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SERVICES TEXTBOOK OF EXPLOSIVES

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PREFACE

This comprehensive revision of the Services Textbook of Explosives textbook is the first since 1988 and the first to be published electronically. It is the work of leading experts from the UK energetic materials community, credited at their individual chapters. Co-editors Steve Murray, former Head of the Department of Engineering and Applied Science at Cranfield Defence and Security and Neil Turner, formerly the MOD UK National Authority for Qualification of explosives, were supported by an editorial board comprising Martin Sloan and Adrian Carp (Defence Ordnance Safety Group); Ian Scattergood (Defence Academy); Steve Hiscock (Navy Explosives Safety); Bruce Martin (DEMS Training Regt); Malcolm Cook (AWE) and Geoff Hooper (Cranfield University). Phil Gill and Matt Parker (Cranfield University) and Justin Fellows (Dstl) provided invaluable and advice during final drafting. Their contributions are gratefully acknowledged

Since 1998 a huge amount of work has been published in the scientific literature, expanding our foundational knowledge and understanding of explosives chemistry and detonics. Policy, process and regulation continue to evolve with legislation and new governance structures, notably the creation of the Defence Safety Authority and the Defence OME Safety Regulations superseding Joint Service Publications. Materials such as cast-cured polymer bonded explosives (PBX) that were new and novel are now in widespread use, enabling a transformation in the vulnerability of munitions.

Looking forward, new manufacturing techniques like Resonant Acoustic Mixing and flow-synthesis will couple with Artificial Intelligence and Machine Learning, producing new ingredients and useful formulations at a pace that would astound our predecessors, heralding a transformation of the energetic materials enterprise from manufacture to end user. We intend to update this textbook regularly, not quite a living document perhaps but one that maintains utility and relevance in the coming years.

Phil Cheese

DOSG Energetics Group Leader & CoEEM Technical Director

August 2020

CHAPTER 1
INTRODUCTION TO THE TEXTBOOK

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1 INTRODUCTION TO THE TEXTBOOK

Author – S G Murray (Cranfield University)

1.1 PURPOSE OF THE TEXTBOOK

1.1.1 Background

The last edition of the Services Textbook of Explosives was written in 1988 and produced as Joint Services Publication (JSP) 333. While most of the science and technology in that edition remains current there has been significant changes to legislation with the introduction of MSER (2005) (1) now superseded by Explosives Regulations 2014(2) and in Explosives Safety Management within the MOD, with new Regulations including JSP 520 *Safety and Environmental Management of Ordnance, Munitions and Explosives over the Equipment Acquisition Cycle*.

Further changes have been the development and introduction of MOD Insensitive Munitions (IM) policy and its effect on munition design and choice of explosive formulations. Many of the explosive materials cited in the 1988 edition are now obsolete and can be found in the History of Explosives chapter. Those explosives currently in service are in the chapters that relate to explosive materials.

To produce this textbook, subject matter experts from academia, industry and the MOD were chosen as chapter authors. An Editorial Board with representatives from Service users and academia provided oversight for suitability of purpose.

1.1.2 Target Audience

This textbook is intended to assist all of those in the MOD that acquire, use or manage Ordnance, Munitions and Explosives (OME), including the Royal Navy, Army, Royal Air Force and MOD Civilians. A significant effort has been made to engage with all potential users of this textbook. It has been recognised that different technical levels will be relevant across a wide range of potential users. To reach the widest audience, each chapter, where appropriate, is structured to have a basic introduction at Awareness level, then with greater detail for Practitioners and finally information relevant to Experts in that subject.

1.1.3 Purpose

The textbook is to provide an electronic edition that brings up to date the 1988 edition with content that is accurate and comprehensive.

1.2 STRUCTURE OF THE TEXTBOOK

The textbook is designed to provide information on how explosives work, how they are applied in weapon systems and how their safety may be ensured through testing and regulation. Other sources of information that provide further detail or more in-depth analysis are referenced and summarised where appropriate. For example, Joint Services Publications such as JSP 520 cited above and MOD explosives regulations (JSP 482) are relevant to explosives in the defence environment. It is not the purpose of this textbook to repeat their contents; instead this document details the fundamental principles that underpin explosives in defence.

The textbook is structured around 5 themes:

1. An introduction to the defence requirements for explosives and a history of explosives that have found service use.
2. The relevant legal and regulatory frameworks, policies and standards relevant to services use of explosives and safety management.
3. The science behind how explosives work their chemistry, toxicity, detection and effects.
4. Explosives currently employed in weapon systems and explosives of interest in defence such as improvised and commercial explosives.
5. The processes applied to ensure they are safe and suitable for service use including qualification, life assessment, vulnerability assessment and electrical safety.

The textbook is designed and constructed to be read electronically and has been mapped to provide, within the text, hyperlinks between a subject and supporting material to avoid the need for repetition. Chapters will contain references together with a bibliography of additional source material.

1.3 DEFENCE REQUIREMENTS FOR EXPLOSIVES

1.3.1 Defining Explosive

There are several ways that an explosive can be defined. In simple terms an explosive is the energetic component or filling within a munition. For a more detailed definition often the reference document is Recommendations on the TRANSPORT OF DANGEROUS GOODS[3] which includes the definition:

"Explosive substance is a solid or liquid substance (or a mixture of substances) which is in itself capable by chemical reaction of producing gas at such temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are included even when they do not evolve gases."

Further definitions include:

"Pyrotechnic substance is a substance or a mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions."

"Explosive article is an article containing one or more explosive substances."

For the purpose of transport, all of these are classed as Dangerous Goods Class 1 – Explosive. It also should be noted that the publication states that "Transport of explosive substances which are unduly sensitive or so reactive as to be subject to spontaneous reaction is prohibited." The definition of explosives for the purpose of safe, practical use within the MOD excludes substances that can produce an explosive or pyrotechnic effect but would be considered unsafe to use. These are not excluded from explosives that are improvised and employed in criminal acts including terrorism and these are included in the textbook in Chapter 16.

One further type of explosive is the mixture of a flammable gas, vapour or finely powdered solid with a gaseous source of oxygen, usually air. These may be produced by accident or intentionally as a weapon type and are known as fuel-air explosives as described in Chapter 9 (see 9.4).

Many dictionary definitions of the term 'explosive' assume that an explosive is a substance that will produce an explosion. However, as noted above, pyrotechnics are classed as explosives, most of which do not display that property. Taking this argument further rocket propellant can be a substance that by chemical reaction produces gas at high temperature but again does not produce an explosion but instead produces thrust.

The one common characteristic that covers all substances that may be encompassed in the definition of 'explosive' is that they are chemicals or mixtures of chemicals that all produce heat by self-sustained chemical reaction. Many also produce gas as a product of this reaction but the speed of reaction may vary considerably. Fast reactions, where the explosive charge is all consumed in thousandths or millionths of a second, lead to explosion whereas slow reactions lead to sustained burning for timescales generally measured in seconds.

1.3.1.1 Defining explosion

An explosion is often defined as a rapid expansion of gas capable of causing damage. An explosion can be created by more than just an explosive and can be caused by three means; physical, chemical and nuclear. It is considered that the largest explosion ever witnessed on earth was a physical explosion. The eruption of the volcano known as Krakatoa in August 1883 allowed sea water to pour in to the collapsing caldera where it immediately was converted to its gaseous state. The expansion created a blast, which has been estimated as having the equivalence of 200 million tonnes of TNT. Here a change of state from liquid to gas created the gaseous expansion in a timeframe necessary to

form a blast wave. A more common physical explosion is simply the bursting of a pressure vessel where high pressure gas can expand rapidly on release.

Nuclear explosions also create rapid gas expansion but in this case it is created by the immense heat released in the nuclear fission or fusion process that simply expands anything in contact with that source of heat. For an above-ground nuclear explosion this would be the surrounding air. Chemical explosives also release heat on explosion but this is insufficient on its own to heat the surroundings to cause rapid gas expansion. To create an effective chemical explosion both heat and gas must be released together thus producing the necessary conditions.

A more correct description of an explosion would be a rapid expansion of gas capable of performing work. For example when a gun is fired there is a controlled explosion inside the breech and barrel of the gun when a rapid expansion of gas certainly occurs in thousandths of a second. The sound of gunfire is then an audible explosion coming from the rapidly expanding hot gas as it exits the muzzle at very high pressure.

1.3.2 Explosives for Application in Defence

1.3.2.1 The Role of explosives in defence

Ever since the discovery of Black Powder, or Gunpowder, explosives have provided advantage on the battlefield over weapons operated by human effort. Until the recent development of Directed Energy Weapons such as lasers all weapon systems relied on explosives for their effect, whether this was a gun propellant for pistols and rifles, rocket propellant for missiles or warhead explosives for artillery shells. Even nuclear weapons rely on conventional explosives to trigger the nuclear explosion.

Explosives provide the energy for delivery systems to gain access to remote targets and then often the destructive effect to neutralise or destroy them. As pyrotechnics they provide support to operations through the provision of signalling with coloured light and smoke, illumination, screening and distraction. Complex munitions themselves will often rely on pyromechanisms as part of their operating systems as do military aircraft. Safe, reliable and effective explosives are critical to the operations of all Armed Forces.

1.3.2.2 Categorisation of explosive types

Explosives for defence use are normally categorised as:

- High Explosives (for warheads, shells, grenades, demolition charges, mines, etc.)
- Propellants
    - Gun propellants
    - Rocket propellants
- Pyrotechnics

Another way of categorising explosives is by the process through which they release their energy:

- High Explosives
- Low Explosives

High Explosives detonate (see 7.1.2) creating a shockwave within the explosive that has the ability to shatter anything in contact with that explosive but also due to the speed of explosion the ability to produce the damaging effect through rapid gas expansion known as blast (see 9.1.1). Low Explosives undergo a burning reaction (lsee 7.1.1) where heat transfer not shock causes the explosion process to occur. Propellants and pyrotechnics are Low Explosives. It is not uncommon for explosives to be grouped as High Explosives, Propellants and Pyrotechnics although there is a fourth group, Pyromechanisms (see 15.1.1), which are explosive articles that have links to Propellants and Pyrotechnics and are designed to use explosive energy to provide motive force.

A third way that explosives are categorised is in regard to the ease by which they can be initiated. The terms used are Primary and Secondary Explosives where Primary Explosives are easily initiated and are used as the way an explosive event is started whereas Secondary Explosives are more difficult to initiate and they will form the main explosive component of, say, a munition such as the main filling in an artillery shell. Explosives for practical use are chosen to be clearly in one group or another as the use of Primary Explosives must be carefully controlled to avoid a damaging accidental initiation.

This has led to the Explosive Train (see 6.1.1) concept in fuzes where a very small amount of Primary Explosive is physically separated from an adjacent explosive pellet until the fuze arms and brings them together. Until arming occurs an accidental initiation of the Primary Explosive will not propagate to the adjacent pellet. Both High and Low Explosives have examples of Primary and Secondary Explosives although fuzing normally is applied to warheads and not to propellants or pyrotechnics.

1.3.2.3 Military, commercial and improvised explosives

For the most part the textbook considers aspects of services explosives, however, for defence purposes there is an interest in commercial and improvised explosives. Commercial explosives (see 11.5) for quarrying, blasting and demolition are, in most cases, quite different to military explosives in that cost is a major factor in their choice; they are produced in large quantity and generally will have a short shelf life. The only exception is in the use of certain plastic explosives in civil demolition that are similar if not identical to those employed by the services. However, there may be occasions when service personnel may wish to use commercial explosives and therefore they are included in the chapter on High Explosives with the main purpose being to show how they differ from the service explosives normally employed.

Improvised explosives (see 16.1) are particularly relevant to certain parts of the MOD therefore a chapter is included in the textbook. These are not explosives as normally defined as Dangerous Goods Class1 as they are often too sensitive

or too unstable to be accepted as a practical explosive. However, by all other definitions they act as explosives in their ability to either cause explosion or self-sustained burning to provide incendiary effects.

1.3.2.4 Performance, safety and reliability

Explosives for defence use are normally chosen to maximise the output matched to their application but other considerations are also applied to find explosives that are safe and suitable for service use. Unlike commercial explosives, service explosives can have long storage life, experience much lower or higher temperatures or be subject to attack during operations. A balance must be made between performance requirements and the need to minimise the likelihood of inadvertent initiation through instability or physical insult while their performance must not be degraded during their storage life or operations and reliably perform as designed.

There always will be a balance between performance, safety and reliability. For example, to increase safety it may be sensible to use a very insensitive explosive; however, this may make it difficult to initiate reliably. There are some explosives that are very high energy but are quite unstable and spontaneously decompose and become useless, or worse, very sensitive and therefore hazardous in a very short time. There are vast numbers of chemicals that potentially could exhibit explosive properties but only a few have found use in practice. Some of the factors that can affect the choice of explosives for service use are given in the following sections.

1.3.2.4.1 Performance

Propellant performance is based on its ability to produce heat and gas providing high pressures that can accelerate projectiles in a barrel or provide thrust from a rocket motor nozzle. High Explosives, for some applications, also rely on gas expansion to produce blast and underwater effects (see 9.1) but for other warheads acceleration of metal is the primary required effect (see 8.1). High Explosives normally are chosen to optimise one effect or the other. For example, some large air delivered bombs are designed to give blast as their main output and so gas expansion is the main requirement and creation of fragments is relatively insignificant. A Shaped Charge (see 8.4) anti-tank warhead, however, is effective through the collapse of a metal cone and production of a very high velocity metal jet with blast being insignificant in its effectiveness.

1.3.2.4.2 Ease of initiation

The ease by which an explosive can be initiated will always be a factor in the choice for particular applications. This is called the sensitiveness (see 20.2.1) to various stimuli such as impact, friction, heat, flame and electrostatic spark when considered from the perspective of accidental initiation and sensitivity when considered from the perspective of designed initiation. Primary Explosives exhibit properties that demonstrate they are easily initiated, which is why they are used as the first element of an explosive train (see 6.1.1).

Secondary Explosives have to be less easily initiated than Primary Explosives for their safe application although must still be capable of reliable initiation from a designed stimulus.

1.3.2.4.3 Chemical stability

Explosives are chemicals or mixtures of chemicals which can undergo further chemical reactions. There are three main concerns with the stability of explosives, the first is that the explosive chemicals themselves are unstable and begin to break down spontaneously and small quantities of decomposition products may themselves accelerate further decomposition. Secondly, there is the potential for contaminants including moisture to react with the explosive. The third issue is that of compatibility (see 20.4.1.1.1), that is, the explosive reacting with other substances to diminish the safety or performance properties of the munition. An example of this would be the adhesive that binds a rocket propellant to a rocket motor casing which could promote decomposition of the propellant. Service explosives are required to have very long shelf lives and can be exposed to thermal extremes which can magnify these problems.

1.3.2.4.4 Physical properties

Service explosives are solid materials and the physical properties of these solid explosive materials affect their suitability for different uses. In manufacture the explosive may need to be extruded or passed through rollers where viscosity at elevated temperatures is important for example in the manufacture of rocket propellant. For High Explosives maximising density may be required to give optimum performance while brittleness in an explosive should be avoided as this makes them prone to violent response in an accident. Elasticity, coefficient of expansion and softening temperature can affect the integrity of an explosive charge and its adhesion to the munition casing, which can have negative effects on safety and performance.

1.3.2.4.5 Ease of manufacture

The manufacture of High Explosive munitions requires the explosive to be filled in to casings. This must be taken in to consideration as the filling process can influence performance, safety and cost. It has been commonplace to employ formulations based on TNT as it melts at 81 °C allowing safe melt casting. However, there are drawbacks in that TNT contracts in volume when changing from the molten state to a solid. This can produce voids and cracks in the filled munition if not carefully controlled and if the explosive charge is accelerated very rapidly, for example as the filling of an artillery shell, this can lead to accidental ignition leading to an explosion within the barrel.

Among other manufacturing considerations is the complexity of chemistry needed to create the explosive material. If many reaction steps are required this can be costly. Equally the cost of precursor chemicals will influence choice.

1.3.2.4.6 Availability and cost

Unlike commercial explosives cost has less influence on the choice of explosive although it must be understood that the overall cost is the cost of the materials and of the manufacturing processes such as filling. Usually the explosive component of a munition or weapon is a relatively small percentage of the overall costs the weapon. What is becoming important is continuity of supply for precursor chemicals or explosives used to produce formulations. A good example of this is availability of ammonium perchlorate that is a key component in composite propellant for rocket motors. Another example is the availability of cotton linters for the manufacture of nitrocellulose.

REACH is a European Union regulation concerning the Registration, Evaluation, Authorisation and restriction of Chemicals that came into force on 1st June 2007[4]. Its purpose is to provide a high level of protection of human health and the environment from the use of chemicals. It is already affecting explosives manufacturing processes and in future may become even more restrictive. This is likely to have a major impact on the choice of future explosives.

1.4 REFERENCES

[1] Manufacture and Storage of Explosives Regulations 2005
[2] The Explosives Regulations 2014
[3] UN Recommendations on the Transport of Dangerous Goods - Model Regulations, Eighteenth revised edition, 2013
[4] The REACH Enforcement Regulations 2013

CHAPTER 2
HISTORY OF EXPLOSIVES

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2 THE HISTORY OF EXPLOSIVES

Author - G Hooper (Cranfield University)

2.1 THE GUNPOWDER ERA

2.1.1 The Origins of Black Powder

The earliest explosive and for several centuries the only one in existence, was gunpowder. Since it pre-dated guns by at least a century and probably several centuries, it is better referred to in the early historical context as black powder. It is a mixture of potassium nitrate (saltpetre, or nitre), charcoal and sulphur. Although the proportions of the ingredients have not always remained constant, the nitrate has always been the major component and was for a long time the most difficult to obtain. This fact is the main line on which historians have worked for over a century in trying to establish beyond doubt the origin of black powder, but so far without success or likelihood of it.

Some writers have suggested that black powder was developed from 'Greek Fire', which was an incendiary mixture used in the naval defence of Byzantium against the Arabs in the 7th century AD (CE) and later. This alleged connection is based on the belief that the earliest type of ‘Greek Fire’ contained potassium nitrate in addition to thickened petroleum distillate. The theory is now discredited, although later versions of the mixture probably did contain the oxidant salt.

The invention of black powder presumably stemmed from the discovery by some person unknown that potassium nitrate, when strongly heated, assists the combustion of flammable material. Potassium nitrate does not occur naturally in large quantities or a pure state, but it is formed in a crude state when organic matter decays on moist ground. The nitrate is washed into the soil by rain and if a long spell of dry weather then follows, the nitrate appears on the surface as a whitish efflorescence. An alert person would have noticed that burning material exhibited an enhanced glow when brought into contact with the efflorescent salt and the same investigator, or a later one, then would have found that a prepared mixture of the white material with charcoal would burn quite vigorously. Although sulphur occurs naturally in regions of volcanic geology, its addition to the mixture is less likely to have been accidental and was probably an experiment made in the fullness of time, with the resulting discovery that the ternary mixture was more easily ignitable.

The climatic conditions which most favour the natural formation of potassium nitrate are found in China, India and North Africa among other places. The two regions which have been claimed as the birthplace of black powder are China and North Africa, but no firm documentary proof of either claim has ever been produced. Documents which are cited by some researchers as evidence are disputed by others on grounds of inaccurate writing, incorrect translation or unsound inference. The most important source so far found which indicates a Chinese origin of black powder is the Wu Ching Tsung Yao; a Chinese treatise

on military techniques which is believed to have been completed in AD (CE) 1044. It describes various mixtures of sulphur and saltpetre with resins, charcoal etc., which were of an incendiary or deflagrating nature. Sometimes arsenic and other toxic substances were added to the compositions to produce poisonous smokes, an early use of chemical warfare. The treatise indicates that by AD (CE) 1000 the Chinese had developed some types of explosive grenade and bomb which were projected by catapult, but there is no mention of what we now call guns. Wu Ching Tsung Yao's first recorded black powder formula had a potassium nitrate level of ~55 % (w/w), sulphur content of ~20 % (w/w) and carbonaceous content of ~ 25 % (w/w).

Even if the rival claim for a North African invention of black powder is unsubstantiated, it seems at least likely that the knowledge of the substance was eventually transmitted by the Arabs through the Middle East and thence to Europe. There it came to the notice of certain scholars, one of whom was the Englishman Roger Bacon (born *circa* 1214, died 1292). Bacon graduated c.1240 and became a Franciscan friar c.1257, but he was a man of many intellectual interests. He obtained some crude potassium nitrate, which by 1225 was being imported from India *via* Venice and which was also being found in European countries as efflorescences in stables. Bacon succeeded in purifying the nitrate by recrystallisation and used it to make some effective black powder. In about 1249 he wrote an account of this and other work, entitled 'De Secretis Operibus Artis et Naturae et de Nullitate Magiae' and sent it to the Pope. Bacon was careful to conceal the details of the powder in a cypher and they remained in that form until decoded by Lt. Col. Henry Hime, RA, in his notable book 'Gunpowder and Ammunition', 1904. Bacon's composition was interpreted as potassium nitrate 41.2 % (w/w), charcoal 29.4 % (w/w) and sulphur 29.4 % (w/w).

Although Bacon was secretive about his work with black powder and was eventually discouraged by the Church from continuing it, certain of his contemporaries, particularly Albertus Magnus (c.1200-1280), were less reticent about the substance. Thus by the end of the 13th century knowledge of black powder was widespread in Europe and it is said that it was already in use for the breaching of fortifications by mining.

2.1.2 The Advent of Firearms

The next development was the invention of the gun to make use of the propulsive property of black powder, which had not been investigated by Bacon. The circumstances of this invention are unknown, but a manuscript of 1313 belonging to the city of Ghent states that in that year the use of 'bussen' was first originated in Germany by a monk. Another Ghent manuscript of the following year mentions guns being manufactured in the city and exported to England. Some writers have identified the alleged monk as one Berthold Schwarz of Cologne, but this connection and even the real existence of Schwarz have been much disputed. The earliest extant English record of a gun is an illustration in a manuscript by Walter de Millemete, dated 1325, showing a bottle-shaped piece discharging a dart-like projectile. There is documentary

evidence that brass cannon and iron balls were ordered by the Council of Florence in 1326. A late 14th century author stated that cannon were used by Edward III of England in Scotland in 1327. They were certainly used by the English at the battle of Crécy, 1346 and were quite common in Europe by the end of the 14th century.

2.1.3 The British Gunpowder Industry

The manufacture of black powder, which we can henceforth call gunpowder, was at first a scattered industry in several European countries and few reliable records have survived. During the 14th century most of the powder used in England was imported, but by 1461 written mention was made of a 'powder-house' in the Tower of London. At that time, or later, powder was actually mixed there and also at Porchester Castle in Hampshire. Early records of other English mills are scarce, but there is believed to have been one at Rotherhithe by 1555 and several others by 1560. The supply of powder with which to fight the Spanish Armada in 1588 was, however, found inadequate and after that a more formal system of contracts was instituted by the Government.

In 1621 the Lords of the Admiralty were appointed as Commissioners for Saltpetre and Gunpowder and the official collection of saltpetre from farm buildings was authorised, causing much disruption and resentment. At this time the law permitted the manufacture of powder only in factories licensed by the Admiralty, but there were several illicit factories operating in southern England. In 1641 an Act of Parliament provided for the free importation and manufacture of powder, but this was revoked in the following year. In 1664 control of the industry was passed to the Board of Ordnance, which was based in London and the contracting mills were accordingly situated in the Home Counties, mostly on tributaries of the Thames. These waterways provided both motive power for the machinery as an alternative to horses and a means of transport to the magazines which were situated along the shores of the Thames estuary. The Lea valley in Essex had, at different periods, some eight mills, including Waltham Abbey where powder was made from before 1560 until the 1940s. Another ancient powder factory at Faversham in Kent continued production of gunpowder and later safety fuze, until 1934.

In 1672 the importation and manufacture of powder were again freed by Act of Parliament. In the same decade the use of powder for mineral blasting was introduced into England, first in Staffordshire and later in Somerset and Cornwall. Thenceforth powder ceased to be a mainly military and sporting commodity and its manufacture spread to all those parts of Britain where there was a ready sale for it. In 1685, however, the Government once again imposed licensing controls on the industry and these have continued in some form ever since.

The British Government continued to procure its powder for military purposes by contract until 1760, when it acquired the Faversham mills. In 1781 the factory was destroyed by an explosion and the Government considered abandoning it, but on the advice of Major William Congreve, Deputy Comptroller of the Royal

Laboratory at Woolwich, they retained and rebuilt it. Later, in 1787, the Government also acquired the Waltham Abbey complex, which was to become particularly productive during the Napoleonic Wars up to 1815. There was a great improvement in the quality of the powder made in these two factories under the supervision of Major Congreve and, from 1814, his son William Congreve the younger, of military rocketry fame. For example, it became possible to reduce the charge weight of powder for naval guns from half the weight of the shot to one third. Congreve gave vivid demonstration of the improvements that he had made at the mills under his supervision by organising firing trials at Marlborough Downs in 1809/10. Taking a standard 10 inch shell and a 9 pound gunpowder charge he compared the range achieved by powders made at the government owned mills and those made by private contractors (Table 2-1).

Table 2-1 Performance of Gunpowder by Manufacturer

Public/Private Ownership	Mill Name	Range in Yards
Gunpowder from King's Mills	Royal Gunpowder Factory Waltham Abbey	4430
	Royal Powder Mill Faversham	4360
Private Contractor's Gunpowder	Pigou	4270
	Butts	4187
	W.Taylor	3922
	Bridges	3898
	Taylor & Co	3861
	Kitchener	3801

Eventually the Government sold the Faversham factory in 1832 and the Irish one at Ballincollig, Co. Cork, in 1834, after which Waltham Abbey remained the only Royal Gunpowder Factory. Its processes and safety methods were continually improved and prizes were awarded for its products in the international exhibitions of the time.

During the first half of the 19th century new, privately-owned gunpowder mills were set up in many parts of Britain to supply the expanding industries of coalmining, quarrying and railway construction. Later in the century, when gunpowder began to give way to the new High Explosives, many of these mills were closed down, but others were adapted to the new products and survived until the First World War, when they produced military explosives for the Government.

2.1.4 The Improvement of Gunpowder

Throughout the centuries when gunpowder was in large-scale production its composition and quality were steadily improved. The earliest gunpowder was simply a fine mixture of the three ingredients. Its ballistic performance was poor because it burned slowly, the flame being unable to pass easily through the mixture. The powdered nitrate readily absorbed moisture and moreover the ingredients tended to separate out during transportation. These problems were overcome by 'corning' the powder. This involved moistening the mixture, forming it into cakes, and then breaking the dried cakes into granules which were then sieved into a range of sizes. Corned powder was being manufactured by 1425. At first it was used only in handguns, since the faster burning produced pressures too great for the ordnance of the time. These latter pieces continued to be loaded with fine powder, known as 'serpentine powder' from a particular type of cannon, but by the 16th century the constructional strength of guns had increased sufficiently to allow the use of corned powder in them. Meanwhile hand grenades and explosive cannon shell were also being filled with corned powder, but most ordnance fired solid shot.

From about 1680 corned powder was improved by 'glazing' the grains, that is, tumbling them in barrels to round the good grains and to pulverise the weak ones, the remains of which were then sieved out. Another significant improvement was made in the 18th century by pressing the mill-cake in screw-presses, thus producing denser and harder grains which burned more steadily. In the following century the screw-presses were replaced by hydraulic ones. Another innovation was the coating of the grains with graphite during the glazing process. The original object of this was to retard the ignition of the grains in guns, but it was found also that it increased resistance to the ingress of moisture, which if present in more than a minimum percentage badly degrades the ballistic performance of the powder.

Over a long period the composition of gunpowder was improved by a steady increase in the nitrate content and in England this trend evolved as shown in Table 2-2 (based on fortuitously surviving formulae rather than definitive ones):

Table 2-2 Changes in Gunpowder Formulations

Year	Potassium Nitrate (% w/w)	Charcoal (% w/w)	Sulphur (% w/w)
1350	67	22	11
1560	50	23	17
1647	67	22	11
1670	71.5	14.5	14
1742	75	12.5	12.5
1781	75	15	10

The higher nitrate content was permitted by the greater availability of the salt, while the increased rate of burning which resulted was controlled by the glazing and increase in density.

The traditional use of potassium nitrate as the oxidant has not always remained unchallenged. In 1788 Count Claude Berthollet, who two years earlier had first prepared pure potassium chlorate, attempted to substitute it for the nitrate, but the result was a violent explosion in the mill, killing two people. Subsequent attempts on the same lines have similarly failed due to the high sensitiveness (see 20.2.1) of chlorate-sulphur mixtures to impact and friction.

During the final years in which gunpowder was commonly used as a propellant the size of ordnance, especially naval guns, increased considerably and by 1880 calibres were as large as 40 cm. If the barrels of such guns were long in proportion and rifled, this necessitated increasing the size of the propellant grains so that they continued to burn and maintain the gas pressure for many tens of milliseconds while the projectile was accelerated and rotated along the bore. There was also a requirement for the initial pressure to be kept within limits, to avoid overstressing the gun. The existing powders, consisting of irregularly shaped grains no more than about 13 mm across, were unsuitable for these purposes. In 1860 the American General Thomas J. Rodman experimented with very large powder grains for big guns, formed as compressed discs 2 cm to 5 cm thick and of a diameter to fit the bore, with perforations through the discs. Ignition occurred initially within the holes, giving a steadily increasing burning surface or what we now call progressive burning. Rodman proved both mathematically and experimentally the superior ballistic performance which resulted. The British Services found, however, that the discs in Rodman's 'perforated cake cartridge' broke up too easily during handling and transportation so they did not adopt it. Instead they concentrated on increasing the density of the powder and also increased the size of grains by cutting the mill-cake into large cubes by means of knife edges. These propellants were known as 'cut powders' or 'pebble powders'. In 1869 pebble powder 'P' was approved for all gun charges heavier than 18 kg (40 lb). This had sides of 16 mm (5/8 inch) and later a larger grain called P2, with 38 mm (1.5 inch) sides, was introduced for 30.5 cm (12 inch) guns. In 1881 Rodman's principle was applied by the British Service in a modified form known as 'prismatic powders'. The grains were pelleted in the shape of hexagonal prisms 2.5 cm high and 3.5 cm between opposite sides. Those for the largest guns had one axial hole, while those for smaller pieces had a ring of seven holes. The grains were packed into cartridges in such a way that the holes formed continuous channels for the initiating flame.

In 1883 brown powders, also known as 'cocoa powders', were introduced from Germany for breech-loading guns. They contained an incompletely carbonised charcoal and burned with satisfactory slowness but were less easily ignitable than the earlier powders. In 1887 a still slower powder, 'EXE', was introduced, containing two grades of charcoal. This was the last development in the artillery field before the general introduction of cordite. Thus in the last three decades before gunpowder propellant was superseded by nitrocellulose types, its

efficiency was pushed to the limit by the advances in the engineering of large guns. Moreover, principles of internal ballistics were established which were later adapted to the different rheology and superior thermochemical performance of 20th century propellants.

2.1.5 Black Powder War Rockets

The foregoing notes relate mainly to the use of black powder in guns. In view of the great importance of rocketry in present-day armaments, some mention should be made of the parallel employment of powder in rockets. The origins of the rocket, like those of black powder, cannot be dated with any certainty, but are probably Chinese. Although the early Chinese appear to have lacked the technology to contain the high pressures necessary for a gun, it would not have been difficult for them to pack black powder into a bamboo tube, with an axial hole in the charge and perhaps a constriction at the rear. They would then possess what a later writer was to call ‘ammunition without ordnance'.

A notable early book, 'Liber ignium ad comburendos hostes' ('Book of fires for burning the enemy'), by the pseudonymous Marcus Graecus (Marcus the Greek) and dated by some as early as the 8th century AD, describes a form of rocket, but it is generally agreed that the first recorded use of the rocket in war was in the defence of Kai Fung Fu In China 1232. The rocket was also used for celebratory fireworks, probably from a much earlier date. This custom spread to Europe in due course and became of increasing commercial Importance from about 1400 onwards. Contemporaneously, war-rockets were used to some extent in mainland Europe and in 1561 there appeared in France a 'Treatise upon several kinds of war-fireworks'. The tradition appears to have persisted in Europe throughout the 17th century, although war-rockets never surpassed ordnance in importance. It is said that by 1688 rockets of up to 50 kg (120 lb) had been successfully fired in Germany.

Meanwhile, in India the war-rocket was used at Delhi in the 14th century before guns were introduced there. Much later, in 1792, British troops serving with the East India Company were hard-pressed when bombarded by a rocket-equipped force of 5000 men belonging to the Maharajah of Mysore in an action on the island of Seringapatam. The rockets used were of two kinds, explosive and incendiary and were quite small, 20 cm to 30 cm long and 3.75 cm to 5 cm in diameter. At this time the British Army had never used war-rockets and after a similar occurrence in 1799 the Ordnance Office sought expert help in developing such a weapon. It fell to Captain (later Sir) William Congreve (1772-1828) to do this. In experiments at the Royal Laboratory at Woolwich around 1805 he developed several types of missile. Initially the rockets had side-mounted brackets which were used to attach wooden sticks of differing lengths, according to the sizes of rocket, but in December 1815 Congreve demonstrated a new design of rocket that had the stick screwed centrally into the rocket’s base plate and directing the exhaust through a ring of small nozzles around the edge of the plate. The cases were originally of paper but Congreve soon made a change to sheet iron. The most common type of rocket had a total

weight of 14 kg (32 lb) and a range of 2700 metres. It could be fitted with an explosive, incendiary or the recently adopted shrapnel warhead.

The Navy considered Congreve rockets well-suited to the attack of land targets from sea and in that role they were equal to the best guns of the time in terms of range, moreover exerting no recoil forces. There remained, however, a problem with their accuracy, making them unsuitable for the attack of point targets. The rockets were used in large numbers in naval bombardments at Boulogne in 1806 and at Copenhagen and Walcheren in 1807. By 1813 war-rockets were in use by the Army and played a small but crucial part at the battle of Leipzig in that year and were also used during the American War in the following year. It was the use of ship-launched Congreve rockets by the British in the bombardment of Fort McHenry in the US in 1814 that inspired the fifth line of the first verse of the United States' National Anthem, "The Star-Spangled Banner" with the words "and the rockets’ red glare, the bombs bursting in air".

In Russia there was military interest in rockets from an early date and a factory was founded in Moscow in 1680 to produce pyrotechnic rockets for the army of Czar Peter the Great. Later the works was moved to St. Petersburg and war-rockets on the lines of Congreve's were developed there, having a range of 5 km. These were used in the Russo-Turkish War of 1828-9 and the Crimean War of 1853-6.

In the British Army Congreve rockets continued in service until 1865, when they were superseded by a type named after their designer, Lt. Col. E.M. Boxer (1833-1898), Superintendent of the Royal Laboratory, Woolwich. They had a gunpowder propellant of improved composition.

Meanwhile William Hale, a mechanic of the Royal Arsenal, had invented in 1845 a stick-less rocket which obtained its stability in flight by part of the exhaust gases causing the rocket to rotate or spin on its axis. This was achieved by three exhaust holes in the rocket which were each surrounded by curved vanes for producing the rotation. The design failed to impress the British authorities but Hale sold the manufacturing rights to his rockets to the U.S. Government through an agent for the then not inconsiderable amount of $20,000 for use during the Mexican War of 1846-1848 where they had some success. This was the first battlefield use of Hale rockets. It was eventually adopted by the British Service in 1867, but was never a reliable weapon, being seriously inaccurate and prone to bursting of the propellant case. From about 1870 improvements in rifled ordnance rendered the military rocket obsolescent in most countries and in the UK only minor modifications to the Hale rocket were made up to World War I, in which it was not used and after which it was withdrawn. The next decade was to see a new era in the history of rocketry.

2.1.6 The Decline of Black Powder

The use of gunpowder, both as a gun propellant and as a shell filling for the British Services, had virtually ended by 1900. Since that time gunpowder has been used mainly in igniters for gun cartridges, in expelling charges for carrier shell, in time rings for fuzes, in safety fuse (invented by William Bickford in

1831) and in a variety of pyrotechnic roles. At present gunpowder is not being manufactured by UK factories, but is imported.

The British Army uses the word ‘Fuze’ to define all such devices, however, all other branches of the Services and safety authorities refer to 'Safety Fuse' to differentiate this type of fuze from mechanical fuzes.

2.2 EARLY LEGISLATION ON EXPLOSIVES SAFETY

Gunpowder is a hazardous material to manufacture and store because it is readily initiated by sparks and sometimes by impact or friction. Accidental explosions in gunpowder mills were frequent throughout the centuries and although casualties in any one incident were not usually heavy the total rate was high. The usual effect on victims was severe burns rather than the avulsion and missile injuries caused by High Explosives. As we have seen, the earliest Acts of Parliament relating to gunpowder were intended only to secure the Government's supply of it and to keep powder out of the hands of political enemies. However, from 1719 onwards legislation was enacted to reduce the frequency of accidents and to minimise their effects on the general public. In that year an Act was passed to limit the amounts of powder kept or carried in the Cities of London and Westminster and suburbs thereof, but Government powder was exempted and this policy of Crown exemption from such legislation has been maintained to the present time. Further Acts passed in 1725, 1742 and 1749 successively tightened control and the Gunpowder Act of 1772 was a wide-ranging one regulating the making, keeping and carriage of gunpowder within Great Britain. The next major step was the Gunpowder Act of 1860, which incidentally was the first such Act to stipulate protection against lightning. This hazard to gunpowder storehouses had been of concern to the Government since at least 1769 when a church in Brescia, Italy, was struck, exploding 100 tons of powder stored within it and causing heavy casualties and damage. The British Government had afterwards installed lightning conductors at its Purfleet magazines.

The 1860 Act was poorly enforced and accidents from various causes continued to occur at civil premises, although the safety record of Government explosives was good. Eventually the Explosives Act of 1875 provided for tighter and more centralised control of the manufacture, keeping, sale, carriage and importation not only of gunpowder but of the newer explosives which by then existed. The traditionally responsible attitude of the Services towards explosives was reflected in the appointment of a retired officer, Col. Sir Vivian Dering Majendie KCB, who had urged and guided the new Act, as the first permanent Chief Inspector of Explosives. The 1875 Act is still the basis of much of the extant UK explosives legislation, which is discussed in Chapter 3.

2.3 EARLY PRIMARY EXPLOSIVES

2.3.1 The Origins of Primary Explosives

Although gunpowder was for long the only known explosive suited to practical purposes, other explosive substances had been discovered by about 1600. These included the fulminates of gold and silver, highly sensitive and dangerous compounds which existed only as scientific curiosities and for entertainments by fairground showmen. Their first discoverer is not known, but gold fulminate was described in 1602-4 by the pseudonymous Basil Valentine, who is believed to have been the author Johann Thölde (or Thölden) of Hesse. The Dutch chemist Cornelius Van Drebbel, who worked for the British Navy, is said to have incorporated gold fulminate as an initiating compound in munitions used against the port of La Rochelle in 1628. If this is true it was a development well ahead of its time. Silver fulminate was prepared, though perhaps not for the first time, in 1788 by Berthollet, who has already been mentioned. The slightly less sensitive but almost equally violent fulminate of mercury was probably first prepared by Johann Kunckel von Löwenstern (1630-1703) and was formally described in a paper by Edward Charles Howard FRS In 1800. Furthermore, sensitive mixtures of potassium chlorate with other substances existed from the 1780s onwards, as mentioned.

2.3.2 The Use of Primary Explosives in Small Arms

In the early 19th century some of these primary explosives, as we now term them, found a crucially important practical use in the initiation of gunpowder charges in firearms. One of the problems which had restrained the early development of small arms was the difficulty of creating flame outside the breech in all weathers and causing it to pass through a small hole to the propellant charge at the intended moment of firing. The early match-lock was succeeded in turn by the wheel-lock and the flint-lock, but by the early 19th century there was a great need for a fully enclosed initiation system which was quick and easy to load, unaffected by wind or rain and which would be practically instantaneous in its action, that is, which would not hang-fire.

The first radical step in this direction was taken by a clergyman, the Rev. Alexander John Forsyth (1769-1843) of Belhelvie, Aberdeenshire. In 1805 he invented a percussion lock for a sporting gun, using a mixture of potassium chlorate, charcoal and sulphur dispensed in loose, discrete portions from a receptacle fixed to the gun. Forsyth drew his so-called 'scent-bottle lock' to the attention of the Master-General of Ordnance, who asked him to adapt it to military use. This was attempted by Forsyth but he failed to satisfy the authorities and later spent many years and much money in the legal defence of his patent.

Forsyth's original idea was eventually superseded by that of enclosing the portions of primary explosive in separate metal caps and substituting mercury fulminate for the chlorate mixture. Several inventors worked on these lines and the first successful one seems to have been Joshua Shaw (1776-1860), an

English expatriate in Philadelphia, USA, in 1814. The London gunmaker Joseph Egg is believed to have obtained the idea in 1815 from Shaw, who did not patent it until 1822. Other claimants to the invention of the percussion cap included the Briton Joseph Manton (1816) and two individual Paris gun-makers, Prélat (1818) and Deboubert (1820). In 1823 E. Goode Wright of Hereford published an important paper based on his practical experiments with fulminate caps and among the gun-makers who utilised this knowledge commercially the most successful was Frederick Joyce of London in the following year.

The next development was the invention of a cartridge containing the cap, propellant and ball, to be, loaded into the breech from the rear. The potential benefits of a breech-loading system had been understood for centuries. However, engineering technology had not been sufficiently advanced to provide adequate obturation (gas-sealing) without the help of an expanding cartridge case, which in turn needed an internal percussion cap. A pin-fire cartridge was produced by Lefaucheaux In 1836, the first centre-fire systems in about 1853 and the first really successful centre-fire gun by Daw in 1861.

All these guns were sporting types: military authorities were reluctant to adopt the very latest inventions to Service weapons, hence the British Army did not begin converting its existing muskets to a percussion system until 1831, using the technology of ten years previously. The filling of the cap was changed from straight mercury fulminate to a mixture of 33 % w/w fulminate, 50 % w/w potassium chlorate and 17 % w/w powdered glass. The first purpose-designed percussion rifle to enter military service anywhere was the Prussian needle-rifle invented by Johann von Dreyse in 1838 and which continued in service until after 1870. The first British Service rifle designed for percussion firing was the 0.577-inch Snider in 1866, which took a brass centre-fire cartridge designed by Col. Boxer. By that time the cap filling had been changed to 37.5 % w/w mercury fulminate, 37.5 % w/w potassium chlorate and 25 % w/w antimony sulphide. Between 1885 and 1889 the calibre of British Service rifles was reduced from 0.450-inch to 0.303-inch and the cap composition for the new ammunition was that shown in Table 2-3 and remained with little alteration until World War II.

Table 2-3 Cap Composition from Late C^{19th} to WWII

Mercury fulminate	15 % w/w
Potassium chlorate	35 % w/w
Antimony sulphide	45 % w/w
Sulphur	2.5 % w/w
Mealed gunpowder	2.5 % w/w

In the foregoing paragraphs it can be seen how some simple primary explosives made possible a profound improvement over the crude firearms of older times and paved the way for the development of the far superior firepower possessed by present-day small arms.

2.3.3 Early Primary Explosives in Artillery Weapons

The invention of the small arms percussion cap was adapted in due course to ordnance ammunition. Previously, the propellant in cannon had been ignited by a powder-filled tube, called a firing tube, which passed through a hole in the breech and was itself ignited on the outside by a portfire. In about 1840, this firing tube was modified into a rather cumbersome percussion device by Marsh, the first Chemist of the Royal Laboratory, Woolwich. This, in turn gave way in 1845 to a neater form of tube to which a percussion cap was fitted. In about 1853 friction tubes were introduced: these consisted of a friction bar coated with a potassium chlorate/antimony sulphide mixture, with minor additions of gunpowder, sulphur and powdered glass, housed in a body containing mealed gunpowder. A pull on a lanyard ignited the mixture and thus fired the gun.

The first 'galvanic' (electrical) firing tube was approved for proof and experimental firings in 1856 and after further development work by Frederick Augustus Abel (1827-1902), the War Department Chemist, electrical firing was adopted by the British Service in 1866. (It was, of course, only applicable to warships and permanent fortifications). The tube contained copper sulphide, copper phosphide and potassium perchlorate and it required a high voltage. Low-voltage electric tubes were adopted in 1878.

While this work was being carried out on the initiation of propellants, some progress had also been made in the initiation of projectile fillings. In 1846 the percussion cap was first used to ignite time fuzes in shell, the cap being fired by set-back action upon the firing of the gun. This invention was credited to Quartermaster Freeburn RA. Soon afterwards, in 1850, came a percussion device to explode the shell on impact, invented by Cdr. Moorson RN.

2.4 REPLACEMENTS FOR GUNPOWDER

2.4.1 Nitrocellulose

The pioneering discoveries which eventually led to the supersession of gunpowder for major purposes between about 1870 and 1895 had been made several decades earlier. Advances achieved in organic chemistry at that time included the preparation of new compounds by the action of nitric acid, or of mixed nitric and sulphuric acids, on certain parent compounds. The products in some cases were explosive in nature. However, the theory and practice of analytical chemistry at that time were insufficiently advanced to prove their exact composition and molecular structure. Some of their discoverers, moreover, appear to have been more intent on turning their achievements to profit than on making full scientific investigation of the new explosives, while others did neither; they quickly lost interest and went on to other things.

In 1833 Professor Braconnot of Nancy, France, found that starch dissolved in nitric acid to give a readily flammable white precipitate which he called Xylöidine. Five years later Theophile-Jules Pélouze (1799-1868), Professor of Chemistry at Basle University, carried out the first orthodox preparation of

nitrocellulose, closely followed by Professor Rudolf Böttger (1806-1887) of Frankfurt-on-Main who discovered it independently a few months later.

The German chemist Christian Friedrich Schönbein perceived great civil and military possibilities in his product and soon travelled from Basel to Germany and England where he demonstrated the use of nitrocellulose for rock blasting and as a propellant for ordnance and small arms. In England the sole right to manufacture nitrocellulose was acquired from Schönbein by Messrs. John Hall of Faversham, Kent, who built a factory there for the purpose. However, on the 14 July 1847 a spontaneous explosion of nitrocellulose destroyed the factory and killed 21 people. Similar explosions occurred in France at Vincennes and Bouchet, after which production of nitrocellulose ceased in both countries for many years.

In Austria Baron Wilhelm Freiherr von Lenk of Wolfsburg, a prominent figure in connection with military explosives, had worked since 1849 on improving Schönbein's method of manufacturing nitrocellulose and retained much faith in the product. He had a factory built at Hirtenberg near Vienna and production began there in 1853. Von Lenk tried his nitrocellulose as a propellant in 12-pounder guns but they were damaged by it. Then in 1863 there was a spontaneous explosion of nitrocellulose in the magazine at Hirtenberg. Von Lenk meanwhile travelled to England and had taken out patents for his method of manufacture. Messrs. Prentice & Co. of Stowmarket, Suffolk, started to manufacture nitrocellulose by Von Lenk's method, but a disastrous explosion destroyed the factory and was followed by yet another at Steinfelder Heath, near Vienna, in 1865. After this the Austrian Government followed other European ones in prohibiting the manufacture of nitrocellulose.

Clearly some method of making the product more stable was needed. John Tonkin of Pool, Cornwall, took out a patent in 1862 for a mixture of nitrocellulose with gunpowder, which was not a commercial success but the patent was notable as the first one which specified the pulping of nitrocellulose. The definitive remedy for the instability problem was published by Frederick Abel in 1866-7 under the title of 'Researches on Guncotton', following his work for the British Government at Woolwich and Waltham Abbey. Abel recommended pulping, boiling and more thoroughly washing the product. The way was now clear for the development of nitrocellulose as one of the most important explosives ever discovered. Despite one more spontaneous magazine explosion at Stowmarket in 1871, which the reporting inspector attributed to sabotage, production was begun at Waltham Abbey in 1872. Abel's stabilisation process was later improved by Robertson, who reported his work in 1906 and since then the manufacturing process has remained largely unchanged.

2.4.2 Early Smokeless Powders

Because of the disastrous explosions of nitrocellulose, Schönbein's demonstrations of its propulsive properties in 1846 were not successfully followed up for many years. In about 1864 a Prussian artillery officer, Captain

J.F.E. Schultze, developed a propellant made from a mixture of nitrated wood and potassium nitrate. This propellant burned too fast for use in rifles but was found suitable for shotguns and smooth-bore ordnance. It was manufactured for a time from 1869 at Eyeworth in the New Forest and in Austria from about 1870. The Austrian manufacturer, F. Volkman, patented an improved version of Schultze powder called Collodin, which was partly gelatinised with a mixture of di-ethyl ether and ethanol. This mixture has a strong solvent action on nitrocellulose of up to medium nitrogen content (12.6 % N), a fact which was discovered by the American J. Parker Maynard in 1847.

The next significant advance in propellants was a superior shotgun powder, patented in 1882 by W.F. Reid and D. Johnson of the Explosives Company at Stowmarket. This was called EC powder and consisted of nitrocellulose mixed chiefly with potassium nitrate and barium nitrate. The grains were partially gelatinised by ether/ethanol solvent, and then hardened. EC powder was manufactured in Green Street Green, near Dartford in Kent.

The first smokeless powder which was safe for use in rifled ordnance and small arms was invented in 1884 by the French physicist Paul M.E. Vieille (1854-1934) and was called Poudre B. The 'B' is said to have stood for 'blanche' to distinguish the new composition from Poudre Noire, or black powder. Another explanation of the initial is that Vieille dedicated the powder to a noted French soldier of the day; Gen. E.J.M. Boulanger and possibly both explanations are valid. Poudre B was made from a fully gelatinised blend of nitrocellulose of two different nitrogen contents, forming a dough. This dough was rolled into thin sheets, and then cut into square grains, which were then dried. After trials the new propellant was adopted by the French Government for the Lebel rifle and larger weapons.

2.4.3 Early Nitroglycerine Explosives

The propellants mentioned thus far were all of what is nowadays called the single-base type, the universal base being nitrocellulose. In order to outline the next step, namely the introduction of double-base propellants, it is necessary to go back to 1847. In that year Ascanio Sobrero (1812-1888), Professor of Applied Chemistry at the University of Turin, Italy, first prepared the liquid High Explosive nitroglycerine (glyceryl trinitrate, or propane-1,2,3-triol trinitrate). He noted its violent explosive properties and dangerous sensitiveness (see 20.2.1) but did not establish its chemical structure: this was not achieved until 1887, by Hay and Orme Masson. Nor did Sobrero attempt to exploit the substance commercially. Others, including the Russians Zinin and Pietruszlwski in 1854, experimented in filling artillery shell with liquid nitroglycerine as a main charge, with attendant grave hazards and unsatisfactory results. Nikolai Zinin brought nitroglycerine to the notice of the Swedish inventor Immanuel Nobel, who then attempted to use a mixture of gunpowder and nitroglycerine in sea-mines required by the Russians for the Crimean War. This mixture also was not a success.

Later, in 1862, Nobel and his third son Alfred Bernhard (1833-1896) set up a factory in Stockholm for the production of nitroglycerine as a blasting explosive. Unfortunately their customers experienced difficulty in inducing the liquid to detonate satisfactorily in boreholes, while contrarily there was much danger of it detonating in bulk during transportation. The latter fact was demonstrated by the blowing up of the steamship 'European' with the loss of 74 lives in 1866. There were also major accidental explosions at Krummel in Germany, San Francisco in the USA and in Sydney, Australia. The Nobels' own factory was destroyed in 1864 by an explosion in which the youngest son and four other employees were killed. Thereafter Alfred Nobel discovered a suitable absorbent (kieselguhr) for nitroglycerine and from 1867 he marketed the mixture as a blasting explosive under the name of Dynamite, with great commercial success. More importantly for the future of explosives generally, in 1864 he invented the detonator, using mercury fulminate which by then was in common use for initiating cartridges in firearms.

Alfred Nobel’s pioneering work in the 1860s to 1880s, although mainly directed at the fast-expanding commercial blasting market, included some experiments of military interest. In 1867 two fellow Swedish chemists, C.J. Ohlsson and J.H. Norrbin, took out the first patent for ammonium nitrate-based explosives, which they called, generically, ammoniakrut. This patent was purchased by Nobel, who made some use of it at the time but was hindered by the hygroscopicity of the nitrate. Since then ammonium nitrate has become the most important ingredient of commercial explosives and for long periods has also been used extensively in military ones.

In 1875 Alfred Nobel discovered that nitrocellulose of fairly low nitrogen content dissolves in nitroglycerine, forming a gel which was the most powerful explosive of the time and even today has few rivals. He called it Blasting Gelatine. From this discovery stemmed a large family of blasting explosives in which other substances, such as inorganic nitrates and cellulosic materials, were incorporated with the gel to make Gelatine Dynamites, Gelignites and Semi-gelatines. The first two categories were originally distinguishable, but nowadays are virtually identical. These new explosives, although bringing further vast profits to Nobel and his competitors, were of little military usefulness because of their high sensitiveness (see 20.2.1) and short shelf life.

2.4.4 Double-base Propellants

In 1887 Nobel made a further important discovery, this time one of great military significance. He found that a mixture of nitroglycerine, nitrocellulose and camphor could be rolled into thin sheets and then cut up into grains to form a gun propellant, which was named Ballistite. This was the first 'double-base' propellant. It was patented in 1888 and is still used in some countries at the present time. The nitrogen content of the nitrocellulose used is about 12.6 % N.

In view of the adoption of Poudre B by the French Government in 1886, the British Government had set up a committee to report on the possibilities of smokeless powders for use in the British Service. The committee took an

interest in Ballistite when it became available. Finally they recommended the development of a double-base composition generally similar to Ballistite but made with nitrocellulose of higher nitrogen content (13.1 % N) and which therefore required the use of acetone as a solvent in its manufacture. This composition was to be extruded in the form of cords and was hence called Cordite. It was patented in 1889 by the British Government in the names of two members of the committee, Sir Frederick Abel and James (later Sir James) Dewar, though most of the experimental development was done by Dr. W. Kellner, who had succeeded to Abel's position as the War Department Chemist. Production of Cordite was commenced at the Royal Gunpowder Factory, Waltham Abbey, in the same year and the new propellant was finally introduced into service in 1893. Nobel then sued the British Government for the infringement of his patent and there followed a protracted court action which hinged on the definition of 'solubility' as applied to nitrocellulose. Eventually Nobel lost his case, as did Sir Hiram Maxim who also sued the Government in connection with his own patent.

The original Cordite, known as Mark I although later variants did not carry mark numbers, contained 58 % of nitroglycerine, giving it a high combustion temperature. When it was used extensively in the Boer War (1899-1902) it was found to cause excessive erosion of the gun bores, so for artillery ammunition it was replaced in 1901 by a ‘cooler' propellant containing only 30 % of nitroglycerine and called Cordite MD ('Modified'). Cordite Mark I continued for a number of years to be used in small arms, which at that time included very few machine guns. Cordite MD was used in large quantities in World War I. At one stage in the Great War supplies of acetone were inadequate and a Cordite containing nitrocellulose of lower nitrogen content (12.2 % N) was introduced, so that gelatinisation could be done with ether/ethanol solvent instead. This composition was called Cordite RDB. Another propellant used by the Allies in the war was the single-base powder NCT (T - tubular), which contained nitrocellulose of 12.6 % N content. NCT was manufactured in large quantities in the USA and on a smaller scale in the UK. Two other imported American powders of the time were NCY and NCZ and some NCY was made in Britain.

2.4.5 Other Replacements for Gunpowder

Up to the late 19th century gunpowder served all the purposes of military explosives except that of a primary explosive. Then, with the introduction of the new nitro-compounds and nitrate ester explosives, the choice of compositions for specific requirements became wider. Patents for all kinds of explosives proliferated and military authorities had to instigate much research and development work to ensure that the explosives selected for particular requirements were safe, reliable and effective. It has been seen how two nitrate ester High Explosives, nitrocellulose and nitroglycerine, were adapted to a deflagrating role as gun propellants. It is now time to look at the developments in the detonating role of explosives, which prior to 1914 was mainly confined to explosive shell for the Army and Navy, torpedoes and mines for the latter and some demolition stores for both Services.

In 1865 Abel patented the manufacture of Guncotton blocks, Guncotton being the name for the most highly nitrated grades of nitrocellulose, containing more than 12.9 % N. Following Nobel's invention of the detonator, Abel's assistant, E.O. Brown, discovered in 1868 that a dry block could be made to detonate by this means and soon afterwards he and Abel found that the detonation of a dry block could be passed on to a wet one. (This was a case of practice being well ahead of theory, for the theory of detonation was then only in its infancy). These blocks, kept wet primarily for safety but incidentally giving better explosive performance in that condition, were used for many years packed into the capacious warheads of torpedoes and in sea mines. Up to 1900 the weight of each block was limited to 3.6 kg (8 lb), but afterwards the Hollings process introduced by the New Explosives Co. at Stowmarket enabled blocks as large as 227 kg (500 lb) to be produced. Small blocks of Guncotton were used by the British Army and the Royal Navy as demolition stores right up to World War II, when they were superseded by plastic explosive.

2.4.6 Replacements for Warhead Explosives

2.4.6.1 Picric acid

A nitro-compound which received much attention from explosives chemists in the late 19th century was picric acid (2,4,6-trinitrophenol). It was first discovered by Glauber in the early 18th century when he treated such substances as wool and horn with nitric acid. In 1771 Woulff prepared picric acid by the action of nitric acid on silk. Seven years later Hausmann prepared it by the action of the same acid on indigo. In 1843, Laurent, nitrated phenol. For many years picric acid was used only as a dyestuff, chemists believing that it was undetonable because of its heavy deficiency of oxygen. However, certain picrates were found to be useful ingredients in explosive mixtures with potassium nitrate and charcoal known as Designolle powders (1869) for fillings in shell and torpedoes. These powders were not used in Britain, but at about the same time Abel suggested a mixture of ammonium picrate and potassium nitrate as a shell filling to replace gunpowder and in 1874 the manufacture of picric acid as a precursor to the picrate salt was authorised for the Royal Gunpowder Factory.

Meanwhile, in 1871 Dr. Hermann Sprengel, the celebrated German scientist, discovered that picric acid could, after all, be made to detonate. Little notice was taken of this, however, until 1885 when the Frenchman Eughne Turpin patented the use of picric acid in all kinds of hollow projectiles and in various physical forms. Several countries adopted the idea, including France, where picric acid and its physical modifications were known as Melinite. In Britain trials of picric acid-filled shell were carried out at Lydd in Kent and in 1888 the cast explosive was approved for Service under the name of Lyddite. Lyddite-filled shell were first used by the British in action at the battle of Omdurman in the Sudan in 1898 and continued in use until the early years of the First World War. A later variant of Lyddite contained dinitrophenol in addition to picric acid, reducing the melting point so that the mixture could be more safely poured into shell. This mixture was called Shellite in the United Kingdom and Tridite or MBT in other countries.

For the efficient detonation of Lyddite shell a large and powerful exploding system was found necessary. The British used for this a revised version of Abel's mixture of ammonium picrate and potassium nitrate, in proportions 43:57 % w/w. This was called picrate powder. Confined in a steel tube known as a gaine, it did not require a detonator since it burned to high-order detonation when ignited at one end by the time fuze or impact igniter.

The most serious disadvantage of picric acid as a Service explosive was its tendency to react with any metals with which it remained in prolonged contact. The metallic picrates thus formed are very sensitive to impact and friction and their detonation is sufficiently violent to detonate in turn the main body of picric acid. Numerous routine precautions against this hazard had to be taken during the manufacture and filling of Lyddite and in both Germany and Britain a safer filling was sought at the turn of the century.

2.4.6.2 Trinitrotoluene (TNT)

In 1902 the Germans adopted as a shell filling the High Explosive 2,4,6-trinitrotoluene (TNT), which had been first prepared in 1863 by J. Wilbrand, himself a German. They called it Fp-02 (Fullpulver, or filling powder, of 1902). During the next three years several commercial explosives manufacturers in the UK tried to interest the British Government in its possibilities, but after trials the response was negative because TNT, or trotyl as it was then called in Britain, was slightly less powerful than picric acid and moreover had the same need for an inconveniently large exploder. It was not until about 1907 that the net superiority of TNT over picric acid as a shell filling was officially recognised in Britain and its production for this purpose was commenced there. Even then the scale of manufacture remained small until after the outbreak of war in 1914.

2.4.6.3 Tetryl (CE)

The problem of inadequate exploder systems in shell, which had troubled the British Services for a number of years, was largely solved in 1910 by the approval of Tetryl, otherwise known as CE (Composition, Exploding), for this purpose. Tetryl (2,4,6-trinitrophenylmethylnitramine) had been first prepared by Mertens in 1877. It was found to be a good 'intermediary' explosive (this term has since fallen out of use) but was suitable only for use in TNT-filled shell, being chemically incompatible with picric acid. In the UK, Tetryl went into large-scale production early in the Great War and remained in use until recent years in most countries, being replaced because of its toxicity. It was only in the latter part of the twentieth century that it began being replaced in British Service, mainly by wax-coated RDX compositions known as the Debrix series. These in their turn became unavailable after the closure of the Bridgwater facilities and the consequent loss of RDX manufacture in the UK.

2.4.6.4 Ammonal

An important development during the Great War was the addition of aluminium powder to certain military explosives in order to enhance their air blast or

cratering effects. Aluminium powder had been used in pyrotechnics since 1894 and in 1897 Deissler took out a Belgian patent for its use in explosive compositions.

In 1904 Fedherer suggested the use of a mixture of TNT, ammonium nitrate and aluminium as a High Explosive. This mixture, called Ammonal, was used commercially before the war as a blasting explosive and during the war the Royal Engineers used a version known as Military Ammonal, which was essentially an aluminised Amatol. Its most famous use was in General Plumer's huge trench mines at the battle of Messines Ridge in 1917, when 19 simultaneous detonations were heard in London, 140 miles distant and reportedly in Dublin also. Military Ammonal was also used as a filling for grenades, aircraft bombs and the wire-cutting pipe charges known as 'Bangalore torpedoes'. It continued in use until World War II when superior aluminised compositions replaced it. A similar Service composition was called Alumatol and a well-known commercial version called Burrowite, produced from 1931 to 1963, was also used in the Service.

2.5 PRIMARY EXPLOSIVES IN THE EARLY C^{20th}

During the late 19th and early 20th centuries mercury fulminate compositions were universally used for the initiation of ammunition. Early in the 20th century fuze design became more diverse and stab detonators, as distinct from percussion ones, became common, but the versatile fulminate compositions, provided they remained in good condition proved adequate for these devices also. The main disadvantage of mercury fulminate was its short shelf life under hot, humid conditions and since the British Army and the Royal Navy had to be equipped to fight in any part of the world, a replacement for fulminate was sought. This applied to its two separate functions, detonative ('disruptive') and igniferous.

In 1890-91 Curtius first prepared the azide salts of lead, silver and mercury and of these the lead salt appeared to be the most useful for detonators of all kinds. The hazards of manufacturing and handling it prevented its adoption for many years, but it was used in some commercial blasting detonators from about 1908 and was used in fuze detonators in the 1914-1918 war, first by the Germans and then to some extent by the British. Lead azide, in an unmixed state, gives a stronger detonative effect than does an equal weight of mercury fulminate and also has a longer shelf life, but it is less sensitive to flash, percussion and stabbing. Therefore new compositions and configurations had to be developed to adapt lead azide fully to the exacting requirements of fuze detonators and it was not until 1925 that lead azide detonators became common in the British Service. Since then there has also been some use of silver azide for special applications. Among the constituents of primary compositions which were newly introduced in connection with lead azide were lead styphnate (the lead salt of 2, 4,6-trinitroresorcinol) and tetrazene (an abbreviation of 1-5-tetrazolyl-4-guanyltetrazene monohydrate). The latter was first prepared by Hoffman and Roth in 1910.

2.6 THE ORIGIN OF MILITARY PYROTECHNICS

2.6.1 Early History

No historical starting point for the invention of pyrotechnics is universally agreed. The incendiary mixture known as 'Greek Fire' is often quoted as an early example of that particular branch of the art believed to date from C^{7th} when it was employed in naval battles by the Byzantines. Although there have been suggestions that it contained saltpetre (potassium nitrate), a well known ingredient of modern pyrotechnics, it is more likely that it consisted of a flammable hydrocarbon such as naphtha probably with a thickening agent and acted like napalm, a mixture of liquid hydrocarbon thickened with a soap-like material.

Much of the history of pyrotechnics is linked to that of black powder, because black powder conforms to the definition of a pyrotechnic as well as being an explosive and a propellant and many historical pyrotechnics have been merely modifications of the basic black powder composition. This is also true of some present-day pyrotechnics. The early rocket, which may have pre-dated 'Greek Fire', is central to the history of pyrotechny because the black powder which it contained served to provide both propulsive force and a visible and audible signal. Such a versatile device could be put to a range of purposes, from warfare to entertainment.

In England, the earliest involvement of the armed forces in rocketry was in the field of public entertainment. Although the art of making and displaying fireworks reached mainland Europe in the 14th century, it did not become common in England until three centuries later. Then, starting in 1613, public firework displays were provided in London by the Government to mark special occasions. The Government followed the example of other European countries in entrusting overall charge of these displays to the military authorities. Hence, from 1613 to the end of the 18th century, important displays in London were in the hands of the Master-General of the Ordnance, at whose disposal were military equipment (mortars etc.) and trained and disciplined soldiers. Sometimes, however, presentation of the displays was delegated to others and on at least one occasion (1749) the result was conflagration and fiasco.

The military involvement led to the employment of pyrotechnists in the Ordnance Department, where they were known as Firemasters and to the manufacture of fireworks in the Royal Laboratory, which was the forerunner and eventually the headquarters, of the Royal Gunpowder Factories. Big displays were expensive: the one to celebrate the Peace of Ryswick in 1697 cost £12,000, a very large sum in those days. For the ill-fated celebration of the Peace of Aix-la-Chapelle in 1749 a total of 10,650 rockets, shells and pinwheels were made at the Royal Laboratory and the cost amounted to £14,500. A huge temporary structure was erected on 17 April 1749 in the northern part of St James's Park, now known as Green Park, for a firework display organised by the famous Italian pyrotechnist, Giovanni Niccolo Servandoni in collaboration with the Royal Laboratory at Woolwich, but the evening ended in chaos when

one wing of the structure caught fire. There was no further state display until 1814. In that year of peace the King of Prussia Tsar Alexander and the emperor of Austria's representative Prince Metternick, visited London were to see a brilliant display organised by Sir William Congreve (the younger), a close friend of the Prince Regent.

2.6.2 Incendiary Mixtures

The more serious aspects of military pyrotechnics can also be said to have begun in earnest in the 17th century. By the 17th century delivery of such mixtures was effected by firing a 'carcass' or 'fireball' from mortars or howitzers. An early type of fireball was a strong canvas bag filled with a mixture of 'meal powder and coal sprinkled with brandy or oil of petrol'. Later, such mixtures were fired in rockets. At the end of the 19th century incendiary mixtures were revolutionised by the availability of powdered aluminium. The capacity of elemental aluminium to reduce the oxides of other metals with the evolution of heat had been first noticed by Tissier in 1856 and later by Beketov in the 1860s, but the metal was then still rare and expensive. From 1895 Dr. Hans Goldschmidt took out patents for the production of metals from their oxides by reduction with aluminium. The mixture of iron (III) oxide with aluminium powder was given the proprietary name of Thermit, or Thermite and after some years of use as a commercial welding agent it became used in incendiary bombs. Military Thermite as used in aircraft bombs and shell during World War I typically consisted of 76 % (w/w) magnetic iron oxide and 24 % (w/w) aluminium. Once ignited, it was usually scattered by a small explosive charge for the best effect. The British aircraft-dropped 'Baby Incendiary Bomb', the 6.5-oz Mk IV, had a tin-plate body containing 'Daisite', a mixture of 57 % (w/w) Iron oxide, 17.5 % (w/w) aluminium and 25 % (w/w) sulphur. British incendiary 4.5 inch and 8 inch shell for use against easily flammable targets were filled with a complex mixture described by the traditional name of carcass composition. The World War I ingredients were mainly potassium nitrate, aluminium, sulphur and resin, with minor additions of antimony sulphide, tallow, turpentine and mealed powder. A number of British, French and German weapons contained white phosphorus (WP).

In World War II the Luftwaffe dropped 1 kg Thermite-filled bombs of magnesium alloy in large numbers on British cities and later the RAF dropped its 1.7 kg version on Germany on an even larger scale. The British filling was typically SR306 (SR - Superintendent of Research, RARDE, Fort Halstead), a Thermite modified by the addition of barium nitrate and a little boric acid. (The Americans called this type of filling Thermate). Both sides supplemented Thermite bombs with large ones containing thickened oil. The British also used benzole (commercial benzene) gelled by rubber and containing white phosphorus, sometimes with added sodium nitrate and aluminium. Such mixtures were known as phosphorus incendiary gels (PIGs). The total weight of incendiary bombs dropped on Germany by the RAF in World War II was 196,335 tons, compared with 234,312 tons of HE bombs. The Americans carried out a great deal of research into incendiary warfare. For close air support of land forces they developed the use of drop-tanks containing gelled petrol, dispersed by a

small HE charge and ignited by White Phosphorus. The most successful gelling agent was a powdered compound soap of aluminium naphthenate and aluminium palmitate devised by Prof. L.F. Fieser in 1943 and known as Napalm. This name in time became used to describe the whole filling. The incendiary bombs with which the USAAF destroyed large areas of easily flammable buildings in Japanese cities in 1945 were mostly of thickened oil or gelled petrol types. Napalm bombs have been used in many conflicts since World War II. Their tactical role is as much for killing or demoralising enemy personnel as for orthodox incendiary use against easily flammable targets. In general, white phosphorus and thickened petroleum fillings, including the flamethrower fuels used since World War I, are outside the definition of a conventional pyrotechnic. Among the more humane applications of heat-producing pyrotechnics In World War II was the British invention of self-heating food cans by Caldwell and Gillies and compositions for starting camp-fires in wet conditions.

2.6.3 Flare and Photoflash Compositions

Military pyrotechnic flares are used for two distinct tactical purposes, illumination of the surrounding terrain and as a visible signal to convey a pre-arranged message. Illuminating projectiles known as 'light-balls' were used by the British at least as early as the Napoleonic Wars (1799-1815). In about 1820 potassium chlorate was first used for colouring pyrotechnic flame in conjunction with appropriate metallic salts and signal flares then became practicable. According to a contemporary Prussian treatise on pyrotechnics, the British Navy used coloured rockets for signalling at sea, in ten different shades. It was later found that this was far more than could be reliably distinguished in all circumstances. Illuminating light-balls were fitted with parachutes by the time of the Crimean War (1853-6). The early flare compositions were of poor luminosity, but they were greatly improved from about 1865 by the inclusion of magnesium powder. In 1878 a new type of star shell was introduced into British Service, fired from a 6.3 inch mortar and containing 21 magnesium stars which gave good illumination. These shells were used successfully in the Afghan War of 1878-80 and in the campaigns on the North-West Frontier of India. British star shells were still being improved in the early 1900s and at about that time a pistol-sized version of the flare projectile was invented by and named after, Edward W. Very (1874-1910) of the US Navy. The use of pyrotechnic flares became very important during World War I, especially on the Western Front as the conflict degenerated there into trench warfare on a vast scale. Telephones were unreliable, radios few and any other form of signalling entailed exposure of personnel to enemy fire. The rapidly increasing use of aircraft also created a requirement for pyrotechnic signals. An example of the latter was wingtip flares containing barium nitrate, sulphur and aluminium for white light and strontium nitrate instead of the barium for red light. Illuminating flares still relied on barium nitrate/magnesium mixtures.

In Britain the large amount of hasty research and development necessitated by the World War I growth of pyrotechnics was carried out by the Research Department, Woolwich, which had been formed in 1907 to deal with problems of

ordnance originating from the Boer War. After the war the Department continued its pyrotechnics research in a fundamental way and by 1939 many definitive principles of modern pyrotechny had been established there, putting Britain in the forefront of the technology. One of the earliest discoveries, made in 1923, was that sodium nitrate, hitherto excluded from flare compositions because of its hygroscopicity, could, with suitable precautions, be used in magnesium flares in place of the usual barium nitrate, giving greatly improved luminosity. British illuminating flare compositions of the inter-war period, such as SR562 and SR563, comprising mainly magnesium and sodium nitrate, were used throughout World War II and for long afterwards. Work was also continued on coloured signal flares. The potassium chlorate in these was replaced, in most cases, by the less sensitive potassium perchlorate, the other ingredients being magnesium and an appropriate colouring salt. Another area of research was in photoflashes for aerial photography at night. This form of reconnaissance had been pioneered by the British in 1918. The early flash bombs contained mixtures of magnesium and/or aluminium with an oxidant salt, but this made an aircraft carrying such stores susceptible to instant destruction if hit by enemy fire, so ways were devised of dispersing the finely divided metals in the air where they were ignited as a dust cloud. As the duration of burning could be measured in milliseconds these were essentially fuel-air explosions.

2.6.4 Smoke Compositions

Smoke has been utilised since time immemorial for signalling and also for screening the activities of one military force from another. During the Napoleonic Wars 'smoke-balls' were fired from ordnance. In World War I screening smokes were used on land and at sea. Naval smoke-screens could be easily produced by reducing the air supply to the ship's furnaces. For use on land, smoke was disseminated from 'ground candles' or from shells or grenades. Smoke shells and grenades were mostly filled with white phosphorus. Ground candles used by the British typically contained potassium nitrate, pitch, sulphur, borax and glue. Towards the end of World War I the French and Americans used screening smoke mixtures of metal powders and chlorinated hydrocarbons and in 1920 Captain Henri Berger of the French Army patented the use of zinc powder with carbon tetrachloride. This and similar compositions became known as Berger mixtures. They continued to evolve in several countries and in the UK they took two different forms, of which one, the CTC type, contained Berger's original oxidant. The other type contained the closely related compound hexachloroethane which is, more conveniently, a solid and these were called the HCE type. The British Army used both types in World War II but preferred the HCE type, using mixtures of hexachloroethane, calcium silicide, zinc oxide and potassium nitrate, which were designated by such numbers as SR269M or PN800. The Americans used, up to 1941, a mixture called HC, more like Berger's original one and comprising zinc powder, hexachloroethane, calcium carbonate, ammonium chloride and potassium perchlorate. However, this frequently underwent spontaneous ignition upon ingress of moisture, so the Americans switched temporarily to the British HCE type. Later they substituted aluminium powder for the calcium silicide. Many

new screening smoke compositions have been developed worldwide since that time, but the HCE type, despite its disadvantages, was retained in the British Service until recently. Similarly there has been little change in the composition of British coloured signal smoke compositions, which were standardised on the potassium chlorate/lactose/volatile dyestuff mixture as far back as World War I.

2.6.5 Delays

Burning delay trains have always been an indispensable part of pyrotechny and of many explosive munitions, probably dating back to the early Chinese fireworks. Explosive cannon shell, from the Middle Ages onwards, incorporated a black powder time fuse and this device was improved, as were several others, by Col. Boxer in the 19th century. Black powder variants, pressed into drilled holes in shell fuzes or in the form of Bickford safety fuse, continued to be the only military delay composition throughout World War I and into the early part of World War II. By then the advent of high-flying bomber aircraft and the consequently increased altitude required of anti-aircraft projectiles, led to a requirement for ‘gasless' delay compositions and these were developed during World War II. However, the first use of gasless delays was by the Americans for grenades in about 1943, because the new delay compositions such as nickel powder/potassium perchlorate/superfloss and lead oxide/silicon were more resistant to damp conditions than was black powder. Since then a large number of non-black powder delay compositions and their related 'first-fire' mixtures have been developed, both for military and civilian pyrotechnic devices and for the burning trains in military explosive stores.

2.6.6 Black Powder in Military Pyrotechnics

This traditional mixture has served the purposes in both military and civil pyrotechny, of a 'primer' or 'igniter', a delay, a propellant, an expelling charge and a noise-making charge and in its mealed form is an ingredient of several other types of pyrotechnic. The ingredients of black powder, separately or two at a time, appear in many other compositions, but black powder combines, in a special way, several useful properties which are contributed by its constituents and which interact with those of the others. Black powder has a lower sensitiveness (see 20.2.1) to impact and friction than many other pyrotechnics. It is chemically compatible (see 20.4.1.1.1) with most (though not all) other pyrotechnic materials and with some High Explosives. It is also relatively cheap. However, black powder has some disadvantages as a pyrotechnic, just as it has as a propellant for guns and rockets and the two most serious ones are the reactivity of free sulphur and the hygroscopicity of charcoal. Modifications of black powder and attempts to replace it altogether, are therefore part of pyrotechnic history.

It has been shown in Section 2.1.4 how the standard 75/15/10 % w/w formulation was arrived at after several centuries, but certain roles of black powder require deviation from those standard proportions. In pyrotechnic rocketry it has long been recognised that the optimum composition of the propellant depends on the weight of the rocket. The powder in a typical World

War I signal rocket contained potassium nitrate 85 % w/w, charcoal 14 % w/w and sulphur 1 % w/w. Some military pyrotechnic rockets still have black powder variants as propellants, e.g. in the United States of America the standard 75/15/10 % w/w composition is slowed by an addition of 9 % w/w calcium carbonate. More usually, such stores nowadays contain a motor grain of single-base or double-base nitrocellulose propellant. The classification of a rocket as a pyrotechnic device depends on its size and function rather than on the nature of its propellant. Single-base propellants, though unsuitable for war-rockets, provide adequate Impulse for signal or illuminating rockets and are sufficiently cool-burning to be used with thin cases and cheap nozzle materials.

In contrast to the rocket propellant composition described above, a World War II black powder time-fuze composition, SR227, contained potassium nitrate 72 % w/w, charcoal 21 % w/w and sulphur 7 % w/w, a considerably different mix for a different role. In another role again, that of an igniter in the early cordite gun cartridges of the 1890s, the sulphur ingredient was suspected to be the cause of degradation of the cordite and so was omitted altogether, the new igniter powder being called ' sulphurless fine grain' (SFG). Its composition was potassium nitrate 70.5 % w/w, charcoal 29.5 % w/w. This powder is still used in British stores which contain other pyrotechnics, as a precaution against possible incompatibilities. The absence of sulphur makes SFG more friable than standard black powder and it is inferior in some other respects, but has some redeeming features.

The substitution of the charcoal in black powder by organic compounds has been attempted for several decades, but only a few candidate substitutes have been found which share the special properties of charcoal. The possibilities include tetranitrocarbazole, first tried by the Germans, potassium dinitrophenate and Bakelite moulding powder. Pyrotechnicians believe that traditional black powder may eventually be replaced by several compositions for different purposes, but not by a single, universal substitute.

2.6.7 Tracer and Incendiary Bullets

From the time of the introduction of elongated rifle bullets in the mid-nineteenth century there were proposals for filling them partly with substances other than lead, mainly for purposes of increased anti-personnel effect or damage to inanimate targets. However, the international humanitarian movement which arose from the sufferings of soldiers in the mid-nineteenth century wars resulted in the 1868 Declaration of St. Petersburg: this banned any projectile of a weight below 400 grams which was 'either explosive or charged with fulminating or inflammable substances'. The declaration was agreed by the major European countries and was reaffirmed in the 1874 Declaration of Brussels. Suggestions continued to be made of bullets of a 'non-ball' nature but there remained inhibitions about using them. Then, from January 1915, the Germans flew Zeppelin airships on bombing raids over Britain, causing civilian casualties. The British, regarding this as inhumane, responded with the use of incendiary machine-gun bullets against the hydrogen-filled craft and destroyed a few on an occasional basis. The Pomeroy bullets contained white phosphorus, which on

firing was squeezed out through slits in the jacket and ignited in flight. These bullets also had some tracer effect and from this developed the use of conventional tracer bullets, first for aerial warfare and later for infantry weapons. There was no international outcry and post 1918 efforts at arms control were concentrated on chemical warfare, which had caused far greater suffering.

The earliest conventional tracer bullets had a magnesium/oxidant salt/binder filling which did not ignite directly from the flame of the propellant and needed an igniter of magnesium/barium peroxide/binder behind it. This had the disadvantage of temporarily blinding the gunner and also giving his position away, so 'dark ignition' compositions were developed to avoid light emission over the first 100 m of trajectory. Another improvement was the use of less bright tracer bullets for night-time use than for daytime. Modern British tracer bullets contain potassium dinitrophenate/barium peroxide mixture. Present-day incendiary bullets contain a mixture of powdered magnesium alloy and barium nitrate. Some types of incendiary bullet, e.g. the De Wilde bullet of World War II, have contained both explosive and incendiary compositions, to scatter the incendiary filling on impact.

2.7 ACCIDENTAL EXPLOSIONS IN WORLD WAR I

By the end of the Great War the cumulative production of TNT in Britain alone had reached 238,364 tons and in addition large quantities of other explosives and propellants were produced. Manufacture on this scale, under difficult wartime conditions, increased the number of accidental explosions to well above the peacetime average. Official labour statistics give only the number of deaths in industrial accidents covered by the Explosives Act 1875 and therefore exclude accidents which occurred on Government premises. Nevertheless, they show an average of 67 fatalities per annum during 1914-18, compared with 9 per annum in 1911-13 and 5 in 1919-21. These figures do not include, for example, the biggest explosion of the war in Britain, which occurred at a TNT purification works in Silvertown, East London, on 19 January 1917 and involved 53 tons of TNT. This explosion, which was heard up to 120 miles northward, killed 73 people and demolished all buildings within 400 yards. The heaviest single death toll from the UK wartime accidents on land was 134 at Chilwell, Nottinghamshire, on 1 July 1918 and this figure also was excluded from the official statistics.

2.8 WORLD WAR I TO WORLD WAR II

2.8.1 Gun Propellants

The vast output and usage of gun propellants by the Great Powers in 1914-1918 provided certain lessons to be learned and in Britain this was done in time for 1939-1945 war insofar as limited financial resources allowed. One lesson was the desirability of developing a solventless process for the manufacture of Cordite, as had been done by the Germans in the Great War. This offered several benefits, including saving on solvents, stoving equipment,

factory space and energy. It would also avoid shrinkage of the propellant grains and remove residual solvent variation both of which factors otherwise have a limiting effect on ballistic reproducibility. Another dividend, not realised until some years later, was the potential use of solventless Cordites in large extrusions for rocket propellants. Solvent Cordites and single-base compositions were not suitable for this purpose because of the uneven shrinkage of the grains on drying and difficulty of removing solvent from large grains without producing internal cavities. However the solvent process is still in use for gun propellants.

The principles employed in the solventless process were not new: they had been employed by Nobel in the manufacture of Ballistite thirty years earlier. Nevertheless, new compositions for the two proposed Royal Navy Cordites had to be developed, these being called SC (solventless, carbamite-stabilised') and HSC ('hotter' SC) respectively. Also, a new plant had to be designed and built to cope with extrusion pressures some 12 times greater than those for solvent Cordites and precautions had to be taken against the consequently increased risk of fire or explosion during extrusion. Eventually Cordite SC was introduced in 1927 for naval use and was manufactured at the Royal Naval Cordite Factory, Holton Heath, Dorset.

For reasons of financial stringency and the accelerating pace of rearmament, the new Land Service propellant introduced in about 1934 had to be manufactured in the older plant at Waltham Abbey and was therefore made by the traditional solvent process. It was named Cordite W after its place of manufacture. In fact the composition was little different from the Cordite MD of the Great War. Only the stabiliser, carbamite, was new and in 1940, when wartime supplies of carbamite were running low, the change had to be partly reversed. Some of the carbamite was replaced by the original mineral jelly and the resulting composition was called WM ('Waltham Modified'). Although Cordite WM was intended only as a temporary substitute it continues to be used in some countries to the present day.

During World War II, as in the previous war, the British used large quantities of imported American single-base propellants. These were called NH ('non-hygroscopic'), FNH ('flashless NH') and M/P (containing potassium sulphate). They were extruded and chopped in the form of short grains and were therefore more convenient than stick Cordites for filling narrow-necked cartridge cases.

Another lesson, not new but re-emphasised in the Great War, was the necessity of developing artillery propellants, which produced less flash than did conventional Cordites. Work already done on this problem before 1914 suggested that metallic salts mixed with the propellant, or loaded in contact with it, reduced flash but also caused an undesirable increase of smoke. In Britain research into so-called 'flashless' propellants (a subjective and somewhat misleading term) was resumed by the Research Department in 1921. It eventually led to the principle of increasing the nitrogen content of the propellant and hence of the muzzle gases, while at the same time lowering the combustion

temperature. To achieve these ends a third High Explosive ingredient, nitroguanidine, was added to the traditional Cordite composition, giving a new series of propellants called triple-base types. For security reasons nitroguanidine was given deliberately misleading pseudonyms: it was at first called 'Petrolitel, then when the particle size was reduced it was called 'Picrite'.

The most promising of the new propellant compositions, first tried in about 1928, was called RDN (N standing for 'Nolite') and contained 55 % (w/w) of nitroguanidine. Production of this propellant began in the late 1930s. Following a succession of small changes to its composition and designation, the standard Land Service version was finally designated Cordite N in 1941 and its 'hotter' counterpart as Cordite NQ. These propellants were used extensively in the latter part of World War II. The name 'Cordite' was officially dropped from all designations in 1950 in favour of 'propellant'. The Royal Navy, like the Army, changed from double-base gun propellants to triple-base ones during World War II, but the Navy has preserved its independence in the matter of compositions and designations. Hence the Naval versions of N and NQ had slightly different compositions and from 1947 were known as NF and NQF respectively. (The suffix F dates back to 1936 and denotes nitrocellulose made from wood cellulose). Later, when the manufacturing process for the Naval propellants was changed to the 'semi-solventless' process, the prefix M ('modified') was added, making the designations MNF and MNQF respectively, although the compositions were unchanged. Nowadays the UK has lost the capacity to make either nitrocellulose or nitrate ester gun propellants and the relevant UK service compositions are country of origin dependant.

2.8.2 Military High Explosives

Nearly all the military High Explosives mentioned in earlier paragraphs were those used in the British Service and represent the mainstream of High Explosive (HE) development, namely a succession comprising guncotton, picric acid, TNT and Amatol. The British Service was traditionally cautious in its choice of explosives and a composition was approved for service only after lengthy trials of various kinds. Financial considerations, though never ignored, did not take precedence over questions of safety, reliability and performance. Other countries, however, did not always arrive at the same conclusions as the UK in the choice of HEs, so a number of High Explosive compounds have been used, or at least tried, abroad which have not hitherto been mentioned in this Chapter. They include the following:

- 1,3,5-trinitrobenzene (TNB)
- Trinitronaphthalene (Naphthite, or TNN)
- Hexanitrobiphenyl
- Hexanitrodiphenylamine (HND or Hexyl)
- Trinitrocresol (Cresylite)
- Ammonium trinitrocresylate (Ecrasite)
- Trinitroanisol
- Hexanitroazobenzene (HNAB)

- Nitrostarch
- 2,4,6-trinitrophenylnitraminoethyl nitrate (Pentryl)
- Hexanitrodiphenyl sulphide
- Ethylenedinitramine (EDNA, or Haleite)

In addition to these single compounds there have been numerous mixtures of them, or of other explosive compounds, with ammonium nitrate or ammonium perchlorate. These two oxidants are powerful explosives in their own right, though ammonium nitrate is a very insensitive one. Ammonium perchlorate was used from early in the 20th century, originally in commercial blasting explosives. Barium nitrate has been used in both civil and military explosives, its most notable military mixture being with TNT and called Baratol. Mixtures of picric acid and TNT, not used in the British Service, were called Picratol. Mixtures of Tetryl with TNT were called, in the USA, Tetrytol, or in the British Service simply CE/TNT.

2.8.2.1 RDX

After World War I the Research Department, Woolwich, sought a new military High Explosive which would be superior to TNT in power and detonation velocity and equal to it in stability. Moreover, it should be compatible with TNT with a view to possible mixtures or composite systems of the two. Attempts made to synthesise hexanitrobenzene proved unsuccessful and the resulting PETN was at first rejected on safety grounds. Finally the Research Department chose cyclotrimethylenetrinitramine, or in more modern terminology 1, 3, 5-trinitro-1, 3, 5-triazacyclohexane, a nitramine High Explosive which was given the designation RDX. (It is said that the 'X' originated when the Research Department (RD) list of explosives, from which the new candidate compound was to have been numbered, was temporarily unavailable and that 'X' was eventually retained because of the derivation of the explosive from hexamine). RDX was first prepared by the German Henning in 1899. He does not appear to have realised its explosive properties, but thought the compound might be useful in the treatment of heart disease. It was patented as an explosive by von Herz in 1920.

The development of a suitable manufacturing process for RDX took the Research Department some years to accomplish, but it was done in time for World War II and production began at ROF Bridgwater in 1939. The Americans and Italians had failed in their own attempts to develop a manufacturing process in the same period, but during the war the British enabled the Americans to adopt the so-called Woolwich process. The Americans called the explosive Cyclonite and the Italians designated it TA. The Germans succeeded in developing their own version of the Woolwich process before the war. They called the explosive Hexogen and used it to a considerable extent.

RDX was found to be an excellent and versatile explosive, but too sensitive to be used in an unmixed state. It could, however, be desensitised in several different ways. For plastic demolition charges it was mixed with various soft, inert materials (phlegmatisers), while for the poured fillings of shell and bombs it

was mixed with TNT. In the USA this mixture was called Cyclotol, or if containing wax, Composition B. Mixtures of RDX, TNT and aluminium were found to be useful high-blast explosives for torpedoes and aircraft bombs and from the former use the UK generic name 'Torpex' was derived. The American equivalent was HBX and the German one was Trialen. The World War I mixtures called Amatols, which were re-introduced in World War II, could be made more sensitive by the addition of a little RDX and these became Amatex. The Royal Navy version of Ammonal, called Minol from its use in sea-mines, became Minolex when similarly sensitised.

2.8.2.2 PETN

The High Explosive pentaerythritoltetranitrate (PETN or Penthrit), first prepared by Rheinisch-Westfaelische Sprengstoff AG in 1894, was investigated by the Research Department in the 1920s but was at first judged to be too sensitive and moreover was not quite as stable as TNT. (PETN is a nitrate ester and these compounds as a class are less stable than nitrocompounds). Despite this original decision, PETN became used in the British Service in several ways during World War II. It was manufactured by the Nobel Co. for the filling of detonating cord and also for some of the earliest plastic demolition explosives, e.g. Nobel's 852. Some foreign-made British 20 mm cannon shell contained the mixture of PETN and TNT called Pentolite and Pentolite desensitised by paraffin wax and nitrocellulose was used in British 40 mm shell under the name of 'Pen D'. The demolition explosive Nobel's 851 consisted of Pentolite 50/50 plasticised with dibutylphthalate and nitrocellulose. During WWII the Germans used desensitised PETN widely for exploder pellets. They also used PETN as a substitute for nitroglycerine in small arms propellants.

2.8.2.3 Primary explosives after WW1

In the period between the wars the search continued for a replacement cap composition for small arms ammunition (SAA), not only because of the shelf life problem with fulminate but because the traditional use of potassium chlorate compositions caused corrosion of the bore in small arms. That these compositions were still in use in more than one country after nearly a century following their first development is shown by data from the 1925 Textbook of Explosives shown in

Table 2-4.

Table 2-4 SAA Cap Compositions Used in Britain and Austria in 1925

	British % (w/w)	Austrian % (w/w)
Mercury fulminate	19	14
Potassium chlorate	33	42
Antimony sulphide	43	34
Gunpowder	2.5	-
Sulphur	2.5	-

Powdered glass	-	10

For a time lead thiocyanate, then favoured in the United States of America, was tried by the British as a replacement for mercury fulminate in the role of sensitiser, but was later rejected. One composition which included it was S.9, as shown in Table 2-5.

Table 2-5 Example of a Thiocyanate Containing Cap Composition (S.9)

Potassium chlorate	24.5 % (w/w)
Antimony sulphide	49.5 % (w/w)
Lead thiocyanate	24.5 % (w/w)
Lead dioxide	1.5 % (w/w)

2.8.2.4 British small arms propellants since WW1

Small arms propellants are not subject to the requirement of minimal flash, but regular ballistics and a long shelf life are obviously necessary and, with the increased use of automatic weapons during and since World War II, low erosiveness is also important. In the 1914-1918 war the propellant in most British 0.303-inch ammunition was MD/T and this was superseded by CD/T, almost identical in composition. Then developments in automatic weapons between the world wars necessitated a 'cooler' and more easily loaded propellant. Imperial Chemical Industries (Nobel Division) developed progressive-burning, single-base propellants called Nobel's Rifle Neonites (NRN). These powders were made on a large scale in this country during World War II and NRN 41 is still in use for 7.62 mm ammunition. For other British small arms some double-base propellants are used.

2.8.2.5 Rocketry between WW1 and WW2

War-rockets were little used in the 1914-18 war. One instance worthy of note was the work of a French naval officer, Lt. Y.P.G. Le Prieur, who developed for the Western Allies, rockets fired against German observation balloons and airships from tubes on the struts of biplanes This was probably the first-ever use of air-to-air rocket missiles. The rockets were fired electrically from the interplane struts supporting the wings of biplanes via a cockpit switch. The switch would launch all the rockets consecutively. The rockets were generally fired at a range of 100–150 metres with the aircraft at an inclined dive angle of 45 degrees. The steeper the dive the straighter was the trajectory and the more accurate the attack. Attacks were made in the direction of the length of the balloon and against the wind, the pilot taking aim via the plane's existing gun-sight. However, the ignition and discharge of each rocket did not occur immediately and a delay varied slightly from one rocket to another. Thus the pilot had to continue to hold the target in his gun-sight and the dive continued until the last rocket discharged.

The rockets successfully brought down observation balloons, but never managed to bring down a Zeppelin, although it was used to defend the United Kingdom from Zeppelin raids. Le Prieur rockets were also used in a ground-to-air role.

2.8.2.6 Russian and German rocket propellants

It is believed, though not proved, that the Germans used rocket-assisted shells in their ultra-long range bombardment of Paris in 1918. From this low state of the art there was a phenomenal development of rocket technology over the next 40 years and rocket propellants proliferated even faster that did gun propellants in the corresponding period of their history, say 1865-1895.

In 1921 some of the territory of Soviet Russia had only very recently been vacated by foreign counter-revolutionary forces. The Communist Government, still feeling itself under threat, took steps to re-arm its forces in the long term with weapons superior to those which had led to the disastrous defeats by the Germans in the Great War a few years previously. The Russians opened a rocket laboratory, later moving it to Leningrad and began to experiment with Cordite as a rocket propellant. The propulsive effect of Cordite is about three times better than that of black powder. Five years later, in 1926, the historic first flight of a liquid-propellant rocket was achieved by the American Dr. Robert Hutchings Goddard (1882-1945), who had been experimenting with rockets since 1912. He used as propellants petrol and liquid oxygen (LOX). Although Goddard's pioneering experiments of the late 1920s were small in scale and were hampered by lack of money and of official encouragement, both Russia and Germany took great interest in them. In 1928 the Leningrad rocket laboratory was renamed the Gas Dynamics Laboratory (GDL). Its work was expanded and by 1930 the Russians had made progress in the rocket-assisted take-off of aircraft, had constructed an 82 mm aircraft-launched rocket and were developing an anti-tank rocket. In 1929 the GDL started building liquid-propellant rocket motors, using petrol and toluene as fuels and LOX and dinitrogen tetroxide as oxidants. The first test flight of a Russian liquid-propellant rocket took place in 1933. By 1936 the Russians were using kerosene and nitric acid as a bi-propellant system. From then on their work was subjected to strict censorship, but it is believed that the liquid-propellant rocket development was aimed mainly at the assisted take-off of aircraft. There was an attempt in 1940-1 to develop a fighter aircraft powered by a kerosene-nitric acid rocket motor, but after flight tests the project was abandoned. As war with Germany became increasingly probable the Russians put ever greater efforts into the development of small, Cordite-propelled missiles. The 1.8 m long, 42 kg BM-13 or Katyusha rocket was developed in great secrecy by A.G. Kostikov and was manufactured from 1941, just in time for use in the defence of Moscow against the Germans. Numerous variants of the BM-13 were produced. Later in the war 82 mm and 132 mm aircraft-launched Cordite rockets were used extensively. The Russians did not use any liquid-propelled missiles during the war because of the German occupation of many of their industrial areas and because of the overriding need to produce simpler forms of ammunition in enormous quantities.

In Germany in the 1920s there was great interest in rocketry, both among scientists in connection with proposed space travel and among military men for new types of armament which would circumvent the 1919 Treaty of Versailles. These two objectives tended to merge, in that certain talented civilian rocket enthusiasts were induced by the German army to work for them. The leading figure from 1930 was Capt. (later General) W.R. Dornberger and from 1932 his chief collaborator was Dr. Wernher von Braun (1912-77). Work was started on the utilisation of Goddard's invention as the propulsion unit in bombardment rockets for a future war. Some bi-propellant motors fuelled by ethanol/water and LOX were developed, first at Kummersdorf-West near Berlin and from 1937, when German rearmament was well under way, at Peenemünde off the Baltic coast. This work culminated in the large-scale production of the 13 tonne V2 (or A-4) rocket missile which was used for the bombardment of England and Belgium in 1944-5, in numbers of some 4,000 rounds. In a separate programme Prof. Helmuth Walter of Kiel worked on various forms of liquid-propellant rocket motor, one of which was used to power the Messerschmitt Me 163B interceptor fighter. Unlike its Russian counterpart this project was brought to a successful conclusion and the aeroplane, despite numerous accidental losses due to fuel explosions, was used in some numbers during 1944-5 and remains unique as the only rocket -propelled fighter ever to have flown operationally. Its bi-propellant motor burned ‘C-stoff’ (a 30 % v/v) solution of hydrazine hydrate in methanol) and ‘T-stoff’, (an 80 % v/v) hydrogen peroxide solution mixed with various hydrocarbon stabilisers).

Concurrently with the previously-mentioned work, the Germans developed several liquid-fuelled rockets for anti-aircraft defence and a large number of Cordite types for infantry use, artillery, anti-aircraft defence, etc, with calibres of up to 38 cm. The largest of these was the three-stage Rheinbote artillery missile of 1944, 11.4 m long and weighing 1.7 tonnes.

Some of the German solid propellants used during the war contained di-ethylene glycol dinitrate (DEGDN) in preference to nitroglycerine, this being a traditional feature of German propellant technology.

2.8.2.7 British and American rocket propellants

In the United Kingdom no work was done on military rocketry between World War I and 1934. In that year Gen. Sir Hugh Elles, Master-General of the Ordnance, acted on reports of German progress in solid rocket propellants and directed a review of their potential application to British weaponry. As a result of this a Rocket Advisory Committee was set up in 1936. Dr. (later Sir) Alwyn D. Crow, Director of Ballistics Research at Woolwich, had advocated the use in rockets of solventless Cordites similar to the naval gun propellant SC ('solventless, carbamite- stabilised'). Some experience in large-diameter Cordite extrusion had already been gained in producing propellants for the catapult launching of aircraft from Royal Navy ships. Rocket Cordites were developed from 1936, originally intended for use in a proposed anti-aircraft rocket barrage system, the Z batteries. The definitive propellants which emerged were Cordite SU ('solventless, unrotated') and its low-flash variant SU/K (containing

potassium cryolite). New presses had to be built for the extrusion of these compositions in diameters of 70 mm (2.75 inches) for the 76 mm (3 inch) unguided anti-aircraft missile and propellants were also produced for the 51 mm and 76 mm air-to-surface missiles and 127 mm bombardment types ('mattress' systems) used by the Army and the Royal Navy. A different rocket Cordite, called RS and containing only 28 % w/w NG as against the 41.5 % w/w in SU, was manufactured for supply to Russia. Comparatively little work was done in Britain during the war on liquid rocket propellants: some effective motors were built in 1941-2 but were not put into operational devices.

In the United States Goddard continued to improve and fly his liquid-propellant rockets right up to 1941, the year in which the United States of America entered the war, but still without attracting Government interest or support. Moreover, the United States Government had not instigated any work on solid rocket propellants until 1939 and so the Americans were well behind the other fighting powers when Japan declared war on them. However, they then made rapid progress and had a number of operational solid-propellant systems by 1945. They were also beginning to develop liquid-propellant missiles.

The German development of the V2 rocket and an even more ambitious project for an inter-continental ballistic missile (ICBM), was interrupted by Allied bombing in 1943 and the plants were therefore dispersed. In 1945, when Germany was invaded from the east and west by the Russians and Americans respectively, each of these Allies captured enough technicians, documents and hardware to assist further development in their own countries. In particular the USA secured the services of Dornberger and von Braun. Thus the former Allies, now becoming mutually hostile, both produced a succession of improved liquid-propellant missiles which became the first-generation ICBMs and satellite launchers of the late 1950s and both nations went on to achieve manned space flight in the following decade. The vanguard of rocket technology, which had started with ambiguous purpose in pre-war Germany, had passed through an unambiguously military phase and returned to a dual role in the post-war period.

The Americans emulated the Germans from 1946 onwards in adapting rocket propulsion to high-speed aeroplanes. The Bell X aircraft were not fighters as was the Me 163B, but aerodynamics research types. The early X-1 and X-2 were powered by ethanol/LOX motors. The later X-15, which flew until 1967, burned liquid ammonia and LOX and reached heights up to 107 km (66 miles) and speeds up to Mach 6.7 (4520 mph). As with the Me 163B there were some fatal accidents due to the nature of the propellants.

2.9 DEVELOPMENTS SINCE WW2

2.9.1 Rocket Propellants

2.9.1.1 Composite solid rocket propellants

During the latter part of the war and for many years afterwards, work was done in the United Kingdom and the United States of America to develop solid rocket

propellants superior to the Cordites. The latter, which are nowadays more usually called double-base or colloidal propellants, had a serious disadvantage in that the propellant grain had to be a loose fit in the motor case, to allow for differential thermal expansion during temperature changes in storage and use. This effectively lowered the important ratio of propellant weight to all-up missile weight. It was thought that if separate fuel and oxidant constituents, instead of two High Explosives, were mixed to form a 'composite' propellant (to which category gunpowder belongs), the judicious choice of a fuel/binder material would permit better designs of motor.

Plastic composite propellants were the favoured British rocket propellants in the 1950s and 1960s and were used in, for example, the boost motors for the now obsolete Thunderbird surface to air missile, the Gosling boost motors for Bloodhound and the rocket motors Raven and Stonechat.

Plastic propellant consisted of a thermoplastic fuel/binder and the oxidant ammonium perchlorate. The usual fuel/binder was polyisobutene (PIB): sometimes, with the addition of ethyl oleate as a plasticiser to improve the low temperature mechanical properties. Some plastic composites have contained polyvinylchloride (PVC). To manufacture PIB and PVC plastic composites the polymer was first dispersed in a heated plasticiser such as dioctyl sebacate to give a mixture known as a plastisol, which is then mixed with the oxidant prior to extrusion and cooling. The plastic propellant was extruded into the motor case, leaving a small axial conduit which was then enlarged to a star cross section, or some other fairly simple shape, by forcing an appropriately shaped mandrel through the centre and then withdrawing it. Plastic propellants had densities between 1.65 g cm^{-3} and 1.75 g cm^{-3}. The maximum practical grain size was limited by the tendency of the propellant to deform under its own weight. Grains up to 57 cm diameter and weighing 1 tonne had been made in the UK. At ordinary humidity levels, plastic propellants produced a moderate amount of smoke containing hydrogen chloride. Plastic propellants burned reliably at temperatures down to –30 °C although their performance was somewhat degraded below about 0 °C.

Polybutadiene propellants were developed in the late 1950s. Polybutadiene consists of a polymer chain which can be either carboxyl terminated (CTPB) or hydroxyl terminated (HTPB). The two types differ in the method of cross linking and HTPB propellants had longer shelf lives. HTPB propellants were and are the most widely used composites in British systems; historic examples range from the Hoopoe motor for the Sky Flash air to air missile and the motor for the LAW 80 light anti tank weapon which burned for only 12 ms. The rocket motors currently used in the ASRAAM and Sea Viper missiles use this propellant type. Cast HTPB propellants have the best low temperature strain capabilities of all solid propellants. They have an extensibility of up to 40 % between +20 °C and -20 °C and this falls only to about 150 % at -60 °C, so they can be safely case bonded for any ambient temperature likely to be encountered.

Much research had been carried out in the United Kingdom up to the late 1970s to improve plastic propellants but by that time rubbery composites had been

found superior, especially in their low temperature mechanical properties. Consequently, plastic propellants then had few applications in military rocketry.

From 1942 the Americans developed plastic composite propellants, the earliest of which contained asphalt and oil as the fuels and potassium perchlorate as the oxidant. Later, when larger motors were required, they found that plastic composites in large diameters were apt to deform under their own weight, so they used instead rubbery polymers as the fuel/binder ingredient. In instances where it was necessary to reduce the energy content of the propellant and its rate of burning, this was achieved by increasing the fuel:oxidant ratio and non-explosive additives, in preference to using ammonium picrite. For many composite propellants, however, there was an opposite requirement, that is, to increase the energy content and this was done by adding aluminium, boron or compounds of boron.

2.9.1.2 Cast double-base rocket propellants

The sub-division of solid rocket propellants into colloidal (double-base) and composites did not end there. During World War II the Germans had experimented with cast propellant grains to retain the advantages of colloidal compositions without the limitation of diameter imposed by the extrusion process. They used formulations such as TNT 50 % w/w DEGDN 17-18 % w/w, NC (12.2 % N) 28-29 % w/w, diphenylamine 0.5 % w/w and carbamite 0.5 % w/w. From these they produced rocket motor grains up to 100 cm long and 53 cm in diameter. The more successful development of cast double-base (CDB) propellants in the 1950s was followed by a further innovation, the incorporation into CDB propellants of ammonium perchlorate and aluminium and such types were called composite-modified cast double-base (CMCDB) propellants .The ammonium perchlorate makes up the oxygen deficit introduced by using nitrocellulose, improving the overall specific impulse. The aluminum also improves specific impulse (see 13.2.3) as well as combustion stability. High performing propellants such that used in Trident D-5, replaced most of the AP with HMX, further increasing specific impulse. The mixing of composite and double base propellant ingredients has become so common as to blur the functional definition of double base propellants. A variant on the theme is Elastomer Modified Cast Double Base (EMCDB) propellants. Here the addition of an elastomeric binder such as cross linked polybutadiene to a CMCDB gives further improvements to the mechanical properties of the propellant, along with a smokeless exhaust.

2.9.1.3 British rocket propellants

As mentioned previously, little work was done on liquid rocket propellants in the UK during World War II. For a time afterwards there was much interest in the relatively successful results achieved by the Germans and during this period the British built and flew two ethanol/LOX research missiles, the RTV-1 and 2. Then UK policy was re-directed towards anti-aircraft defensive systems, which had been the original starting point some twelve years previously, but by now missiles were much larger and control and guidance systems existed. In

defensive systems immediate readiness for use is important and solid propellants satisfy this requirement better than liquid ones do. Hence three important and long-service British surface-to-air missiles, the English Electric Thunderbird (developed from 1949), the Bristol Bloodhound I (developed 1949-1958) and the Hawker Siddeley Seaslug (developed 1949-1962), did not have liquid propellant rocket motors. Instead, all three had solid-propellant boosters, the Thunderbird and the Seaslug having also a solid-propellant sustainer motor while the Bloodhound II, which had been in RAF service since 1964, had two ramjet sustainers. Ramjets, although relying on rocket boost to reach their operating speed, are well-suited to instant readiness roles and this concept was continued with the Hawker Siddeley Sea Dart missile developed from 1962. Two British-built military missiles of the same period had liquid-propellant rocket motors. One was the intermediate-range ballistic missile (IRBM) De Havilland Blue Streak, which had a single stage of two motors burning kerosene and LOX. This project was cancelled in 1960 before flight testing was started. The other missile was the Avro Blue Steel, an air-launched, nuclear-tipped type which had a kerosene/hydrogen peroxide motor and was developed between 1957 and 1960 for use with the RAF V-bomber force. A British-built satellite launcher, the Bristol Siddeley Black Arrow, four examples of which were flown between 1969 and its abandonment in 1971, also had kerosene/hydrogen peroxide propulsion for the first two of Its three stages.

2.9.1.4 American rocket propellants

In the latter part of the twentieth century Britain acquired some large rocket missiles from the USA, some of which have had liquid-propellant systems and some solid. The Douglas Thor, a 50-tonne IRBM deployed by the RAF from 1959, had kerosene and LOX propellants. The JPL Corporal, in service with the Royal Artillery (1957-1967), had as fuel a mixture of ethylaniline, furfuryl alcohol and hydrazine, with inhibited red fuming nitric acid (IRFNA) as oxidant. A problem with hydrazine was its high freezing point of 2 °C thus the Americans began to add unsymmetrical dimethyl hydrazine (UDMH) to hydrazine in order to depress the freezing point. In due course UDMH became a rocket fuel in its own right. The Vought Lance missile, which entered service with the Royal Artillery in 1972, has a UDMH/IRFNA bi-propellant system. American solid-propellant missiles in British Service have Included Honest John (developed 1961-1975) and Polaris, which first flew in 1965. Other important American missiles, not exported to Britain, include Atlas (developed 1951-60) and Titan I (developed 1957-62), both of which have kerosene/LOX propellants and Titan II which has a hydrazine/UDMH/dinitrogen tetroxide system. None of the Western military missiles contains the all-cryogenic liquid hydrogen/LOX system, even though it provides a higher specific impulse that any of the combinations already mentioned. This system has been used only in the upper stages of space vehicle launchers, beginning in about 1960 and in the main engines of the American space shuttle. Some large American ballistic missiles with primarily solid propulsion systems include Minuteman, Peacekeeper (formerly MX) and Pershing.

Many American tactical missile systems such as AMRAAM feature composite propellant rocket motors, For instance AIM-120 AMRAAM is powered by a high-performance rocket motor using reduced smoke HTPB (hydroxyl terminated polybutadiene) propellant.

From what is known of Russian liquid rocket propellants since World War II the preferred types are those of the mainstream British and American developments and the Russians have devoted less research than the Americans into expensive and often elusive improvements.

2.9.2 Military High Explosives

2.9.2.1 HMX

Some time after the production of RDX by the Woolwich process had begun, it was noticed that a crystalline substance akin to RDX was being formed as an impurity to the extent of about 0.1 % w/w. This substance was found to have the same elemental composition as RDX but a relative molecular mass (or molecular weight) one-third higher and also a higher density. The compound was designated HMX (high molecular weight X). Its chemical name is 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane. During the war, when the Americans started the new Bachmann process for RDX production they found that HMX was formed to the extent of about 5 % w/w of the RDX yield. This enabled investigation of its explosive properties, upon which it was found that HMX had a higher velocity of detonation than that of RDX. This fact, together with the higher density, made HMX marginally superior to RDX for certain special purposes. Modifications to the Bachmann process were made in order to increase the yield of HMX and a recrystallisation process was developed to produce the HMX in its preferred β - form and free of RDX. In the UK this work was successfully concluded in 1955 when factory production of HMX was established. The cost of HMX has remained about three to four times higher than that of RDX, which in turn is many times higher than that of TNT. HMX is more sensitive than RDX and is normally used in mixtures with TNT or polymers. UK manufacture of HMX ended with the closure of the Bridgwater factory in 2007.

2.9.2.2 HNS

Hexanitrostilbene (HNS) was developed at the U.S. Naval Ordnance Laboratory in the 1960s. It has a chemical name 1,3,5-trinitro-2-[2-(2,4,6-trinitrophenyl)ethenyl]benzene. It is a yellow-orange solid with a melting point of 316 °C. It is produced by oxidizing trinitrotoluene (TNT) with a solution of sodium hypochlorite. HNS boasts a higher insensitivity to heat than TNT and like TNT it is insensitive to impact. HNS can be used as anti-crack additive, typically at concentrations of ~0.5 % w/w, in TNT or TNT-RDX charges forming micro-crystals within the TNT. It has a detonation velocity of 7000 m/s. Because of its insensitivity and good High Explosive properties, HNS is used in cap relays, detonating cords, transmission cords and booster charges. Thanks to its excellent thermal stability, HNS has been used in perforating and cutting

charges for oil and gas industry when the requirement of high temperature resistance is important. HNS has also been used in space missions; the Apollo 17 mission utilised plastic bonded explosives composed of HNS and Teflon in seismic charges.

2.9.2.3 NTO

3-Nitro-1,2,4-triazol-5-one (NTO) is an explosive ingredient that was investigated as a potential insensitive replacement for RDX in explosive formulations. Although its performance is slightly less than that of RDX, NTO is thermally more stable and less sensitive to hazard stimuli. Manchot and Noll first prepared NTO in 1905 by nitration of 1,2,4-triazol-5-one (TO). A viable synthesis route was reported by Russian workers in the late 1960s. Major interest in the explosive characteristics of NTO, however, developed in the mid-1980s, using a synthesis route based upon the Russian route which involved the reaction of semicarbazide hydrochloride with formic acid followed by a mixed acid nitration. It was not until 1987 that the explosive properties of NTO were widely reported. NTO has improved performance over that of TATB and is much less sensitive to hazard stimuli than RDX. For instance NTO is less sensitive to impact than PETN, RDX, HMX and TNT but more sensitive than TATB. Similarly NTO is less sensitive to friction than PETN, RDX, HMX and TNT and showed similar sensitiveness (see 20.2.1) to TATB. Also it is less sensitive to ignition by electrostatic discharge than RDX and TNT (>4.5 Joules). Data generated in France indicated that the velocity of detonation of NTO (8510 m s^{-1}) was less than those of RDX (8850 m s^{-1}) and HMX (9100 m s^{-1}), comparable with that of PETN (8500 m s^{-1}) and greater than that of TATB (8000 m s^{-1}). NTO in mixtures with DNAN and RDX is used in IMX 104, a standard US fill for artillery shells.

2.9.2.4 TATB

TATB, triaminotrinitrobenzene or 2,4,6-triamino-1,3,5- trinitrobenzene is an aromatic explosive, based on the basic six-carbon benzene ring structure with three nitro functional groups (NO_2) and three amine (NH_2) groups attached, alternating around the ring. TATB was first described in 1888 albeit at that time there was no mention of its use as explosive. In the mid-1950s, the US Navy's White Oak laboratory investigated TATB for use in conventional weapons. TATB was made in pilot plant quantities and its explosive properties were tested at White Oak. TATB is a temperature resistant explosive that is stable at temperatures that exceeded 260 °C. It is a reasonably powerful explosive (somewhat less powerful than RDX, but more so than TNT), but it is extremely insensitive to accidental stimuli. Because of this it has become preferred for applications where extreme safety is required. TATB is normally used as the explosive ingredient in plastic bonded explosive compositions, such as PBX-9502 (95 % w/w TATB / 5 % w/w Kel-F), LX-17-0 (92.5 % w/w TATB / 7.5 % w/w) Kel-F) and PBX-9503 (80 % w/w TATB / 15 % w/w HMX / 5 % w/w Kel-F). Because of its relatively low power it has not been widely accepted for use as a main charge in conventional weapons. It has, however, been

extensively used in booster applications in formulations such as PBXN-7 (35 % w/w RDX / 60 % w/w TATB / 5 % w/w) Viton).

2.9.2.5 ADN

Ammonium dinitramide (ADN) is the ammonium salt of dinitraminic acid. It was originally invented in the Soviet Union in 1971 at the Zelinsky Institute of Organic Chemistry in Moscow, but remained classified until it was discovered independently in the United States in 1989. ADN can be synthesized by different methods, one of which is based on direct nitration of salts of sulfamic acid by ordinary mixed acids (sulphuric and nitric), followed by neutralization and separation of the ADN formed. ADN entered pilot plant production at Eurenco Bofors in Sweden in 1996, on license from FOI. It has a density of 1.81 g/cc and a melting point of 93°C starting to decompose at approximately 150°C. Ammonium Dinitramide is a potential replacement for ammonium perchlorate in composite propellants. It has additional potential as an ingredient in LOVA propellants and as a melt cast matrix for High Explosives. When detonated, pure ADN has a large reaction-zone length and shows a strong non-ideal behaviour. ADN does not contain chlorine; therefore a composite rocket propellant containing ADN and a polymer binder produces minimal smoke and is more environmentally friendly compared with propellants based on AP. However, there are some drawbacks: ADN is relatively shock sensitive and is also sensitive to light and moisture

2.9.2.6 DNAN

One of the first recorded uses of 2,4-Dinitroanisole (DNAN) in ordnance was as a main charge ingredient in Amatol 40 (50 % w/w DNAN, 35 % w/w ammonium nitrate, 15 % w/w RDX) in the warhead of some V-1 flying bombs during World War II. Its use was not necessarily due to any performance gains, but more likely to its availability when higher performance materials such as TNT were becoming increasingly scarce. Two main reasons existed for ongoing interest in DNAN. Firstly, as a less sensitive melt-cast medium than TNT, opportunities exist for the development of less sensitive melt-cast formulations than those presently incorporating TNT. The impact sensitivity of DNAN was found to be very low (Figure of Insensitiveness >200) (see 20.10.2.1), but pure DNAN was found to be more friction sensitive than TNT). The second reason for interest in the material was that it was categorised as a Dangerous Goods Class (DG) 4.1 “Flammable Solid” and was therefore subject to less stringent transportation requirements than DG 1.1 “Explosive” materials, such as TNT. The melting point of DNAN is high (94-95 °C) compared to that of TNT (78-81 °C) and whilst it could be used for casting at this temperature, the melting point could be depressed readily by several degrees through the addition of small quantities of melt-soluble additives such as N-methyl-4-nitroaniline (MNA). DNAN is highly oxygen deficient even when compared to TNT and exhibits much lower crystal density (1.34 g cc^{-1} versus 1.60 g cc^{-1}). These factors militated against its effective use as a stand-alone explosive and historically DNAN has only featured as one of several ingredients in explosive formulations. For example, it is in US service mixed with NTO in IMX-101 for artillery shell fills.

2.9.2.7 CL-20

Hexanitrohexaazaisowurtzitane, also called HNIW and CL-20, is a nitramine explosive developed by the Naval Weapon Centre at China Lake (hence the CL designation), California in 1986 by Arnold Neilsen, primarily to be used in propellants. It has a density of 2.044 gm/cc and a detonation velocity of 9.38 km/sec. It has a better oxidizer-to-fuel ratio than conventional HMX or RDX. While most development of CL-20 has been carried out by the Thiokol Corporation, the US Navy (through ONR) has also been interested in CL-20 for use in rocket propellants, as a replacement for ammonium perchlorate oxidiser, as it has lower observability characteristics as it does not produce high levels of primary or secondary visible smoke. CL-20 is also produced at SNPE in France in quantities of 50-100 kg on an industrial scale pilot plant. The increased power of CL-20 argued for its use in smaller weapon systems. However, CL-20 is rather susceptible to impact and friction, being about as sensitive as PETN. Large-scale tests have mostly used a combination of CL-20 and a plastic binder in a 90-10 ratio. While this plastic-bound explosive has achieved a higher level of stability by separating the CL-20 crystals, the power of the explosive is reduced to roughly the HMX level. CL-20 has not yet been fielded in any production weapons system, but is undergoing testing for stability, economic production capabilities and other weapons characteristics. Until its cost becomes closer to established nitramines, it is unlikely to find general application.

2.9.3 Primary Explosives

During World War II the composition finally chosen by the British for SAA caps was VH2, one of a series patented by von Herz in the 1920s. The composition is given in Table 2-6.

Table 2-6 Composition of VH2

Lead styphnate	38 % (w/w)
Barium nitrate	39 % (w/w)
Calcium silicide	11 % (w/w)
Lead peroxide	5 % (w/w)
Antimony sulphide	5 % (w/w)
Tetrazene	2 % (w/w)

This complex mixture is largely non-corrosive and is still in use, but its method of manufacture has been changed in recent years to the safer and more convenient Eleyprime process, where non-explosive precursor chemicals are mixed and filled into SAA caps. The reaction to produce the active explosives is initiated in the cap itself by adding a drop of water.

For the caps of igniters in grenades and for the primers of QF cartridges, mercury fulminate compositions ('A mixtures') continued in use long after the

Second World War. The composition which largely replaced them, after years of development and trials, was a simple, stable and versatile composition called RD1651 or 'L mixture' as shown in Table 2-7. This composition was approved for service in 1961 and is now widely used in British Service ammunition.

Table 2-7 Composition of 'L' Mixture

Lead 2, 4-dinitroresorcinate	50 % (w/w)
Barium nitrate	45 % (w/w)
Tetrazene	5 % (w/w)

2.9.4 Pyrotechnics

Developments in pyrotechnics since World War II have been manifold, but like those in High Explosives and propellants, they have been mainly concerned with using established materials for new applications and eliminating problems of safety and reliability. Newer uses for pyrotechnics have included propellant igniters and tracking flares for missiles, anti-missile decoy flares, pyrotechnically-operated switches, sound and light simulators for military training, concussion grenades for anti-terrorist operations, munitions for disseminating riot control agents and screening smokes.

2.10 SHAPED CHARGES

In recent decades it has become accepted in military circles that no new explosive formulation is likely to result in an order of magnitude increase in performance over HMX and RDX. Modern explosives research therefore tends to concentrate on ways of making the best use of existing explosives and on identifying and solving problems of safety and reliability. There are numerous ways of utilising explosives to the best advantage, many of them being in the fields of metallurgy, ammunition design and terminal ballistics. Perhaps the classic way of harnessing the violent effect of a High Explosive is the shaped charge (see 8.4.1). This type of charge is based on the fact that when a detonation wave, passing through a charge, emerges into the air via a re-entrant shape in the charge surface, there is a focusing of the wave energy. An enhanced destructive effect is projected along a narrow axis or plane, depending on whether the cavity is conical or wedge-shaped.

The earliest mention of hollow charges occurred in 1792. Franz Xaver von Baader (1765–1841) was a German mining engineer at that time; in a mining journal, he advocated a conical space at the forward end of a blasting charge to increase the explosive's effect and thereby save powder. The idea was adopted, for a time, in Norway and in the mines of the Harz mountains of Germany, although the only available explosive at the time was gunpowder, which is not a High Explosive and hence incapable of producing the shock wave that the shaped-charge effect requires.

The first true hollow charge effect was achieved in 1883 by Max von Foerster (1845–1905), chief of the nitrocellulose factory of Wolff & Co. in Walsrode, Germany.

By 1886, Gustav Bloem of Düsseldorf, Germany had obtained U.S. Patent 342,423 for hemispherical cavity metal detonators to concentrate the effect of the explosion in an axial direction.

The shaped charge effect as we now know it is said to have been discovered the American explosives chemist Charles Edward Munroe (1849-1938), whose name is often given to it. He was working at the U.S. Naval Torpedo Station at Newport, Rhode Island. In 1888 he found, by chance, that if a block of guncotton which had letters indented in its surface was detonated with the lettered surface against a substantial steel plate, the letters became imprinted as a mirror image on the plate. Conversely, if letters were raised in relief above the surface of the explosive, then the letters on the plate would also be raised above its surface. In 1894, Munroe constructed the first crude shaped charge. He made numerous experiments on these lines. His most important discovery was that a cylindrical charge with a deep cavity at one end and initiated at the other, was capable of perforating a steel plate even if that could not be achieved in any other configuration by the same charge weight. Further work was done by Foerster before the end of the century, then by Egon von Neumann, who, with Westfaelische Sprengstoff AG, took out patents between 1910 and 1914, having rediscovered the phenomenon.

No use was made of the shaped charge principle in the 1914-18 war, but before the 1939-45 war more work was done, some by Lodati (1932) and Neubauer (1937), but most of it in great secrecy and, at the time, in anonymity. The fundamental improvements were in providing a stand-off between the cavity and the target and most importantly inserting a conical metal liner against the surface of the explosive in the cavity. The advent of the high-performance explosives RDX and PETN also greatly enhanced the efficacy of the system. The introduction of the metal liner cannot be ascribed with certainty to any particular worker. For instance, the miniature but highly penetrative effect of indented blasting detonators had been exploited long before the 1930s. In a 1954 paper, R.J. Eichelberger, himself a noted worker in liner research, credited the first recognition of the importance of the liner to the American R.W. Wood and dated it as 1936. Similar research, however, was being duplicated in several countries, accelerated by the threat of war and advances in tank design and assisted by improvements in ultra-high-speed photography. British workers in the field, during and immediately after World War II, included Sir Geoffrey I. Taylor, N.F. Mott, A.R. Ubbelohde, D.C. Pack, W.M. Evans, R. Hill and T.L. Tuck.

By the middle of World War II some shaped-charge infantry weapons were in use for the attack of armour, notably the British PIAT, the American Bazooka and the German Panzerfaust and there were hollow charges for demolition also. One serious limitation of the principle had been established, namely that it is not effective in gun-fired, fast-rotating projectiles. However, post-war advances in

small, subsonic guided missiles provided suitable delivery systems. The shaped charge has other military uses besides the attack of armour, including anti-personnel mines, excavation devices and cutting charges. In recent years it has also found increasing civil application, especially in the offshore oil industry, underwater excavation and, on land, the demolition of steel structures.

2.11 PHYSICAL MODIFICATIONS OF EXPLOSIVES

Although it is primarily the chemical nature of the base ingredient of an explosive composition which determines its safety, reliability and performance, a need often arises to alter the physical or mechanical properties of a charge by means of additives. For instance, nitroglycerine has appeared in many guises ever since the time of Alfred Nobel. Guncotton for use as a High Explosive was kept permanently wet. In some countries picric acid was mixed with wax to desensitise it against impact initiation when used in armour-piercing shell. The high-performance explosives PETN, RDX and HMX introduced between 1920 and 1945 are too sensitive to be used unmixed and many different additives have been employed with them for reasons of safety or other needs. The addition of grease or oil to RDX during World War II gave rise to the 'PE' series of plastic explosives in the British Service and to composition C-4 in the USA. These mouldable compositions were found far superior to guncotton slabs or blocks of TNT, in that they could be made up into charges of any required shape for improvised demolitions, allowing ideal coupling of the charge to the target material. Later, RDX and PETN were also mixed with the low-molecular weight polymer poly-isobutene, giving the RDX-based 'sheet explosive' (SX) in the UK and the PETN-based 'Detasheet in the USA. These flexible sheets are similarly useful in small-scale demolitions. As with other aspects of explosives technology, what appears to be a simple concept often takes a surprisingly long time to perfect. In the foregoing cases much experimentation and testing was necessary before exactly the right additives and manufacturing techniques were discovered. In particular, great care has to be taken to avoid chemical incompatibilities and these take time to become apparent.

In the past, under the stress of wartime conditions, explosive mixtures have been developed which might be disapproved of in peacetime. During World War II the Germans incorporated PETN or RDX into a matrix formed from out-dated propellant and thus made a hard, waterproof High Explosive composition which they called Nipolit. It could be machined to accept a fuze and could therefore be made into mines or grenades without the use of containers. This was the forerunner of modern developments in both propellants and High Explosives. In the last four decades the use of high-performance explosives in the warheads of supersonic missiles has produced requirements of high mechanical strength in the explosives and resistance to prolonged aerodynamic heating. These demands have led to a proliferation of compositions comprising RDX or HMX bonded with polymers of high molecular weight, giving hard or resilient materials as required. Each of these compositions has involved much research and testing to ensure that the explosive in the missile warhead remains safe, reliable and effective even after long-term service under conditions far from

ideal. The requirement of high mechanical strength has in some cases been met by the incorporation of chopped polymer fibres. This technique and some of the early plastics-bonded compositions tended to produce compositions which are rather sensitive to impact or friction. Recently considerable developments have taken place in plastic bonded explosives (PBXs) and these are described in the following section on Insensitive Munitions

2.12 HISTORY OF THE DEVELOPMENT OF INSENSITIVE MUNITIONS

During the 1960s and 1970s enemy targets such as tanks and submarines were becoming increasingly hard to defeat, so the challenge to weapon designers was to develop increasingly powerful explosives. For the defeat of main battle tanks the shaped charge was the warhead of choice and 60/40 RDX/TNT was replaced with explosives such as EDC1S (70.1 % w/w HMX / 4.0 % w/w RDX / 24.5 % w/w TNT/ 1.4 % w/w Wax/HNS/X28M). The fillings for torpedoes changed from Torpex or H6 to composite explosives such as PBXN-103 (27 % w/w Al / 40 % w/w AP / 33 % w/w NC/TMETN/TEGDN) and then PBXN-105 (7 % w/w RDX / 25.8 % w/w Al / 49 % w/w AP / 18.2 % w/w PEG/BDNPA/F). The improved performance, however, came with a penalty, that was that they featured undesirable responses to hazard stimuli such as impact or fire.

From the early 1960s onwards a series of events occurred which persuaded the international community of the need for munitions which would react relatively benignly to unplanned stimuli. One of the first incidents that served to focus attention on the importance of munition sensitivity occurred in 1965. A fire, set by enemy action, occurred at the ammunition storage area at Bien-Hoa air base in Vietnam. Within a short time, munitions detonated spreading the fire. Fire and secondary explosions destroyed the entire ammunition storage area at the air base. Thirty-three Servicemen were killed and many tons of ammunition was lost. Shortly after this incident, the US Army initiated a program at the Aberdeen Proving Ground, Maryland to study ammunition storage and ways to minimize sympathetic detonations of munition stockpiles.

From October 1966 to November 1988, there were four flight deck accidents on U.S. aircraft carriers that involved fires and munition explosions. Two hundred and twenty sailors and naval aviators were killed and seven hundred injured. Ninety-six planes, each costing more than 20 million dollars, were either destroyed or severely damaged. The ships were forced to leave the operational areas and undergo extensive repairs in shipyards. The material damage alone cost the US Navy over 1.3 billion dollars.

In addition, in US service between 1965 and 1973, there were sixteen in-bore premature projectile explosions in large calibre gun barrels. Fires and secondary explosions destroyed three ammunition storage areas in Vietnam. In these incidents fifty-nine people were killed, many were injured and the material damage was extensive.

Back in the 1950s aerodynamic heating problems had been encountered with munitions carried externally on high-speed aircraft and with warheads on some tactical missiles. There was at least one case at the White Sands, New Mexico test range where a TNT-based explosive warhead on a surface to air missile had exploded violently before reaching the target. This was attributed to molten explosive being forced into critical areas where pinching, friction or heat can cause it to react explosively. In short, TNT-based explosives were deemed to be unsuitable for this application.

These various events conspired to persuade the US Department of Defence (DOD) to explore how the damage resulting from the inadvertent initiation of munitions could be reduced. Specifically they wanted munitions which could reliably fulfil their operational requirements on demand, but which were designed to minimize the violence of a reaction and subsequent collateral damage when subjected to unplanned stimuli. These were to become known as “Insensitive Munitions”. Unsurprisingly many governments, including that of the UK, France, Canada and Australia developed an intense interest in the Insensitive Munitions concept.

In order to address the aerodynamic heating and vulnerability problems the US laboratories developed Plastic Bonded Explosives (PBXs) for use in their warheads. These first PBX’s were pressed materials and were based on technology developed at the Los Alamos National Laboratory, Los Alamos, New Mexico and Livermore National Laboratory, Livermore, California. An example is PBXN -101 which is HMX in a polystyrene binder. They were followed by cast curable materials developed by all three services. These were mostly based on RDX or HMX in tough rubbery binders. An example is PBXN-106 which is RDX in a polyurethane binder.

At about this time work had begun on the development of HMX and RDX based gun propellants to reduce the vulnerability of tank ammunition. LOVA (LOw Vulnerability gun Ammunition) is the acronym used to describe these nitramine-based propellants. These formulations were similar to the PBXs. Like the PBXs the LOVAs were hard to ignite and they either extinguished or burned slowly at atmospheric pressure.

TATB had been made in pilot plant quantities in 1955 and 1956 at the US Navy’s White Oak laboratory and its explosive properties had been tested. At the time, because of its relatively low energy and its undesirable loading complexity (it needed to be pressed and then machined), TATB was not accepted for use as a main charge in conventional weapons. These tests had, however, demonstrated that TATB was a very insensitive High Explosive and this property interested the Department of Energy (DOE) scientists involved in a program to replace the sensitive HMX formulations then used as the conventional explosive charge in nuclear weapons. The low energy and the processing complexity were a secondary concern for the DOE scientists. The DOE interest in this very insensitive explosive came as a result of U.S. Air Force accidents that occurred, respectively, in Polomares, Spain in 1966 and Thule, Greenland in 1968. In each of these accidents, a B-52 bomber carrying

nuclear weapons had crashed and spread radioactive material over a wide area.

The clean-up efforts had been extremely costly to the United States. Thousands of tons of contaminated soil, vegetation and debris from the accident sites had to be placed in special containers and returned to the United States for disposal as radioactive waste.

In early 1978, Dr Harold Agnew, the Director of the Los Alamos National Laboratory, proposed a joint DOD-DOE effort to study the use of the TATB as the main charge in conventional weapons. Dr Ruth Davis, then the US Under Secretary of Defence, Research and Engineering (DDR&E), agreed with the proposal and decided to fund the effort. The three Services were directed to provide the money for the DOD-DOE Insensitive High Explosives and Propellants (IHEP) study.

The DOD-DOE IHEP study report was issued in March 1979. The study concluded that the PBX studies and the LOVA work were on course and these materials offered weapon designers a good trade-off between sensitivity and performance. The study group concluded that: “A castable explosive with the insensitivity of TATB or NQ (nitroguanidine) is not available but cast cure RDX formulations will enhance safety through their mild burning response in an enveloping fire and reduced vulnerability to fragment impact.” The study report hardly mentioned TATB, the explosive that was the original basis for the DOE proposed IHEP study.

UK MOD had been actively collaborating with the US DOD over this period, this being subsequently spurred on by events in the South Atlantic. In April 1982 Argentina invaded the Falkland Islands and war followed. On 23 May 1982, the frigate HMS ANTELOPE sank after an unexploded bomb within the ship detonated while a disposal team was trying to defuse it. There were two distinct explosions; the first occurring while the disposal team was defusing the warhead. The second that followed was a secondary mass detonation that destroyed the ship.

On the 8 June 1982 while preparing to unload soldiers from the Welsh Guards in Port Pleasant, off Fitzroy, together with RFA Sir Tristram, the Sir Galahad was attacked by three A-4 Skyhawks from the Argentine Air Force. RFA Sir Galahad was hit by bombs and set alight. A total of 48 soldiers and crewman were killed in the explosions and subsequent fire.

Because of these and other ship incidents in the Falklands war there was a renewed interest in the provision of Insensitive Munitions. It was considered that the severity and consequences of these incidents would have been much less had munitions not responded so violently to the unplanned stimuli.

In the early 1980s the USA shared their thoughts and aspirations for IM with other NATO nations and, through the auspices of AC310, NATO sponsored an Insensitive Munitions Workshop in London in October 1986. Seventy representatives of NATO governments and industrial agencies attended. The

participants of the workshop agreed that the reduction of the sensitivity of munitions used interoperably by the NATO forces was desirable and that new technology could make this goal attainable. They also agreed that the formation of an Insensitive Munitions Information Centre (NIMIC) in NATO could facilitate the exchange of technical information among the NATO countries.

The formation of a NATO Pilot NIMIC located in the United States was proposed. The Pilot NIMIC would formalize plans for establishing a permanent NIMIC at NATO Headquarters in Brussels, Belgium. At the time not all of the NATO countries were interested in participating; however, in May 1988, France, the Netherlands, Norway, the United Kingdom and the United States signed a Memorandum of Understanding (MOU), establishing the Pilot NIMIC. Canada joined in April 1989. Each Nation contributed funds and technical personnel for the project and the Pilot NIMIC was established at the Johns Hopkins Applied Physics Laboratory, Columbia MD. After successfully completing the pilot phase in the United States, the NATO Insensitive Munitions Information Centre moved to the NATO Headquarters in Brussels on 1 May 1991. This is now called the Munitions Safety Information Analysis Centre (MSIAC) and has thirteen member countries.

On 25 September 1990, the UK published Ordnance Board (OB) Proceeding 42657 which laid the foundation for Insensitive Munitions (IM) to be introduced into UK service. This Proceeding was published in response to an increasing awareness in the UK of the benefits that could arise from using munitions that would minimise collateral damage when subjected to unplanned stimuli. The Board considered the application of the Insensitive Munitions technology to UK weapons and published their criteria for Insensitive Munitions. It adopted the same tests and criteria as the US and recommended that "…the requirement for Insensitive Munitions be addressed in Staff Targets and Requirements".

In its Proceeding, the Ordnance Board stated the following: "The benefits of IM will accrue in both peace and war: in peace, the lower risk of adverse events occurring and the reduced accident damage will lead to economies in logistics; and during combat, through improved overall effectiveness by improving safety and survivability of weapon systems. The survivability of the weapon system platform – be it ship, tank or aircraft – in or on which they are carried will be improved; this applies particularly to HM Ships which carry embarked armament stores and to RAF carrying reloads. If such ships are attacked, the embarked armament stores can substantially increase the resultant damage and loss of life, as occurred in the attack on RFA 'Sir Galahad' in the Falklands."

The UK, through the OB, was also deeply involved with the NATO committee AC310 which wrote NATO STANAG 4439, Edition 1, which was issued in 1995 and ratified in 1998. In that STANAG ratifying nations agreed that, whenever it was feasible to do so, Insensitive Munitions should be developed and introduced into service. The UK IM policy, implementing the STANAG, was endorsed by the Systems Area staffs and was promulgated widely within and outside the MOD. It was eventually published in Joint Services Publication 520, now called "Ordnance, Munitions and Explosives (OME) Safety and

Environmental Management for the Equipment Acquisition Cycle". The UK IM policy stated that the vulnerability of the munitions in the MOD inventory would be reduced over time to meet the requirements of STANAG 4439. It went on to state that all new munitions requirements were to stipulate compliance with the criteria for IM set out in STANAG 4439. Formal dispensation was required for any non-compliance, either in the requirement definition or in the procurement solution. Finally it noted that all legacy munitions were to be kept under review to identify opportunities to achieve IM compliance. Formal dispensation was required for any non-compliance, either in the requirement definition or in the procurement solutions sought for MLU, refurbishment or re-provisioning programmes.

The aim of the UK IM policy was to ensure that the risk of munitions causing collateral damage and casualties to civilian and military personnel both in non-operational and operational scenarios was as low as reasonably practicable (ALARP) which in turn met MOD's legal requirement under the Health and Safety at Work etc. Act 1974 (H&SW) to reduce risks to ALARP.

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CHAPTER 3
EXPLOSIVE LEGISLATION AND REGULATION

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3 EXPLOSIVES LEGISLATION AND REGULATION

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NOTE – As regulations and guidance are subject to continuous improvement, the reader should always refer to DSA 02.OME: Defence Ordnance, Munitions and Explosives (OME) regulations for the definitive regulations and guidance.

3.1 INTRODUCTION

This chapter provides the background of the need for regulatory control of explosives and describes the extant regulations. It is recognised that legislation and regulation may change and it should be noted that defence regulations are currently under review with new documents being prepared. The chapter will be updated when the new Defence Safety Authority documents are issued.

Significant aspects of the various regulations are presented, however, for a complete understanding of any specific regulation the relevant document should be consulted.

3.1.1 Explosives Hazards

Explosives materials and devices containing explosives have the capacity to cause harm. When they function they can generate a range of effects that could include blast in air and water, projection hazards, fragments, shock, thermal effects and toxic products. These effects can be used in civil applications such as blasting operations, demolition, special effects and seismology and in military applications for guns, missiles, warheads, military pyrotechnics, demolition stores and safety devices such as aircraft ejection systems. When operated in their design mode explosives have the capacity to cause considerable damage and harm and, in the case of military explosives, are often optimised to cause maximum harm to people and equipment. However that harm can also be realised in the event of an accident involving explosives as the following examples illustrate.

3.1.1.1 Macclesfield Bridge (1874)

In the early hours of October 10, 1874 the barge Tilbury was being towed by a steam tug westwards along Regent's Canal in central London. It had a cargo of sugar, nuts, two or three barrels of benzol and five tons of gunpowder. A naked flame is thought to have ignited benzol vapour and as a result the gunpowder ignited, causing a huge explosion as the barge was passing under the Macclesfield Bridge. The crew were killed, the bridge destroyed and windows were blown out a mile away. The explosion caused such havoc that a detachment of Horse Guards were brought in to help keep order and to ensure safety from wild animals at the Zoo. It was also one of many explosions involving gunpowder that had occurred in the preceding years. At that time

gunpowder manufacture, storage, transport and use were essentially unregulated and this was thought to be a major contributor to the accident.

3.1.1.2 Halifax Harbour (1917)

On the morning of 6 December 1917 SS Mont-Blanc, a French cargo ship laden with high explosives, collided at low speed (approximately 1knot) with the unladen Norwegian vessel SS Imo in Halifax Harbour, Nova Scotia. A fire began on board the French ship that quickly grew out of control. Approximately 20 minutes later Mont-Blanc exploded. The blast was the largest man-made explosion prior to the development of nuclear weapons, releasing the equivalent energy of roughly 2.9 kilotons of TNT. Nearly all structures within an 800-metre (2,600 ft.) radius, including the entire community of Richmond, were obliterated. The blast wave snapped trees, bent iron rails, demolished buildings, grounded vessels, and scattered fragments of Mont-Blanc for kilometres. Hardly a window in the city proper survived the blast. Across the harbour, in Dartmouth, there was also widespread damage. A tsunami created by the blast wiped out the community of Mi'kmaq First Nations people who had lived in the Tuft's Cove area for generations. Approximately 2,000 people were killed by blast, debris, fires and collapsed buildings, and an estimated 9,000 others were injured.

Relief efforts began almost immediately, and hospitals quickly became full. Rescue trains began arriving from across eastern Canada and the north-eastern United States, but were impeded by a blizzard. Construction of temporary shelters to house the many people left homeless began soon after the disaster. The initial judicial inquiry found Mont-Blanc to have been responsible for the disaster, but a later appeal determined that both vessels were to blame. There are several memorials to the victims of the explosion in the North End.

3.1.1.3 USS Forrestal (1967)

On 29 July 1967, the aircraft carrier USS Forrestal (CVA-59) was part of a task force operating in the Gulf of Tonkin off North Vietnam. A 5-inch Zuni rocket loaded in the pod under the wing of an F-4 aircraft was accidentally fired. The warhead crossed the flight deck, struck an A-4 aircraft puncturing the fuel tank, and igniting a fire. Two A-4 aircraft each loaded with two 500 pound bombs and SHRIKE missiles, one A-4 loaded with two 500 pound and two 750 pound bombs, and seven A-4’s each loaded with two 1,000 pound bombs were engulfed in the fire.

Sailors on the hangar deck were pushing bombs and missiles over the side of the ship. Chief Aviation Boatswain’s Mate Gerald Farrier, took a fire extinguisher and tried to reach a bomb that was already in the flames. It detonated in front of him and the blast and bomb fragments decimated the first wave of fire fighters as they were approaching to fight the blaze. A further series of fires and explosions ensued causing further damage.

The consequence was that 131 servicemen lost their lives with a further 161 injured. The carrier was to return to the US for major repairs and was out of

commission for almost 10 months. 21 aircraft were lost as was a considerable quantity of munitions.

The Forrestal incident was one of several explosive accidents involving US aircraft carriers. These included the USS Oriskany where 44 were killed with 138 injured and the USS Enterprise where 28 servicemen were killed with 314 injured. None of the incidents involved enemy action.

3.1.1.4 Enchede (2005)

The Enschede fireworks disaster was a catastrophic fireworks explosion occurring at the SE Fireworks depot on 13 May 2000 in the Dutch city of Enschede.

The incident commenced with a fire which resulted in a series of explosions. The first explosion had a strength in the order of 800 kg TNT equivalence, while the strength of the final explosion was within the range of 4000–5000 kg TNT. The biggest blast was felt up to 30 kilometres (19 mile) from the scene. A 40-hectare (100 acres, or 0.4 square kilometres) area around the warehouse was destroyed by the blast. The explosion killed 22 people including four firefighters, and injured 947 people. 400 homes were destroyed and 1500 buildings damaged. The fire spread to the nearby Grolsch Beer brewery which had an asbestos roof. It was later demolished and closed. Fire crews were called in from across the border in Germany to help battle the blaze; it was brought under control by the end of the day.

Ten thousand residents had to be evacuated, 1,250 people were made homeless and damages eventually exceeded 1 billion guilders (€454 million).

3.1.1.5 Lessons Learnt

Each of the examples cited were unintended events and were subject to significant post-accident enquiries. They illustrate that when an accident involving explosive occurs the consequences are often very serious. These accidents led to major loss life in the case of Halifax, Forrestal and Enchede, major damage to infrastructure in the case of Halifax, Enchede and Macclesfield Bridge a significant loss of military capability in the case of Forrestal and Halifax and major environmental impact at Enchede. Furthermore these are not isolated incidents. The USS Forrestal incident was one of four serious aircraft carrier incidents involving explosives that occurred over a 20 year period. At a global level there have been many other explosives accidents involving pyrotechnics and military or civil explosives during their manufacture, transportation, storage, use and disposal.

Given the relatively high frequency of such events and the often serious consequences one could conclude that activities involving explosives are high risk. As such there is a need for such activities to be carefully controlled and managed. One of the principle tools to achieve such control is a body of legislation and regulation.

3.2 EXPLOSIVES LEGISLATION

3.2.1 Explosives Acts 1875 and 1923

Following the 1874 explosion at Macclesfield Bridge at the centre of the Nation's capital there was considerable pressure to introduce legislation to control the manufacture, storage, transport handling and use of explosives. The result was the 1875 Explosives Act. This legislation which remained extant for more than a century provided the foundation for explosives law and regulation in the UK and in many other countries. The 1923 Act added some minor amendments to the original 1875 Act.

The Acts required that places where explosives were manufactured, and stored and handled were licensed and that they were constructed and operated in such a way that reduced the risks of explosion. It also introduced the concept of classification of explosives and that the prohibition of particularly hazardous materials. The new licensing regime placed obligations on local authorities and government and introduced an inspection regime to satisfy the Secretary of State that operators were complying with the law. Many of the licensing principles laid down in 1875 are still applicable today and are widely applied around the globe.

The Explosives Act 1875 and 1923 (EA75) and subsequent Orders in Council made under the Acts were not applicable to Crown Establishments with the exception that any person who enters an explosives area without permission, or any person within an explosive area committing an act liable to cause an explosion without proper authority is subject to instant arrest. Hence Crown establishment and in particular those in the Defence domain had to develop and maintain regulations that mirrored the requirements of (EA75).

3.2.2 Other Explosives Legislation

Whilst EA75 served the community well, additional legislation has been enacted since its introduction to further control aspects of explosives activity.

3.2.2.1 Carriage of dangerous goods by road

The Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations 2009 (Carriage Regulations 2009) & The Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations (Amendment) 2011 (Carriage Regulations 2011), together with the European agreement ("Accord européan relatif au transport international des marchandises dangereuses par route", known as ADR) regulate the carriage of dangerous goods including explosives by road and are highly prescriptive. The GB regulations were substantially restructured for 2009 with direct referencing to ADR for the main duties. Amending regulations were made in 2011, mainly to reflect changes to the EU Transportable Pressure Equipment Directive. The Carriage Regulations 2009 (SI 2009 No1348) came into force on 01 July 2009. These regulations are aligned to ADR, A European agreement covering the

classification, packaging, labelling and transport of all classes of dangerous goods. It also details the duties by all participants in the supply chain, including loaders, packers, hauliers' etc.

The Carriage Regulations 2009 place general duties on everyone with a role in the carriage of dangerous goods, and specific duties on those in the transport chain, i.e. consignors, carriers, loaders, packers, etc. The main duties are now covered by a single regulation, namely Regulation 5.

JSP800 Volume 4b details the MOD arrangements in implementing the Carriage Regulations, including class 1 Explosives, and offers advice and guidance to ensure that Units and users remain in compliance with the statutory requirements.

3.2.2.2 Dangerous Substances in Harbour Area Regulations (DSHAR) 1987

Statutory Instrument 37/1987 regulates all classes of Dangerous Goods including explosives (Class 1) for carriage, loading, unloading and storage in harbours and harbour areas. It is supported by an Approved Code of Practice (ACOP). In accordance with DSHAR Regulation 5, the regulations apply to all harbours and harbour areas in Great Britain including any premises or activities in the territorial waters of Great Britain, including any premises or activities in the territorial waters of Great Britain to which the HSW Act applies. The regulations do not apply to nuclear weapons or their components.

The Secretary of State for Defence may, in the interests of national security by a certificate in writing, exempt from all or any requirements or prohibitions imposed by these Regulations:

1. Her Majesty's forces
2. Visiting forces within the meaning of any of the provisions of Part 1 of the Visiting Forces Act 1952
3. Any headquarters or organisation designated for the purposes of the International Headquarters and Defence Organisations Act 1964
4. Any person engaged in the carriage, keeping or supply of any military explosives, if that person is under the direct supervision of a representative of the Ministry of Defence

And any such exemption may be granted subject to conditions and to a limit of time and may be revoked by a certificate in writing at any time.

3.2.2.3 Manufacture and Storage of Explosives Regulations (MSER)

MSER provided guidance on the regulations on the manufacture and storage of explosives. These regulations covered the manufacture storage and handling of all explosives including: blasting explosives; propellants; detonators and detonating cord; fireworks and other pyrotechnic devices; ammunition; and other explosive articles such as airbags and seat belt pre-tensioners.

The activities covered included manufacture of explosives and intermediate products for on-site mixing, storage, and other handling operations such as:

fusing of fireworks; the assembly of fireworks displays from components; filling shotgun cartridges. The regulations did not cover the transport or use of explosives.

MOD had a disapplication from certain parts of MSER, for instance the regulations covering the licensing of premises. DSA 03.OME Part 3 incorporates those aspects of MSER which are applicable and details any alternative arrangements for the MOD where MOD was disapplied.

This regulation was revoked when Explosives Regulations 2014 (ER 2014) were enacted that included similar or identical requirements.

3.2.2.4 The Control of Explosives Regulations 1991 (COER)

The Control of Explosive Regulations (COER) 1991, Statutory Instrument 1531/1991, including amendments made under the Manufacture and Storage of Explosives Regulations 2005 (MSER 2005), placed duties on those with responsibility for explosives.

COER regulated any person (including a body corporate) who acquired; had access to; possession of or control over any explosives, save those explosives specifically exempted from COER. These regulations created a number of requirements, breaches of which constitute offences contrary to section 33 of the 1974 Act. These were:

- Acquiring and or keeping Explosives without an explosive certificate Regulation 7
- Transferring explosives to a person not authorized Regulation 8
- Knowingly employing a "Prohibited Person" (as defined in Regulation 2) Regulation 9(1)
- A "Prohibited Person" acquiring, handling or having control over explosives Regulation 9(2)
- Failure to keep records Regulation 12
- Failure to report loss of explosives Regulation 13.

This regulation was revoked when Explosives Regulations 2014 (ER 2014) were enacted that included similar or identical requirements.

3.2.2.5 The Firearms Act 1968 (as amended)

Since 1968, the act has been extensively amended. Following the Hungerford massacre, the Firearms (Amendment) Act 1988 extended the class of prohibited weapons. Following the Dunblane school massacre, two acts were passed, the Firearms (Amendment) Act 1997 and, after the general election that year, the Firearms (Amendment) (No. 2) Act 1997, which in effect banned almost all handguns. The Policing and Crime Act 2017 brought clarity to aspects of the act, following a recommendation from the Law Commission.

The Act is in several parts and covers:

1. PART I PROVISIONS AS TO POSSESSION, HANDLING AND DISTRIBUTION OF WEAPONS AND AMMUNITION; PREVENTION OF CRIME AND MEASURES TO PROTECT PUBLIC SAFETY
    a. General restrictions on possession and handling of firearms and ammunition
    b. Prohibition of certain weapons and control of arms traffic
    c. Special exemptions from sections 1 to 5
    d. Prevention of crime and preservation of public safety
2. PART II FIREARM AND SHOT GUN CERTIFICATES; REGISTRATION OF FIREARMS DEALERS
    a. Grant, renewal, variation and revocation of firearm and shot gun certificates
    b. Issue etc. in Great Britain of documents for European purposes.
    c. Registration of firearms dealers
    d. Supplementary
3. PART III LAW ENFORCEMENT AND PUNISHMENT OF OFFENCES
4. PART IV MISCELLANEOUS AND GENERAL

3.2.2.6 Placing on the Market and Supervision of Transfers of Explosive Regulations 1993 (POMSTER)

The Regulations, Statutory Instrument 2714/1993, were mainly concerned with safety requirements for explosives and security controls on their transfer. They applied to explosives intended for use in the civil sector

The transfer controls required competent authorities to approve movements of explosives within, through and between Member States of the EU. These controls supplemented domestic security controls on acquisition and keeping of explosives in the Control of Explosives Regulations 1991 (COER).

Ammunition regulated or prohibited by virtue of the Firearms Act 1968, pyrotechnics and any explosives which it is shown to be intended for the lawful use by the armed forces or policy of any country are exempt.

Explosives transferred outside the MOD for disposal were not considered to be intended for the lawful use of the armed forces. If the disposal is by destruction, regulation 8, “Transfer of Explosives” applied. If the disposal was by means other than destruction, the explosives are being placed on the market and POMSTER fully would apply.

The main requirements of Regulation 8 were:

- Before transfer of any explosive covered by the Regulations can take place, including movements wholly within GB, the consignee must obtain the written approval of the competent authority for the country where the transfer will terminate -HSE in the case of movements terminating in GB. The recipient competent authority document (‘transfer document’), or a certified true copy, must accompany the explosives throughout their journey.

- The person responsible for the transfer, normally the consignor or shipping agent, is required to notify the relevant authorities of the Member States through which the movement will take place to obtain their approval. HSE is the relevant authority for Great Britain.
- No person may supply explosives unless they are satisfied that the recipient has obtained the necessary transfer document.

This regulation was revoked when Explosives Regulations 2014 (ER 2014) were enacted that included similar or identical requirements.

3.2.2.7 Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR)

The Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR) are concerned with protection against risks from fire, explosion and similar events arising from dangerous substances used or present in the workplace. They set minimum requirements for the protection of workers from fire and explosion risks related to dangerous substances and potentially explosive atmospheres.

The key requirements in DSEAR are that risks from dangerous substances are assessed and eliminated or reduced.

The Secretary of State for Defence may, in the interests of national security, by a certificate in writing, exempt:

1. any of Her Majesty's Forces
2. any visiting force
3. any member of a visiting force working in or attached to a headquarters
4. any person engaged in work involving dangerous substances, if that person is under the direct supervision of a representative of the Secretary of State for Defence

from all or any of the requirements or prohibitions imposed by these Regulations and any such exemption may be granted subject to conditions and to a limit of time and may be revoked at any time by a certificate in writing, except that, where any such exemption is granted, suitable arrangements shall be made for the assessment of the risk to safety created by the work involving dangerous substances and for adequately controlling the risk to persons to whom the exemption relates. Further information can be found in JSP 375 Leaflet 56.

3.2.2.8 Identification and Traceability of Explosives Regulations 2010 (ITOER)

The Identification and Traceability of Explosives Regulations 2010 (ITOER) require that explosives for civil uses are uniquely identified and can be traced from the production site through to their final use. This is to help prevent misuse and theft and help authorities trace the origin of lost or stolen explosives. The Regulations implement EC Directive 2008/43/EC. This regulation came into force April 2012.

ITOER applies to every explosive except:

a. pyrotechnics, for example flares or fireworks
b. ammunition
c. unpackaged explosives transported and delivered for direct unloading into the blast-hole, for example in pump trucks
d. explosives produced in-situ for immediate use
e. explosives for legal use by the military or police

The main duties of the Regulations are:

a. Product identification – explosives manufactured in or imported into Great Britain shall be uniquely marked with an alphanumerical code and barcode
b. Record keeping – any person who manufactures, imports, distributes or acquires or keeps any explosives included in the Regulations must keep a record of the explosives: (c) for a period of 10 years and provide the enforcing authority with contact details so that information in their records can be accessed at any time.

Although MOD is broadly exempt from these regulations the matter of disposal or military sales of items when no longer required by MOD may pose some problems. This matter is being addressed via HSE and the ELR process which is still under review.

3.2.3 Explosives Regulations 2014

3.2.3.1 Introduction

Despite the introduction of MSER the UK explosives legislation remained complex. The HSE therefore worked with stakeholders to review the legislation and to consolidate, modernise and simplify the legislative arrangements. The result was the Explosives Regulations 2014 (ER2014) which came into force on 1st October 2014. ER 2014 consolidated and therefore revoked a number of explosives regulations. It has brought together the requirements of health and safety related explosives legislation into a framework based around common topics such as authorisation, safety, security and placing on the market. As a result of the consolidation the Approved Code of Practice to the Manufacture and Storage of Explosives Regulations 2005 (L139) has been withdrawn. Guidance relating to the security of explosives (HSE Circular 1/2005), and guidance on the placing of civil use explosives on the market (L66) was also withdrawn.

3.2.3.2 Changes to the regulatory framework

The main changes to the regulatory framework include:

- Merging registrations into the licensing system
- Allowing local authorities to issue licences up to 5 years, aligning them with equivalent HSE/police-issued licences.
- Extending licensing to address storage of ammonium nitrate blasting intermediate (ANBI).

- Exceptions for keeping higher hazard and desensitised explosives without a licence have been updated.
- Tables of separation distances have been restructured to better allow for sites with more than one store; the tables have also been revised to cover quantities of explosives greater than 2000k.
- A revised list of explosives that can be acquired or acquired and kept without an explosives certificate from the police.
- The repeal of the Fireworks Act 1951, as its remaining provisions have been superseded by the Pyrotechnic (Safety) Regulations 2010.
- The regulations are supported by a suite of overarching and subsector guidance namely:
    - L150 focuses on safety provisions
    - L151 covers security provisions

3.2.3.3 Safety provisions – L150 Safety Guidance

The guidance in L150 is for anyone who has duties under the safety provisions of the Explosives Regulations 2014 (ER2014) (SI 2014/1638). It is particularly relevant to duty holders such as employers, private individuals and other people manufacturing explosives, storing larger quantities of explosives or storing explosives that present higher hazards or greater risks of initiation. The publication provides overarching technical guidance that will help duty holders to comply with the safety provisions in the Regulations. It also identifies detailed topic-based and specialist guidance and provides background information that supports subsector guidance. It also contains material relevant to enforcing authorities such as local authority trading standards officers, the police, fire and rescue services and other emergency services.

The Guidance sets out general principles of safety in explosives operations. For example high standards of safety need to be in place before explosive operations start and they should remain in place, and be effective, for as long as the explosive operations continue. It is generally difficult or impossible to regain control of an event involving explosives once control has been lost. The safety provisions of ER2014 provide the regulatory framework for identifying and implementing these standards of safety and are based on generally recognised principles of safe operation in the sector.

There are ten general principles underpinning the safety provisions of ER2014. These principles should form part of the arrangements and working practices of anyone undertaking explosives operations:

- People undertaking explosives operations should be competent to carry out their particular roles.
- The particular hazards associated with the explosives should be understood.
- The sources of energy that could cause the explosives to initiate should be identified.

- Appropriate safety measures should be part of a planned and proportionate system of work to control all sources of energy that could cause an initiation.
- Particular care should be taken where an activity involves the application of energy to an explosive to ensure that this is controlled.
- So far as reasonably practicable, the quantity of explosives, extent and duration of exposure to the hazard should be minimised.
- The number of people exposed to the hazard should be limited to the minimum necessary for the activity in hand.
- Precautions should be in place to prevent an explosives event from escalating if an initiation does take place.
- Precautions should be in place to protect people if an initiation does occur.
- Robust systems should be in place to make sure that the necessary precautions are in place and remain effective.

Applying these principles should result in arrangements and safe systems of work which ensure that:

- Suitably qualified and experienced people are engaged in all elements of the explosives operations.
- The properties of any explosives being manufactured or stored are known and/ or understood.
- The hazards presented by the explosives under the conditions of their manufacture or storage will have been identified and assessed.
- Reasonably practicable steps are taken to segregate activities involving explosives from activities that do not involve explosives.
- Wherever reasonably practicable, sensitive explosives are desensitised during processing or storage.
- Explosives are not introduced into multi-stage processes until as late as possible.
- The amounts of explosive present in production and packing areas are limited to that needed for the work in hand.
- People are not exposed to explosives hazards unnecessarily.
- People in close proximity to explosives areas are provided with an appropriate level of protection from harm.
- Changes in processes and procedures are not made until checks have been made to see that all the control measures remain appropriate.

3.2.3.4 Regulatory framework

The safety provisions in ER2014 comprise four whole regulations and some elements of a fifth regulation. 41 The four whole regulations are:

1. Regulation 26 requires anyone manufacturing or storing explosives to take appropriate measures:
    - to prevent fire or explosions

- to limit the extent of fire or explosion including measures to prevent the spreading of fires and the communication of explosions from one location to another
- to protect people from the effects of fire or explosion

2. Regulation 27 requires people storing explosives to maintain separation distances, identifies the circumstances in which separation distances do not need to be applied, and identifies how separation distances are applied to certain sites that are granted a licence by HSE or ONR.
3. Regulation 28 requires anyone discarding or disposing of explosives, or who is decontaminating explosive-contaminated items, to ensure, so far as reasonably practicable, that they are undertaking those activities safely.
4. Regulation 29 prohibits the manufacture and storage and import of pyrotechnics containing sulphur and/or phosphorus mixed with chlorates without the approval of HSE.

Regulation 13 relates to the grant of licences but also includes safety provisions. It allows:

- HSE and ONR to prescribe separation distances at most of the sites they license as an alternative to the 'fixed rules' approach required by regulation 27.
- HSE and ONR to prescribe certain activities that will be subject to the provisions of the licence at most of the sites they license to take account of potential interactions between those activities and the manufacture and/or storage of explosives that takes place at that site.
- All licensing authorities to reinforce the requirements of regulation 26 as they relate to the sale of pyrotechnic articles at a site which is licensed for the storage of explosives.

3.2.4 Security Provisions L151 - Guidance

The security guidance publication is for anyone who has duties under the security provisions of the Explosives Regulations 2014 (ER2014). It is particularly relevant to duty holders:

- Acquiring, keeping and transferring relevant explosives
- Manufacturing, storing, transferring and placing on the market civil explosives
- Manufacturing, possessing or transferring plastic explosives
- It provides background information and detailed specialist and technical guidance that will help duty holders to comply with the security provisions in the Regulations.
- It also contains material relevant to enforcing authorities such as local authority trading standards officers, the police and fire and rescue services.

In relation to the security of explosives the following principles should be considered and applied:

- Explosives have the potential to be misused and that misuse can cause both harm to people, the damage or destruction of property and infrastructure, and disruption to wider daily life.
- In addition, inadequate controls can result in unauthorised people having access to places where explosives are manufactured, stored, kept or used which can increase the likelihood of a fire or explosion occurring through inappropriate actions or behaviours.
- Robust security controls need to be in place before explosive operations start and they should remain in place and be effective for as long as the operations continue.
- The security provisions of ER2014 provide the regulatory framework for identifying and implementing these security controls and are based on generally recognised principles of secure operation in the sector.

2.3.4.3 Regulatory framework

The security provisions in ER2014 can be found in three parts of the Regulations.

1. Part 10 comprises three regulations which relate to the prevention of the unauthorised access to, or acquisition of explosives. The three regulations are as follows:
    - Regulation 30 requires anyone who manufactures, stores or keeps explosives to take appropriate measures to prevent unauthorised people having access to either the places where the explosives are manufactured, stored or kept or to the explosives themselves. It also places a prohibition on people entering; – stores; – buildings used for manufacture; and – sites and places with marked boundaries; without the permission of the licensee and provides a framework for the removal of unauthorised people from the site.
    - Regulation 31 provides a framework for the lawful transfer of relevant explosives.
    - Regulation 32 prohibits the employment of prohibited persons in positions where they handle or control relevant explosives. It also prohibits the prohibited person from acquiring, handling or controlling relevant explosives and restricted substances for their own purposes.
2. Part 11 comprises five regulations which relate to the traceability of civil explosives, the records to be kept for both relevant and civil explosives, and the reporting of losses of relevant explosives. The five regulations are as follows:
    - Regulation 33 provides a framework for the unique identification of civil explosives.
    - Regulation 34 provides a framework for the attribution of manufacturing site codes for civil explosives.
    - Regulation 35 requires records to be kept for relevant explosives and identifies the information that those records should contain. It also

identifies those people who are not required to keep records and states that when regulation 36 comes into force, explosives that are both relevant explosives and civil explosives will only need records to be kept under regulation 36.

- Regulation 36 came into force on 5 April 2015 and requires records to be kept for civil explosives. The regulation also identifies what those records should contain and those people who are not required to keep records of civil explosives.
- Regulation 37 requires duty holders to report losses of relevant explosives. It provides a framework for the information on the loss that should be reported and requires duty holders to have proportionate systems in place to identify that a loss of a relevant explosive has occurred.
- Regulation 36 requires records to be kept for civil explosives. The regulation also identifies what those records should contain and those people who are not required to keep records of civil explosives.

3. Part 12 comprises one regulation relating to plastic explosives:
   - Regulation 38 prohibits the manufacture, transfer and import of plastic explosives unless they are marked with a detection agent.

3.2.4.1 The MOD and EA2014

The application and extent of EA2014 is limited. A number of regulations do not apply to defence activities:

- Regulations 4,5,11,19,21,22,31,32,35 and 37 do not apply to any explosive nuclear device.
  - Regulation 5 does not apply to the acquisition or keeping of explosives by or on behalf of the Crown, in respect of any explosives which is in premises occupied on behalf of the Crown for, or is intended for use for, naval, military or air force purposes or the purposes of the department of the Secretary of State having responsibility for defence or that of the Secretary of State having responsibility for home affairs or the service authorities of visiting forces or any headquarters or organisation designated for the purposes of the International Headquarters and Defence Organisations Act 1964(a).
- Regulations 6, 7, 12 to 14, 16 to 18, 20, 23 and 27 do not apply to the manufacture or storage of explosives, at any site under the control of the Secretary of State having responsibility for defence, or held for the purposes of a visiting force or headquarters, under a scheme approved by that Secretary of State which:
  a. provides for their safe manufacture and storage
  b. prescribes:
     i. separation distances or
     ii. a combination of separation distances and other safety measures, which are designed to ensure a standard of safety which is equivalent to that ensured by the separation distances, prescribed by regulation 27 and Schedule 5.

- Regulations 6, 7, 12 to 14, 16 to 18, 20, 23 and 29 do not apply to explosives which, for reasons of public safety or protection of property, are undergoing ordnance disposal by:
    - persons under the direction of a member of Her Majesty's Forces or civilian employees of the department of the Secretary of State having responsibility for defence authorised in writing by that Secretary of State to carry out ordnance disposal.
- Regulations 8 and 39 to 42 do not apply in respect of the transfer of civil explosives to, by or on behalf of, or where, following the transfer, the explosives are in the possession of:
    - The Crown in respect of any civil explosives which are intended for use for the purposes of the department of the Secretary of State having responsibility for defence or that of the Secretary of State having responsibility for home affairs.

3.3 ORGANISATIONAL ARRANGEMENTS

3.3.1 MOD and the Law

3.3.1.1 Introduction

The Secretary of State's (SofS) Policy Statement for Health, Safety and Environmental Protection (HS&EP) applies to everyone and all organisations within Defence and who conduct activities on behalf of Defence, including contractors and MOD's partner organisations. It explicitly identifies Top Level Budget Holders (TLBHs) and Chief Executives (CEs) of both Defence Executive Agencies (DEAs) and the Defence Infrastructure Organisation (DIO) as having responsibilities for meeting this policy for Duty Holding, where appropriate, and compliance with the statutory requirements. In doing so, they are required to describe their management arrangements, including the delegations to those managing activities on their behalf and ensure that at every level, both military and civilian, are suitably and sufficiently trained and provided with relevant information and access to resources to ensure compliance with the Policy Statement.

3.3.2 Director General, Defence Safety Authority (DG DSA)

The Policy Statement and the DSA Charter authorises the Director General, Defence Safety Authority (DG DSA) to:

a. Empower suitably qualified and experienced Crown servants to regulate HS&EP activity across Defence where it enjoys disapplications, exemptions or derogations from statutory requirements, where there is no statutory requirement or where assurance of specific hazardous activities is required.
b. Provide independent investigation of accidents and be the primary Convening Authority (CA) for safety-related Service Inquires (SIs).
c. Be the Defence Authority for HS&EP.

3.3.2.1 DSA01.1

DSA01.1 amplifies the Policy Statement and describes:

a. The HS&EP legislative framework that applies to Defence and how this is addressed by Defence policy
b. The responsibilities for the management of HS&EP across Defence
c. The requirements and arrangements for managing HS&EP risk in Defence
d. The requirements for checking and reporting HS&EP performance
e. The requirements for ensuring competence and providing information, training and instruction
f. The arrangements for regulation, assurance and enforcement of HS&EP in Defence activities

3.3.2.2 A failure in HS&EP management

A failure in HS&EP management has the potential to be detrimental to the health and safety of people, the environment, organisational reputation and ultimately the Department's operational capability. DSA01.1 describes the need for suitable and sufficient HS&EP management arrangements to prevent or minimise adverse work-related health and safety effects, impacts on the environment, organisational reputation and operational capability. The treatment and regulation of such risks are addressed by other DSA regulations and guidance. Legislation SofS's Policy Statement reinforces the requirement for Defence to comply with UK HS&EP legislation, (which includes legislation giving effect to the UK's international obligations). However, as a Department of the Crown, Defence has immunity from prosecution and there are provisions that allow total disapplication, specific disapplication, exemption or derogation from legislation:

a. A non-application of legislation is where an entire set of statutory requirements do not apply to MOD (e.g. Nuclear Installations Act 1965, Air Navigation Order or Control of Major Accidents Hazards).
b. Disapplications from specific parts of statutory requirements (e.g. Environmental Protection Act 1990, Explosive Regulations 2014).
c. Provisions within legislation for exemptions to be granted from specific requirements in recognition of a Defence imperative (e.g. the Health and Safety at Work Act etc. 1974 (HSWA74) permits the SofS to exempt the Department from any or part of the Act by order "to the extent that it appears to him requisite or expedient to do so in the interests of the safety of the State"). Other H&S regulations alternatively specify the exemption in the interests of national security.
d. Derogations are a lessening of a statutory requirement for justifiable practical or operational reasons (e.g. smoking in single living accommodation recognises the distinction from temporary accommodation such as hotels and hostels).

3.3.3 Defence Policy and Regulations

The HSWA74 requires employers to “prepare and, as often as may be appropriate, revise a written statement of his general policy with respect to the health and safety at work of his employees”. For these purposes, the SofS is regarded as the employer and complies with this duty through a Policy Statement. For convenience and consistency, this Policy Statement identifies the key requirements and high-level responsibilities for both health and safety and environmental protection and applies to all Defence activities and its personnel.

3.3.4 Disapplication, Exemption and Derogation

Where there is a disapplication, exemption or derogation from UK HS&EP legislation or where Defence activities are conducted overseas (outside of the requirement to respond to host nations’ relevant HS&EP expectations and cooperate with their HS&EP authorities), the Policy Statement requires Defence to put in place arrangements that produce outcomes which are, so far as is reasonably practicable, at least as good as those required by UK legislation. Accordingly, a fundamental responsibility of the Defence Safety Authority (DSA) is to regulate activities against Defence Regulations where there are disapplications, exemptions and derogations from statute. Defence Regulators are to consult with stakeholders on the maintenance of Defence Regulations that are appropriate to their domains: These regulations are to be coherent, consistent and proportionate to the risk and where possible goal-based across HS&EP Regulatory domains.

3.3.5 Influencing Emerging Legislation

It is essential that Defence is aware of, and can appropriately influence emerging legislation and consider the potential for consequential constraints on Defence capability. It is this awareness that safeguards those circumstances where disapplications, provisions for exemptions are granted, or, derogations are sought. Therefore, DSA is to ensure that emerging and changing legislation is tracked and influenced in order to protect Defence interests and when necessary seek disapplications, derogations or the provision for exemptions to be granted.

3.3.6 Responsibilities for Health, Safety and Environmental Protection in Defence Activities

3.3.6.1 As an employer

The Secretary of State for Defence is regarded as the employer for the purposes of complying with the requirements of UK HS&EP legislation and is answerable to Parliament for ensuring Defence complies with this duty through a Policy Statement that identifies the key requirements and high-level responsibilities for HS&EP management. The Policy Statement is the Defence

policy for complying with HS&EP requirements and applies to all Defence activities and its personnel.

3.3.6.2 Permanent Under Secretary (PUS) role

The Permanent Under Secretary is the Department's most senior official for HS&EP matters. The Permanent Under Secretary (PUS) is to ensure that effective management arrangements and resources are in place to achieve compliance with the Policy Statement. PUS is to include HS&EP performance in the Department's holding-to-account process.

3.3.6.3 DG DSA responsibilities

The Director General, Defence Safety Authority DG DSA is responsible, through a Charter from SofS, for the following responsibilities:

a. Empower suitably qualified and experienced Crown servants to regulate HS&EP for Defence activities in the UK where it has disapplications, exemptions or derogations from UK statutory requirements and Defence activities overseas, outside of the requirement to respond to host nations' relevant HS&EP expectations and co-operate with their HS&EP authorities.
b. To be the primary Convening Authority (CA) for Service Inquiries (SIs) into safety related fatalities, serious injuries and significant loss of major capability. To support him in this function, DG DSA maintains the Defence Accident Investigation Branch (Defence AIB).
c. As the Defence Authority for HS&EP setting standards and taking assurance of compliance by TLBs and Defence Executive Agencies where Defence has disapplications, exemptions or derogations through the Defence Regulators.
d. Providing independent advice to the SofS on HS&EP policy in Defence and evidence-based assurance that the policy is being promoted and implemented in the conduct of Defence activities.
e. Providing the Defence Board with information on HS&EP matters at each meeting and an Annual HS&EP Assurance Report.

3.3.6.4 DSA functions

In support of these responsibilities, the DSA undertakes three main functions:

a. DSA Headquarters (HQ) oversees the management of the DSA, supports the CA for SIs, formulates MOD HS&EP policy and provides independent assurance to the SofS.
b. DSA Regulators regulate: Where Defence has disapplications, exemption or derogation from statutory requirements; overseas; where there are no statutory requirements for unique military activities, and, where statutory requirements exist but the high hazard nature of the activity demands a higher level of Defence assurance.
c. The Defence Accident Investigation Branch (Defence AIB) conducts impartial and expert 'no-blame' safety investigations across Defence in

support of Service Inquires into safety related fatalities, serious injuries and significant loss of major capability.

3.3.6.5 DSA authority

Defence Authority DSA is one of 18 Defence Authorities, which set rules and standards that TLBs must follow to shape delivery of key functions that cut across Defence and are critical to Defence outputs. In accordance with the MOD operating model, “How Defence Works”, Defence Authorities provide these ‘defence directives’ and TLBs’ compliance with Defence Authority directives are assessed as part of the Defence Performance Framework and in an annual assurance report. As the Defence Authority for HS&EP, DG DSA discharges his responsibility specifically through the publication of HS&EP policy requirements and providing an independent Annual Assurance Report.

3.3.6.6 DSA publications

The DSA sets out rules and standards for Defence HS&EP in three broad levels of publications that is consistent with SofS’s Policy Statement:

- Level 1 – Departmental Policy for Defence HS&EP
- Level 2 – Defence Regulations owned by Defence Regulators
- Level 3 – Guidance on complying with Defence Regulations

Level 2 and 3 publications have been developed to replace the plethora of Joint Service Publications including the former JSP482 MOD Explosives Regulations and JSP520 Safety and Environmental Management of OME over the Equipment Acquisition Cycle, two of the main explosives publications in use in the past decade.

3.3.7 Roles of TLB Holders and Chief Executives

The SofS’s policy statement requires TLB Holders (TLBHs) and Chief Executives (CEs) of both Defence Executive Agencies and the Defence Infrastructure Organisation (DIO) to conduct Defence activities in their area of responsibility (AoR) safely, environmentally responsibly and compliant with legislation. In this latter respect, each TLBH/CE discharges the employer’s legal responsibilities, where they apply, on behalf of SofS. These employer’s duties are further delegated by each TLBH/CE to those with direct responsibility for managing Defence activities within their AoRs. Where an individual has such responsibilities, the TLBH/CE is to ensure that they are suitably and sufficiently trained and provided with relevant information and access to resources to ensure compliance with the Policy Statement.

3.3.8 Explosives Regulation in MOD

3.3.8.1 Introduction

Where Defence has disapplications, exemption or derogation from statutory requirements DSA is required to put in place appropriate arrangements that produce outcomes which are, so far as is reasonably practicable, at least as

good as those required by UK legislation. The Explosive Act 2014 as previously described has a number of disapplications for Defence hence DSA regulators are required to produce regulations that achieve appropriate outcomes.

The Defence Ordnance, Munitions and Explosives Regulator (DOSR) is responsible for regulating the majority of explosives and ordnance related activities in MOD. The explosive regulation for which the DOSR is responsible is found in

- DSA 02 - Defence Ordnance, Munitions and Explosives (OME) Regulations
    - Incorporating, Defence Ranges Regulations and Defence Major Accident Control Regulations (MACR)
- Defence Codes of Practice (DCOP) and Guidance Material
    - DSA 03 - OME Part 1 - OME Acquisition
    - DSA 03 - OME Part 2 - In-Service and Operational Safety Management of OME
    - DSA 03 - OME Part 3 - Ranges
    - DSA 03 - OME Part 4 - MACR
    - DSA 03 - OME Part 5 - Lasers

These Regulatory Publications apply to all personnel at all levels in the MOD who have duties and responsibilities for Health, Safety and Environmental Protection (HS&EP) associated with activities involving Ordnance, Munitions and Explosives (OME) (including Lasers), Ranges and Major Accident Control. These Regulations should be read with reference to DSA 01.1 - Defence Policy for Health, Safety and Environmental Protection.

In addition, the Defence Maritime Regulator (DMR) is responsible for the regulation of explosives on ships and submarines.

This chapter will consider the overarching regulation of explosives across the MOD covered by DSA 02 and DSA 03 – OME parts 1 and 3.

3.3.8.2 DSA 02 - Defence Ordnance, Munitions and Explosives (OME) Regulations

3.3.8.3 Introduction

Under UK legislation MOD is disapplied from parts of the Explosives Act 2014. Where disapplications apply the Secretary of State with responsibility for defence has issued a Policy Statement that requires Defence to put in place arrangements that produce outcomes which are, so far as is reasonably

practicable, at least as good as those required by UK legislation. DSA 02 describes in considerable detail what these arrangements are.

3.3.8.4 Applicability

The regulations, issued by the Chief Inspector of Explosives MOD), endorsed by the OME Safety and Environmental Stakeholder Committee (OSESC), and under the authority of DSA are produced for the guidance and instruction of all personnel, both Service personnel and MOD employed civilians (including supporting contracted staff), who are concerned with the management, storage, maintenance, inspection, processing, transport, handling and disposal of explosives and explosives storage facilities within the Ministry of Defence.

The regulations are based on mandatory provisions, in the form of legislation, and on the recommendations of the Explosives Storage and Transport Committee (ESTC) and NATO AC326, which set MOD standards and safety principles. The conditions provided by these regulations and such necessary ESTC recommendations are to be treated as the mandatory minimum safety regime that must be applied to explosives in the MOD.

Explosives in this context include all substances, and materiel containing substances, which are classified as Class 1 in the United Nations Recommendations on the Transport of Dangerous Goods.

Management of explosives safety within MOD, for the maritime environment, is a two-stage process. The first stage addresses the intrinsic explosive safety of the Ordnance, Munitions and Explosives (OME) following the process defined in DSA 02 and described elsewhere.

This process is MOD wide, for all environments and is undertaken by the OME Project Team. The second stage is the integration of the OME into a maritime platform and is undertaken following the processes defined in DSA 02 – Defence Maritime Regulations which identifies OME as a key hazard requiring independent safety approval and certification. Naval Authority Explosives NA (EXP) is formally authorised by the Defence Maritime Regulator (DMR) as an authority that is independent of the Platform Duty Holder and Operational Duty Holder and is responsible for providing safety regulation in the area of Shipborne Explosives hazards.

3.3.8.5 Applicability overseas and in operational theatres

In overseas theatres, ports, anchorages, airfields etc. it is the Secretary of State's (SofS) policy that the MOD applies all relevant UK/EU/International regulation or standards where reasonably practicable and, in addition, comply with relevant host nations standards. Where there is ambiguous regulation or apparent gaps against UK legislation or standards, we are to implement management arrangements that produce outcomes that are, so far as reasonably practicable, at least as good as those required by UK legislation. Where there is no relevant host nation legislation, our internal standards aim to optimise the balance between risks and benefits. This does not mean avoiding

risks but managing them responsibly, on the basis of consequence and likelihood. Where advice or direction is given by means of these regulations for peacetime, it is also normally to be applied during war or periods of tension, as to do otherwise may be seen as indefensible in court. Disobedience of Regulations or Infringements of DSA 02 Defence OME Regulations and any other associated regulations by any person will result in appropriate disciplinary action in accordance with MOD civilian or service procedures.

3.3.8.6 Nuclear weapons facilities

When Nuclear Weapons containing conventional explosives are stored, processed and handled in MOD Explosives facilities they will be subject to the conditions of this document.

3.3.8.7 Safety aspects - general

Although there are many kinds of items in service that require special precautions to be taken in their handling and storage, those containing explosives (including pyrotechnic or incendiary substances and certain chemical compositions) form a special class. Additional precautions are therefore essential, not only to preserve their serviceability, but also to provide the minimum practicable/acceptable risk, not only for personnel handling them, but also to other persons and property. It must always be borne in mind that the regulations contained in this publication deal with items that are potentially dangerous.

All persons employed in the custody and handling of explosives, whether in peacetime, periods of tension, or war, are to apply both the spirit and the letter of the regulations.

3.3.8.8 Fundamental principles

The fundamental principles underlying these regulations are:

The function of an explosive, pyrotechnic or incendiary substance or article is to explode or ignite violently. The greatest care is therefore to be taken at all times during storage, handling, transportation, processing, inspection, trials and disposal.

Explosives, even those with similar characteristics, differ in sensitiveness (see 20.2.1) to heat, friction, shock and impact. They also differ in stability under varying climatic conditions, and in their rate of deterioration.

Whilst explosives are designed to be stable, this stability may decrease if they are poorly packaged or stored. Furthermore, any physical or chemical degradation in an explosive, such as could arise if explosives have exceeded their design life, almost invariably leads to greater sensitivity rather than less.

3.3.8.9 Limiting the risk from explosives

To limit the risk it is advised that:

- All facilities used for storing and processing explosives must be licensed as suitable for the intended purpose. The HSE performs this role in the civil sector and CIE (MOD) Licences all explosives areas controlled by the MOD. For an explosives licence to be issued, CIE(MOD), through the offices of the respective IEs, must be satisfied that the facility will generate risks to people that are ALARP.
- In addition to ensuring that MOD explosives facilities are safe, CIE (MOD) must be assured that explosives safety management /with MOD business and operational imperatives. It is essential that, for example, storage capacity is adequate for forecast defence needs that encompass future strategic assumptions and not just day to day business. It has therefore been the custom to exploit fully the maximum licensable potential derived from Quantity Distances (QDs). However, while licensing for future needs and Safeguarding to protect against encroachment to Site Potential are a necessity, under the ALARP principle, it is not permissible to grant a working licence for more than the explosives quantity that can be clearly justified for the prevailing conditions. Experience has shown that the risk associated with individual
- PES (see 3.6.2.1) licensed and operated under normal MOD rules is normally within the Tolerable Region. In the case of large, complex sites, the cumulative risks from individual licensed facilities within the site will generate a higher cumulative risk.
- In order to demonstrate ALARP for processing facilities, it is necessary to keep the quantity of explosives present that hazard people to the minimum. Accumulations of explosives waiting processing return to store, or dispatch after processing are to be kept to a minimum.
- Concurrent processing of two or more munitions should be avoided since the activities of one processing team places its neighbouring team at risk and vice versa. Whenever concurrent processing of munitions is to be undertaken by 2 or more teams in the same process room, it is essential that the HoE provides evidence that appropriate protection has been afforded to all teams.
- The number of personnel exposed to explosives risks must always be kept to the minimum and all avoidable exposure must be eliminated. All personnel nonessential to that activity must be given appropriate protection from fire and explosion and closely controlled by local procedures laid down by the Duty Holder. Where people in fixed ES (see 3.6.2.1), who are necessarily mentioned on the PES (see 3.6.2.1) licence to enable closer safety management, are put at risk, and it subsequently becomes practicable to move those personnel and their activity elsewhere, it is not acceptable to substitute other personnel or another activity to take advantage of the latitude recorded on the licence. Any new need must be justified in its own right with the realisation that new facilities and activities may require, by law and HSE guidance, much higher levels of protection from risk. For multi-role facilities, the need to temporarily remove from risk those personnel not involved in the current operation must be considered even if it is not prescribed explicitly on the licence.

- The prime principle of ALARP is to think beyond pure licensing regulations as a permissioning system and to consider whether the activity could more reasonably practicably be performed in a safer manner. If safety can be practicably improved beyond the rules here prescribed, then a clear duty exists to do so that must be discharged. It is thus not sufficient to rely upon rules that take no account of local conditions that might demand or allow a greater level of safety provision. Therefore, for example, it might be permissible within these rules to place explosives at a reduced QD from people thus increasing their level of risk, but if an alternative location exists where the activity can be carried out at a greater separation distance, despite any perceived difficulties and inconvenience, that greater protection to life must be afforded. In this case however, the risks associated with relocating stocks should also be considered.
- Clearly, while on operations, in times of crisis or war, such action may not be practicable because other far reaching risks may be increased by not affording the best operational solution to site activity. Therefore, through general agreement with the MOD, the HSE has acknowledged that the Defence Imperative should be taken into account in determining what is reasonably practicable to ensure the health and safety of employees and others involved with defence operations and that training directly related to operations. Personnel responsible for safety must look beyond their immediate surroundings and situation to improve safety where local conditions and practicability exists. This is to be thought of as a necessary and mandatory continuous lateral thinking exercise.
- What is reasonably practicable will inevitably be a matter for judgement. However, by ‘accepting the risk' Duty Holders must satisfy themselves that, in their professional judgement, their decision is supported by thoroughly researched and balanced arguments that can be expected to hold up before searching scrutiny in a Court of Law. The resulting Explosives Licence is therefore to indicate or cross reference, in as much detail as possible, the factors and constraints governing the authorised NEQ limits and the matters that must be addressed, supervised and reviewed for effective safety management.
- However, it is essential for duty holders to note that although there is a general duty to manage risks so that they are ALARP where, in such cases the regulations are limited to “Shall…” or Shall so far is practicable”, in some cases legislation places a greater duty than “Shall so far as is Reasonably Practicable”. EA2014, for example, in relation to the prevention of fire and explosion, the limiting of the spread of fire and explosion and the protecting of people from the effects of fire and explosion places an absolute duty to take appropriate measures.

3.3.9 DSA 03 - OME Part 4 - MACR

The Control of Major Accident Hazards Regulations 2015 (COMAH) are the enforcing regulations within the United Kingdom of the Seveso II Directive which were developed within the EU following the Seveso disaster in

Italy when significant quantities of Dioxin were released into the environment causing serious harm to the environment and local population.

The regulations are applicable to any establishment storing or otherwise handling large quantities of industrial chemicals of a hazardous nature such as explosives or petrochemicals.

The principal aim of the regulations is to reduce the risks of potential major accidents, such as the Flixborough disaster, that are associated with the handling of hazardous substances. The regulations operate on two levels depending on the establishment's status which is divided into two categories, 'Lower Tier' and 'Upper Tier', determined by the size and nature of the inventory.

Lower tier establishments are required to document a Major Accident Prevention Policy which should be signed off by the managing director. A top tier COMAH establishment is required to produce a full safety report which demonstrates that all necessary measures have been taken to minimise risks posed by the site with regard to the environment and local populations. The penalty for unauthorised storage can be severe and companies unsure of whether the COMAH regulations apply should seek advice from trade associations and local health and safety inspectors.

The COMAH Regulations do not apply to:

- An establishment which is under the control of the Secretary of State for the purposes of the Ministry of Defence;
- A headquarters or organisation designated for the purposes of the International Headquarters and Defence Organisations Act 1964 or the service authorities of a visiting force within the meaning of any of the provisions of Part 1 of the Visiting Forces Act 1952.

In order to fulfil the SofS Policy to “put in place arrangements that produce outcomes which are, so far as is reasonably practicable, at least as good as those required by UK legislation”. The MOD publishes and promulgates DSA 03 - OME Part 4 - MACR. These mirror the civil regulations (COMAH).

3.3.10 DSA 03 - OME Part 1 - OME Acquisition

3.3.10.1 Introduction

DSA 03 comprises the DCOP and Guidance notes for OME Acquisition. It explains the requirements needed to demonstrate that the inherent risks from Ordnance, Munitions and Explosives (OME) are either Broadly Acceptable or Tolerable and As Low as Reasonably Practicable (ALARP) for the MOD, third parties and the environment.

It applies to all OME:

- Ordnance e.g., weapons including directed energy, small arms, delivery platforms including barrels, launchers, and fire systems.
- Munitions e.g., missile, shell, mine, demolition store, pyrotechnics, mines, bullets, explosive charges, mortars, air launched weapons, free fall weapons.
- Explosives e.g., propellants, energetic material, igniter, primer, initiatory and pyrotechnics irrespective of whether they evolve gases (e.g. illuminants, smoke, delay, decoy, flare and incendiary compositions).

It is designed to be used by personnel who are responsible for OME employed by or contracted to the MOD.

It contains the policy and direction about the processes involved and the techniques to be applied throughout the acquisition cycle or Manufacture to Target or Disposal Sequence (MTDS).

3.3.10.2 Defence Code of Practice

The DCOP is aimed at the OME Project Team (OME PT) responsible through the complete OME life cycle. It places specific requirements that are mandatory and must be followed by the OME PT. These requirements fall under a number of headings:

Scope

- Defines the meaning of OME
- Details how the risks for OME systems and their components shall be demonstrated at all stages of the acquisition cycle.
- It makes clear that DCOP does not only apply to weapon systems but applies irrespective of the use the OME. It further makes clear that where assessment identifies environments and stimuli that might jeopardise the safety of OME this information must be passed to Duty Holders.
- Where OME comprises a component of a larger system the interfaces with other parts of the system need to be considered. Hence the OME PT is required to define, agree record and control OME system stakeholders as part of the Through Life Management of the system.

Policy

The policy directive makes clear that it is the OME PT and supplier of the system to ensure that all relevant legislation is identified. A compliance assessment against all applicable legislation shall be undertaken of the OME.

Objectives

The OME PT is directed to comply with a number of objectives:

- To manage the OME Acquisition SEMS integrally with other safety and environmental management processes as part of a system of systems.
- To manage OME inherent safety through all stages of the equipment or system lifecycle, in conjunction with identified Duty Holders.

- To define the roles and responsibilities of authorities and personnel, whether the MOD or acting at the direction of the MOD, involved in the management of OME inherent safety.
- To define how their evidence of OME inherent safety will be documented in the Safety and Environmental Case and its validity maintained.
- To identify interfaces with associated authorities and policies.
- To comply with the requirements of these Regulations.
- To comply with DSA objectives specified through DSA Notices, prior to the issue of formal updates to this policy.

Standards

To comply with SofS's policy, the MOD requires evidence within the Safety and Environmental Case that the management and technical standards adopted by the Duty Holder are consistent with best civil and international best-practice as a minimum.

One of the standards to which MOD is committed is that relating to insensitive munitions. The MOD Policy is:

- "The vulnerability of the munitions in the MOD inventory shall be reduced over time to meet the requirements of STANAG 4439.
- All new munitions requirements shall stipulate compliance with the IM criteria. Agreement from relevant FLC/ODH is required for any noncompliance, either in the requirement definition or in the procurement solution, in addition to justification within the Risk Assessment.
- All in-service munitions shall be kept under review to identify opportunities to achieve IM compliance and thereby reduce risk. Prior to replenishing stock (e.g. mid-life updates, repeat buys, etc.), the procurement authority, normally the DE&S OME PT, shall investigate all options for improving IM compliance. Where improving the IM signature is technically achievable but for performance cost or time reasons, and the OME PTL proposes not to pursue improvements, agreement from relevant FLC/ODH is required.

Implementation

Implementation of the DCOP involves consideration of the scope of activity in relation to phases of the acquisition cycle and phases of the life cycle of the OME system such that:

- Safety management activities shall be initiated at the earliest possible stage in the MOD acquisition cycle. Where procurement follows the traditional MOD acquisition cycle, requirements shall be identified for each successive stage, including the specific Implementation and Assurance activities mandated by the OME regulations.
- At the early stages of a project the OME PT shall produce an OME SEMS, setting safety goals and initiating processes in an auditable trail of evidence that demonstrates compliance with individual goals and processes.

- This evolving body of Safety and Environmental Case evidence shall be used as the basis of successive reviews conducted by both the OME PT and the OSRP at key project milestones throughout the acquisition cycle.
- The processes defined by the OME PT shall follow the principles within the DCOP and shall incorporate sufficient flexibility to cope with projects following both a conventional acquisition cycle and alternate acquisition models, for example Off-The-Shelf procurement or Urgent Operational Requirement (UOR).
- All OME shall be assessed against their MTDS. The MOD safety responsibilities extend across the entire MTDS, necessitating PTs to establish a safety management approach that addresses specific safety issues particular to each stage. The Safety Assessment shall also consider the integration of all elements necessary to deliver the defence capability, taking account of associated equipment and platforms, personnel training, maintenance facilities, tactics and procedures.

Safety Requirements shall be established at the earliest stage in the acquisition cycle by the OME PT in close consultation with the capability sponsor.

Each OME PT shall identify and record safety requirements, in consultation with their Capability Sponsor (CS). Safety assessments shall be initiated at the earliest possible stages of the acquisition cycle, addressing the different issues that arise as the Project matures, or requirements alter, throughout the acquisition cycle.

Initial safety requirements shall be developed according to sound design practice or standards such as DefStan 07-85 , with particular emphasis on specifying those safety requirements arising from safety legislation, regulations, standards and the MOD policy. Where production of the Safety and Environmental Case is contracted out, recognition of contractual requirements shall also be given.

For areas of design that are not regulated, appropriate Subject Matter Experts shall be consulted for advice on best-practice and the availability of standards and procedures appropriate to the requirements selected. Adoption of alternative standards to those usually selected shall be justified within the Safety and Environmental Case.

Requirements shall cover the entire system, throughout its acquisition cycle and across the entire MTDS, with due regard for military effectiveness and the system's Safety and Suitability for Service (S^3).

All requirements shall be periodically reviewed to consider the effects of emerging capabilities from new equipment, or the application of new / current military thinking, tactics, techniques and procedures on previous assumptions.

The Safety and Environmental Management System is to be established by the OME PT so that:

- The OME PT's OME SEMS shall be established at the initiation of a Project, and shall be managed, maintained, reviewed and updated through-life.
- The OME PT shall establish a Safety and Environmental Panel (SEP) to manage its SEMS through-life.
- All PTs shall satisfy the requirements of the domain-specific safety regulations relevant to the operating environments for that OME by working within a robust integrated SEMS. For Defence OME Regulations-applied systems, the SEMS shall also provide a description of the PT's system for managing inherent OME safety and complying with the requirements of the regulations. This may be in the form of a stand-alone PT OME SEMS or as an Annex to the main document.
- The content of the PT OME SEMS assumes the existence of an overarching PT SEMS that has been produced to the requirements of an alternative functional safety policy. Where no such document exists, the PT shall develop a comprehensive SEMS to meet the requirements of one, or more, of the domain safety policies.

Allocation of OME Review Category

The level of effort and resources applied to the management of OME safety should be proportional to the complexity of the system and level of risk involved. This shall be determined by the OME PT identifying and assigning an OME Review Category to all OME.

The OME Review Category shall be initially assigned at the earliest possible stage in the acquisition cycle and prior to OSRP assessment, but may change as the project develops and further information becomes available.

The OME Review Category shall also determine the level of review to be undertaken by the OSRP. Systems reviews will be proportional to the risk; therefore Low Risk systems will have a lower level of review than that undertaken for High / Medium Risk systems.

Munitions Life Assessment

Munitions Life Assessment (MLA) aims to promote more effective through-life management of munitions and, as a consequence, the optimisation of munitions' lives.

The tools and techniques of MLA shall be applied to all stages of the MOD acquisition cycle and the MLA principles for Initial Service Life Trials, Service Life Amelioration Methods and In-Service Surveillance (ISS) implemented. The SEMS shall also take due cognisance of the management structures for implementing the MOD MLA policy across the MOD.

Conducting Trials

Conducting trials are necessary to generate evidence to support the Safety and Environmental Case arguments.

Where trials are performed at the direction of the MOD, whether on contractor's premises, UK or foreign ranges or in the service operating environment, the OME PTL (or nominated Duty Holder, including the sponsor) shall have a responsibility for ensuring the inherent OME safety of their equipment under trial, within the boundaries of the operating envelope. Duties Holders are to jointly risk assess any operation outside that envelope. Such trials shall require an OSRP Assurance Statement via an OM.

Safety and Environmental Case Development

DefStan00-56 defines a Safety Case as "A structured argument, supported by a body of evidence that provides a compelling, comprehensible and valid case that a system is safe for a given application in a given operating environment." POEMS (see 19.5) defines an Environmental Case as "A body of evidence that is compiled and maintained throughout the lifetime of a project on its environmental aspects and impacts". In recent years Safety Cases and Environment Cases have been combined together, into a Safety and Environmental Case.

The MOD policy stipulates that a robust body of safety and environmental evidence termed a Safety and Environmental Case shall support all equipment operated by or at the direction of the MOD.

The overall safety of weapon systems shall follow the hierarchical approach by assessing the interaction of all systems with the potential to influence the inherent OME safety, including safe operation and suitability for use. The OME PT shall prepare a Safety and Environmental Case for their system or equipment that complements the higher-level systems or platform Safety and Environmental Cases. The aim is to have a seamless flow of safety information between Safety and Environmental Cases at successive levels, be it equipment, system or platform.

The Safety and Environmental Case shall define the system, its boundaries and its operating environment, with all interfaces clearly identified and effectively managed.

OME Safety and Environmental Case Reports (SECRs) shall be produced periodically and at Key Project milestone (Section 7) in the MOD acquisition cycle from Initial Gate onwards.

As the Project matures, subsequent SECRs shall summarise the results of the formal safety and environmental assessment activities conducted by the OME PT. It shall provide compelling evidence that the OME system complies with relevant legislation and that appropriate OME safety risks are either Broadly Acceptable or Tolerable and ALARP, throughout the MTDS when operated within agreed boundaries.

The SEMS shall articulate those posts that have the authority to sign off residual risks, whether it's the Platform Duty Holder and / or the weapon OME PT, as appropriate. Such approval shall indicate their satisfaction with the

progress of the Safety and Environmental Case and their acceptance of the risks and environmental impacts associated with the project.

Existing OME Safety and Environmental Cases shall be reviewed when changes occur to the modification state; operating environment; or the role of the subject equipment, and the existing arguments justifying the safety claims reassessed.

The OME SECR shall include references to relevant clearances and certificates, as applicable, which support introduction into service including:

- ESTC Hazard Classification
- Explosives qualification.
- Range safety assessments
- Laser safety certification
- IM assessment
- Air carriage clearance
- Aircraft Weapons Air Carriage and Release (Aircraft Self Damage [ASD], Thermal Effects on Airborne Conventional Armament Stores and Equipment [TEACASE] and Aircraft Weapons Ballistic Committee [AWBC])
- Logistic Parachute Delivery Clearance, commonly known as Air Drop Code
- Defence Munitions Approval to Process (ATP) and Approval to Store and Handle Explosives (ASHE)

Risk management

OME PTs shall adopt a risk-based safety management approach to system design and through-life management. They shall demonstrate in their Safety and Environmental Case and SEMS details of their system, its manner of operation, and the operating environments to which it will be subjected. They shall begin implementation of processes that shall identify hazards and provide an assessment of that OME's response to a wide range of credible stimuli at the earliest possible stages of the project. In turn, they shall assess levels of risk presented by the OME and consider reduction of those risks using suitable methods to control consequence and / or probability, and seeking appropriate advice from OME Safety Advisors and Subject Matter Experts. They shall consider the balance between operational benefits and options for mitigation, by avoiding the imposition of inappropriate controls and justify their decisions accordingly.

OME Safety Submission

DSA requires that all OME systems are assured for compliance against these regulations. Assurance of inherent OME safety shall be through the independent review of documentary evidence undertaken by an OSRP

The OME PTL shall present OME Safety Submissions for OSRP review at key project milestones throughout the MOD acquisition cycle. These shall include:

- Initial Gate
- Main Gate
- Entry to Service
- In-Service changes
- Withdrawal from Service

In addition to these main milestones, the OSRP Secretariat shall be notified at any stage of the MOD acquisition cycle where changes affect assumptions about the inherent safety of the system.

The OME SECR shall provide sufficient detail to satisfy the OSRP that relevant legislation and standards are complied with, that residual risks are either Broadly Acceptable or Tolerable and ALARP statements are comprehensive, credible, robust and proportionate.

Where an OME Safety Advisor and / or ISA is appointed by the PT, all relevant conclusions drawn from advice and / or audit reports shall be included in the OME SECR to provide support to safety arguments and declarations.

The issue status of all OSRP Assurance Statement shall be recorded and monitored for currency.

Appointment of an OME Safety Advisor

Unless the OME PTL can demonstrate that sufficient OME safety competence exists within their PT to fully discharge the responsibilities defined in this DCOP, they shall obtain external specialist advice from a source that can be demonstrated as independent.

Management of Safety Information

As the Safety and Environmental Case includes a ‘body of evidence’, identifying, obtaining and managing the evidence it is of the utmost importance. The OME PT shall put arrangements in place to manage the identification, obtaining, updating, configuration control and review of safety related documents and information; ensuring that urgent safety related information is made visible to all relevant Duty Holders / Users without delay.

Transferring the Safety and Environmental Case

Where an OME system is to be transferred to another management authority, it shall be the joint responsibility of the existing acquisition and operating authorities to ensure that the Safety and Environmental Case is complete and up to date. The handover and acceptance criteria shall be systematic and documented.

3.4 CLASSIFICATION OF EXPLOSIVES

3.4.1 Background to Classification

Explosives are dangerous goods. It has been agreed by the United Nations (UN) that dangerous goods should be classified so that those handling them can understand the dangers which they pose. This facilitates their transportation across national boundaries. The UN has published a set of model regulations(1). These are used to inform each nation's own legislation to ensure the there is a consistent approach to the handling of dangerous goods.

Within Europe, more specifically, the United Nations Economic Commission for Europe (UNECE), 48 Countries (Contracting Parties) have agreed the arrangements for the transportation of dangerous goods by road(2) also known as ADR. In accordance with ADR explosives must have been assigned a classification by the Competent Authority of the Contracting Party before they are transported by road and this is regulated in the UK by The Carriage of Dangerous Goods and Use of Transportable Pressure Equipment (Amendment) Regulations 2011.

3.4.2 The Process of Classification

'Classification' is a technical process that identifies and considers the hazards posed by explosive substances and articles as packaged for transport.

The Competent Authority of a Contracting Party to ADR must assign the classification of explosive materials before they can be transported by road within Great Britain. The process involves assessing an explosive to determine whether or not there is a danger of fire/explosion that would jeopardise safe transport in terms of:

- thermal stability i.e. the response to heat and flame
- sensitiveness (see 20.2.1) towards mechanical stimuli i.e. the response to impact and friction
- response to dropping an unpackaged article, packaged article or packaged substance from a height of 12 metres.

The final stage of the process is to assign the explosive to – or exclude from – Class 1 of the UN classification scheme for the transportation of dangerous goods by assessing its behaviour in terms of:

- mass explosion of a single package
- propagation potential towards other packages or from a non-packaged article to another
- mass explosion, dangerous projections, radiant heat, violent burning or other dangerous effect when packages are involved in a fire
- hazardous effects outside the package arising from accidental ignition or initiation of contents.

An explosive assigned to Class 1 is given an appropriate UN Serial Number, hazard division and compatibility group, depending on its composition, type, and hazard.

A Competent Authority is a body designated or recognised to carry out duties under transport of dangerous goods regulations. In Great Britain:

- HSE is the Competent Authority for the classification of non-military explosives.
- Military explosives, i.e. explosives under the control of and/or in connection with the execution of contracts for the Secretary of State for Defence are classified by the Defence Ordnance Safety Regulator (DOSR) of the Ministry of Defence.
- The arrangements for the classification of military explosives are set out in DSA 03.OME Part 2 (JSP 482).

Once the Competent Authority has agreed the classification, it issues a Competent Authority Document (CAD). An industry guide provides further details[3].

3.4.3 The Role of HSE

As Competent Authority, HSE:

- assigns classification of non-military explosives where a CAD does not exist
- recognises the classification of explosives whose classification has been assigned by the Competent Authority of a country that is not a Contracting Party to ADR
- issues a CAD, which records the classification granted, and any appropriate conditions

HSE lists all GB-classified explosives on the LOCEF database, which can be found on the Explosives Web Community internet site[4]. Registration is required to access the site and access is free.

3.4.4 Classification of Military Explosives

3.4.4.1 The Role of the Defence Ordnance Safety Regulator (DOSR)

DOSR is the UK Competent National Authority for the classification of military explosives. DOSR-TL is delegated as the Ministry of Defence Classification Authority. Classifications awarded by the HSE and the DOSR are normally, but not necessarily, acceptable to each other.

The only exception to this policy is for Serviceable ACA’s which have been previously classified for transportation of explosives. The furniture of these containers may be modified to enable on Unit transportation of prepared for use natures e.g. Armed Fire Bottles, Countermeasure Flares etc. These transit containers are to be painted RED and be suitably marked with the contents and

Hazard Division. A transit container may be used for on Unit storage whilst awaiting fitment or disarming.

With the exception of the storage of explosives retained for Research and Development or Evaluation purposes and Bird Control Explosives, all, explosives must be classified by the DOSR before they can be stored or transported by the MOD. The DOSR-TL, after review, issues the classifications on behalf of DOSR. These classifications are taken into use immediately.

All explosives stored for Research and Development or Evaluation at Fort Halstead or Porton Down do not require formal classification by DOSR. These explosives must be assessed by appropriately authorised competent persons and allocated a suitable Hazard Division and Compatibility Group prior to storage. For any subsequent movement on, e.g. transport on the public road, the explosives must be classified by DOSR, using either the Temporary or Provisional process. DOSR Classifications are detailed in the Defence Ordnance, Munitions and Explosives (DOME) database. The awarding of a classification does not imply the item is safe to store and transport. The classification is only applicable to items that are assessed as safe to store and transport by a competent person.

It is important to understand that a DOSR classification is not the only requirement to permit storage or transport. Other legal and procedural requirements to enable safe storage and transport are detailed within DSA 02 Defence OME regulations and DSA 02.OME Part 1 (e.g. UN Package Certification and Safety Case Reports). The DOSR classification also guides the correct response by emergency services in the event of an accident.

3.4.4.2 Method of Obtaining a Classification

The DOSR is the only authority in the UK for assessing and classifying military explosives, including those imported for British and Visiting Forces, and foreign munitions for either transhipment to or within theatre, or for information gathering purposes. Military Explosives having HSE or Foreign Competent Authority Certification require classification by the DOSR. It is illegal to transport Military Explosives by road or rail within the UK without DOSR classification.

It is the responsibility of the appropriate MOD Branch or PT sponsoring the Staff Requirement or Main Supply Contract to initiate action to provide the DOSR with all the necessary information to classify the item(s). They should also provide funds for any tests that the DOSR consider necessary for classification.

3.4.4.3 Assigning a Classification

Explosives may be assigned a classification by one of the following methods:

- on the basis of UN test results and information supplied
- by analogy with a similar explosive previously classified by HSE or DOSR
- technical argument through documentary evidence

- by recognising the classification assigned by the Competent Authority of a country that is not a Contracting Party to ADR
- for fireworks that are manufactured in Great Britain or a country that does not have a Competent Authority – UN default classification scheme

The DOSR process of classification of military explosives as packaged (when stowed and transported in such a condition) consists of the allocation of the appropriate:

- HD, as a result of tests or by analogy
- CG
- UN Number and UN Proper Shipping Name selected from the Dangerous Goods List, ('The Orange Book')

The Test Scheme used by DOSR and other competent authorities is that detailed in Part 1 of the UN Manual of Tests and Criteria. The sections concerning military explosives are repeated in NATO AASTP 3 - Manual of NATO Principles for the Hazard Classification of Military Explosives. The UN Test Scheme relates to explosives as presented for transportation, but MOD has extended its use to cover storage. The UN Manual or NATO AASTP must be referred to for details of the Test Scheme and the sentencing criteria, as outlined below at Figure 3-1.

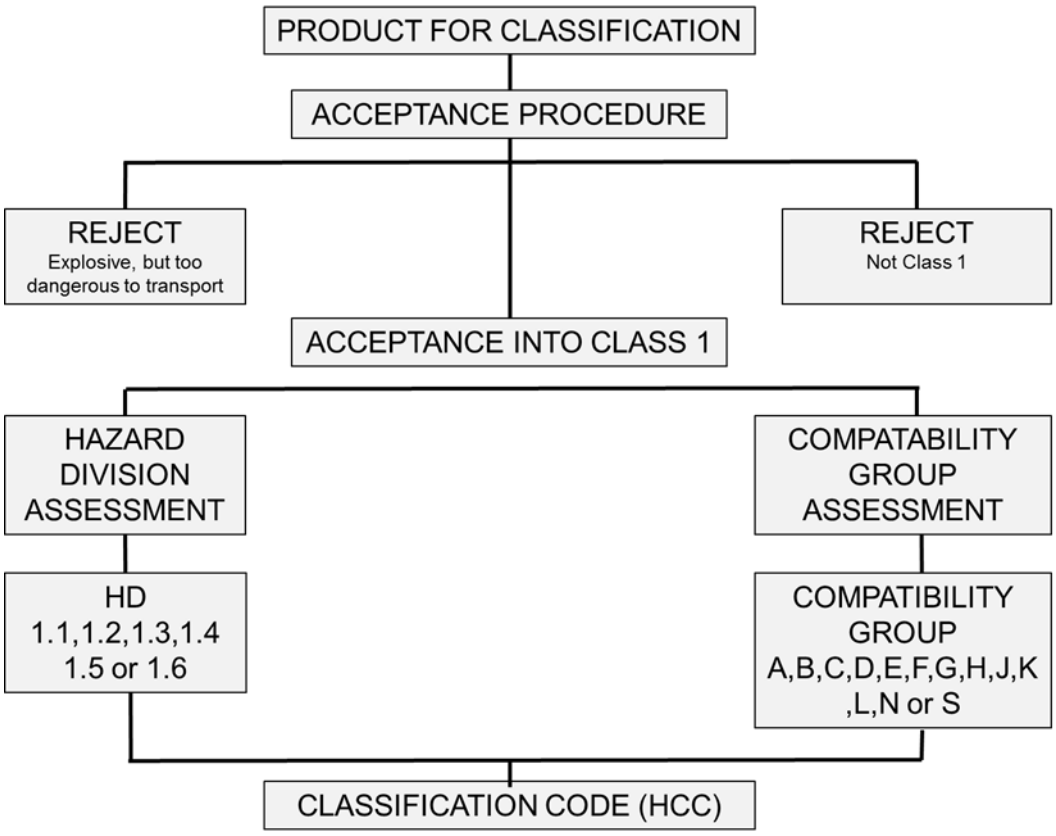


Figure 3-1 Overall Scheme of Procedure for Classifying Substances or Articles in UN Class 1

3.4.4.4 Purpose of the Scheme

The purpose of the scheme is to assign the classification code which is essential for transportation and, in the case of MOD, for storage. Evidence of the behaviour of explosives in their transportation and storage environment is essential to assign a classification code. Where evidence does not exist then practical tests should be carried out. The UN testing scheme is described in detail at Appendix A of this Chapter. The first group of tests, series 1-4 are to decide if the substance should be accepted into class one whilst the second group, series 5-7, is to determine the hazard division. In the absence of clear evidence then the most onerous classification should be applied. Hence if there is no clear evidence that an item is in HD1.3 then it must be assumed that it is HD1.1.

3.4.4.5 Responsibility for Testing

It is the responsibility of the party requiring classification to provide test results for series 1-4 and 5-7 to the Classification Authority as required. The test results should come from a recognised test authority.

3.4.4.6 Packaging

Care needs to be taken to ensure that classification is determined for each condition in which the explosives are stored and transported. The test results from classification tests may vary depending on whether the explosives are packaged or not and the nature of the packaging. Planning the classification test programme will require close liaison with the Classification Authority to ensure that appropriate classification is assigned depending on the nature of packaging during the explosives life cycle.

3.4.4.7 Types of Classification

There are six types of MOD classification:

1. **Permanent Classifications**. These are intended to cover all in-service military explosives in their service packages, in unit loads, or unpackaged articles in handling devices when stored or transported in such conditions. These classifications are identified by a four figure DOSR Serial Number prefixed by the letter ‘P’, e.g. P3254.
2. **Temporary Classifications**. These are intended for allocation to military explosives in the development or final disposal stage, remain extant for a specified period up to a maximum of 10 years, and are automatically cancelled at the end of this period. Temporary Classifications may also be used for Foreign Munitions which are only expected to be stored or transported by MOD resources for a limited period. These classifications are identified by a four figure DOSR Serial Number prefixed by the letter ‘T’, e.g.T2361.

3. **Excluded From Class 1 Classification**. These are intended for articles that satisfy certain conditions and are identified by a four figure DOSR Serial Number prefixed by the letter 'N', e.g. N0025
4. **Provisional Classifications**. These are allocated for the short term storage and one-off transport of military explosives, as defined, during research and development and disposal, normally between MOD sites, but can also be to/from sites under contract to MOD provided the journey begins / ends at a MOD site. Provisional classifications are extant initially for three months. The identifying number for these is determined by the applicant.
5. **EOD Disposal Classifications**. These are awarded to facilitate a need to transport and store EOD arisings prior to final disposal they should be classified in accordance with DSA 03.OME Part 2.
6. **Research and Development (R&D) and Evaluation Classifications**. These are allocated at Fort Halstead or Porton Down only to allow the STORAGE of military explosives undergoing R&D or evaluation (see para 1.1.6). This hazard assessment must be recorded in a register (in a format agreed by DOSR) and retained for audit purposes. This classification CANNOT be used to transport explosives off site.

3.4.4.8 Procedure for Obtaining Classifications

The procedures for obtaining different classifications are set out in DSA 03.OME Part 2. Broadly, permanent, temporary and items excluded from Class 1 must be classified by DOSR whilst provisional, EOD arisings and research explosives can be classified by a competent person with delegated authority from DOSR.

3.4.4.9 Classification of Explosives Belonging to Visiting Forces

Explosives of visiting forces must be classified and marked in accordance with UK legislation. Classifications assigned by foreign authorities must be endorsed by DOSR. The procedure for obtaining endorsement requires information to be supplied in advance to DOSR before any movement takes place.

3.4.5 Other Classification Requirements

3.4.5.1 Classification under the Classification, Labelling and Packaging Regulation

European Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures(5) came into force on 20 January 2009 in all EU Member States, including the UK. It is known by its abbreviated form, ‘the CLP Regulation’ or just plain ‘CLP’. The CLP Regulation adopts the United Nations’ Globally Harmonised System on the classification and labelling of chemicals (GHS) across all European Union countries, including the UK.

Explosive substances and articles must also be classified under CLP and requires manufacturers and suppliers to provide their customers with

information about the hazards associated with their products and to package them safely.

3.4.5.2 Classification under Registration, Evaluation, Authorisation & Restriction of Chemicals (REACH)

REACH[6] is a European Union regulation concerning the Registration, Evaluation, and Authorisation & Restriction of Chemicals. It requires safety data sheets (SDSs) to be provided. REACH is a European system for regulating chemicals imported into the EU in quantities greater than 1 tonne. The detailed CLP and REACH requirements are separate to the explosives classification process.

3.5 EXPLOSIVES LICENSING ARRANGEMENTS

3.5.1 Licensing Principles

Since the introduction of the 1875 Explosives Act it has been a legal requirement in the UK for all sites required to store, handle or process explosives to be licensed. A license is a document that allows the holder to store and/or manufacture explosives. The holder of the license is the person who controls the activities covered by that license such as storage or manufacture and who complies with the conditions of the license.

The license is issued by either, Local Authorities, Police, Health and Safety Executive (HSE) or Office of Nuclear Regulation (ONR) depending on:

- Whether the activity is manufacture or storage
- Whether an explosives certificate from the police is needed to acquire and keep the explosives
- The quantity of explosives
- Whether the separation distances can be met.

In the case of military explosives and MOD facilities the Secretary of State for Defence is authorised to operate his own scheme for Separation Distances (Quantity Distances) and Explosives Licensing.

There may be occasions where, for one reason or another, MOD estate is not licensed by the MOD but by HSE, the Police or Local Authority, and vice-versa. The underpinning intent is to issue the explosives licence to the person carrying out the activity; therefore that person will be accountable for controlling the activity, on a day to day basis; consequently if a person does not have the requisite authority to control the people and activities then they should not be the explosives licensee.

Where a facility is licensed by MOD the relevant MOD Inspector of Explosives will license in accordance with the following principles:

- Explosives buildings, facilities and associated traverse if required, must be constructed to an approved design.

- Where Electrical installations will form part of the building infrastructure then they must conform to the required standard, but they can be to an approval from TA Electrical Safety.
- With certain exceptions, a Lightning Protection System must be installed. Legacy systems are acceptable providing they continue to meet the design and performance criteria applicable at the time of installation, unless legislation or a safety concern requires retrospective action.
- All new explosives buildings are to be commissioned in accordance with ESTC Standard 6 (Requirements for the commissioning, inspection, testing and maintenance of works for explosives facilities in the Ministry of Defence).
- All explosives facilities must be subject to acceptance by the relevant TLB/TFA security service. Any security requirements must be complied with, or where observations allow a HoE to accept a security risk, there must be evidence of such acceptance. All explosives facilities must be subject to acceptance by DFRMO, where DFRMO is the Fire Enforcing Authority. Any requirements of DFRMO must be complied with, or where observations allow a HoE to accept a fire risk, there must be evidence of such acceptance.
- Where DFRMO is not the Fire Enforcing Authority (such as with CCF located in schools) then the TLB/TFA IE is to inform the relevant fire enforcing authority, in writing, to comply with the Regulatory Reform (Fire Safety) Order 2005 Section 42(1)(a). Any requirements made by the relevant fire enforcing authority must be complied with).
- An effective Safety Management System (SMS), appropriate to the explosives activities for which the explosives licences are required, is to be in place.
- There is to be a suitable organisation with the appropriate competences, under the command of the explosives licensee, to operate the SMS and manage the duties required by MoD regulations.

The appropriate Quantity Distances (QDs) should be met. Licences are to be issued on the basis of appropriate protection to people; the underlying principle is that people are to be afforded protection from a fire or explosion and this may be by distance or distance and other safety measures.

Validity of the explosives licence, once issued, is dependent upon continued maintenance of explosives facilities in accordance with ESTC Standard 6; there being no comments restricting or prohibiting the presence of explosives by the security or fire services; no infringements of the QDs; and the continued effective management of the explosives facilities and activities.

Consequences from an unplanned fire or explosion in a PES (see 3.6.2.1), to people within an ES (see 3.6.2.1) external to the PES, can normally be assumed to be at least tolerable if all the Explosives Licences for all the PES on site meet all the normal requirements of the Quantity Distances. Where there is full compliance with DSA 03.OME Part 2 then a Standard Explosives Licence may be issued by the TLB/TFA IE.

Where the requirements of Structural Standards, Electrical Infrastructure, LPS, Fire, Security or Quantity Distances cannot be met, this may not in itself necessarily preclude the issue of an Explosives Licence. Situations may also occur which the prescribed standards do not address. In these cases then a Technical Assessment (TA) or Consequence Analysis (CA) should be made to determine whether the intent of the legislation or regulations is being met and form part of the evidence within a Safety Case (SC).

3.5.2 Technical Assessment and Consequence Analysis

3.5.2.1 Unable to Meet Standard Conditions

There may be various reasons why the standard conditions cannot be met. These may include construction to previous standards; alternative arrangements are already in place; or explosives to be held are less than the minimum assumed by QD tables' minimum separation distances.

3.5.2.2 Choice of Technical Assessment or Consequence Analysis

The TLB/TFA have the option to arrange for a Technical Assessment or a Consequence Analysis (TA or CA) to be conducted by a competent person; this may be someone from within their own chain of command or an external person if the TLB/TFA does not have the competence.

3.5.2.3 The Basic Principle of the TA or CA

The Basic Principle of the TA or CA is to compare the standards that would have been achieved if full compliance with the regulations was met with that that is being achieved in practice. If the TA or CA can demonstrate that the intention of the regulations has been met then this will allow for the authorisation of the explosives licence by the TLB/TFA IE.

3.5.2.4 Failure to Meet Intent of Regulations

If the TA or CA demonstrates that the intent of the regulations has not been met then the licence should not to be issued. If the TLB/TFA still requires a licence then it must comply with the Non Standard Licence procedures.

3.5.2.5 Conditions Imposed on TA or CA

All explosives licences issued on the basis of a TA or CA should refer to the TA or CA and any conditions imposed by the TA or CA should be licence conditions; otherwise the TA or CA assumptions may be invalidated.

3.5.2.6 Infrastructure related TA

Infrastructure related TA will normally relate to either statutory standards or MoD mandated standards. In either case, where the current standard is not being met in practice then the appropriate Technical Advisor should be requested to assess the actual arrangements against the statutory or

mandatory requirements. Particular attention must be paid to any appropriate Approved Codes of Practice (ACoP) or industry best practice.

3.5.2.7 Intent of the Statutory or Mandatory Requirement is Being Met

Where the assessment demonstrates that the intent of the statutory or mandatory requirement is being met, and MoD is in a position to defend itself, then the explosives licence can be issued by the TLB/TFA IE.

3.5.2.8 Continued use of Infrastructure

Infrastructure that has been installed under previous standards, and where there is no breach of safety standards, may continue to be used providing that the performance continues to meet the standards at the time of installation. The exception to this is where legislation, or other safety concerns, may require retrospective action.

3.5.2.9 Explosion Effects CA

Explosion Effects CA must consider the hazards produced in the event of a fire or explosion. These may include:

- Blast
- Primary fragmentation such as from the munitions casing
- Secondary fragmentation such as from the munitions packaging or other munitions
- Debris from the structure or other non-explosives articles present
- Thermal effects from blast or fire
- Toxic effects of gases produced during fire

3.5.2.9.1 Output from the CA

The CA must identify:

- The hazards and level of hazard generated in the event of a fire or explosion
- Any secondary hazards that may be present such as fuel installations etc.
- All people exposed to the hazard and the degree of protection afforded to them
- Whilst the priority is the protection of people, consideration must be given to assets where such assets are critical; their loss may have a strategic impact and be unacceptable.
- The potential consequences to the people and assets exposed to the explosives hazard
- Any other mitigation measures in place

3.5.2.9.2 Comparison of Potential Effects with Full Requirements

The CA must provide a comparison between the potential effects to people and assets exposed to the hazard vs the potential consequences if the full

requirements of the QDs had been met. In order to achieve this it is probable that the effects will need to be modelled. An ESTC approved modelling tool must be used where this is necessary.

3.5.2.9.3 People for Suffering no Greater Harm

Where the CA demonstrates that people exposed to the hazard will not suffer greater harm than that would be expected if full compliance with the QD's/Structural requirements had been met then a Standard Licence can be authorised by the TLB/TFA IE.

The term general public applies to all people, MoD employees, contractors and members of the public who are not involved in the explosives activities for which the licence is required.

3.5.3 Non Standard Licences

3.5.3.1 Issuing a non-standard licence

In principle there should be no Non-Standard explosives licences. However, it may be that the TLB/TFA still requires an explosives licence to support their activity. Depending on the level of residual risk it will be for CIE (MOD) or PUS to determine whether defence will underwrite the risk and therefore allow the issue of an explosives licence.

Where the TLB/TFA believes that in order to meet the Defence Imperative the activity is required, irrespective of the residual risk, and then they must make an application to CIE (MOD), as detailed below. The application must be submitted with sufficient time for adequate scrutiny and possible referral to PUS.

The CA detailed above may require the need to undertake a Quantitative Risk Assessment (QRA) as part of the SC.

The SC may provide a variety of potential scenarios and consequences. The CA will provide an output expressed in terms of Conditional Probability of Fatality based upon the explosion happening; Annual Risk of Fatality for an individual at exposed sites (Individual Risk); and of the surrounding population as a whole (Societal Risk).

A SC must be supported with clear evidence as to the Defence Imperative; what options have been considered; reasons for rejecting options and selection of the preferred option; and the consequences of not being granted an explosives licence.

Where an option exists that meets the standard licence conditions then there will need to be a very compelling argument to support why it has not been taken where:

- The general public are at no greater risk of harm than if they were at the full QD appropriate for the circumstances (PTRD, IBD OR VBD)
- Potential consequences only affect explosives workers and explosives area support workers

- Where the risks, Individual and Societal lie between the Broadly Acceptable and the Intolerable, the Safety Case submitted to CIE(MOD) must be endorsed by an appropriate 1* from the TLB/TFA requiring the activity. The 1* is to have the authority to accept the risks on behalf of the TLB, and confirm that all options have been considered; with reasons as to the appropriateness of the selected option.

Then the TLB/TFA IE may authorise the licence if it has CIE (MoD) endorsement where:

- The general public are at greater risk of harm than if they were at the full QD appropriate for the circumstances
- Where the risks, Individual or Societal, are above the intolerable limit the Safety Case submitted to CIE(MOD) must be endorsed by an appropriate 2* from the TLB/TFA requiring the activity. The 2* is to confirm that all options have been considered; with reasons as to the appropriateness of the selected option. Chap 9 Jan 2013

Then such applications for a licence are to be submitted to CIE (MoD) for comment and then submitted through the TLB/TFA chain of command to PUS for approval.

It is to be noted that any single major industrial incident that may result in 50 or more fatalities overall or 6 members of the general public should be viewed with grave concern. Society is unlikely to tolerate such consequences.

3.5.4 Quantitative Risk Assessment

3.5.4.1 Introduction

Quantitative Risk Assessment (QRA) was introduced into the work of the Explosives Storage and Transport Committee (ESTC) in the early 1990s. A Risk Assessment Study Team (RAST) was later established in the ESTC Support Group to develop the technique, and produced a range of reports in so doing. Using the resulting modelling programmes, a number of studies have now been conducted on a range of MOD explosives areas, and the process has been largely validated. As a result the RAST has been renamed Risk Assessment Team (RAT) and has representatives from each of the Services.

Explosives safety regulations employ Quantity/Distance (QD) rules, based on the likely effect of an accidental explosion. A QRA procedure is used to assist management decisions where there is concern that the QD rules cannot be fully met. QRA estimates the probability of initiations at potential explosion sites in addition to the probability of fatality given that initiation has occurred, and thereby assesses the overall risk to exposed persons. Individual risk is defined as the probability that a single person who is continuously exposed to the stated hazard will suffer a fatal accident during one year. An indication of risks to groups of people whose members may be continually changing (known as societal risk) is produced in the form of a graph of the frequency of accidents that generate N or more fatalities.

Once the results from the QRA are known a judgement can be made as to whether the risks generated are acceptable or tolerable.

The content and form of the QRA are provided in Annex B.

3.6 SEPARATION DISTANCES / QUANTITY- DISTANCES

3.6.1 Introduction

3.6.1.1 Hazards Generated by Initiation

When explosives initiate the hazards generated by the initiation may include air blast, fragments, ground shock, debris and heat which will radiate out from the point of initiation. The closer one is to the point of initiation the more these hazards will be felt. It follows that to protect people or facilities the greater the distance from an explosion the safer one would be. Separating people by distance from explosives has therefore been the principal tool used to achieve their safety and forms a key component in UK civil legislation, MOD regulation, in explosives licensing and in explosives safety management nationally and internationally.

3.6.1.2 Hopkinson-Cranz Scaling Law

The underlying principal is derived from the relationship between the quantity of explosives initiating, the distance from the explosion and the hazard generated by the explosion. The quantity of explosive is related to the hazard by the Hopkinson-Cranz Scaling Law (Equation (**3-1**).

$$D = Z * Q^{1/3} \qquad \textbf{(3-1)}$$

Where: D is the distance in metres; Q is the quantity of explosive; Z is the distance coefficient.

A series of distance coefficients have been agreed internationally by the explosives safety community as representing the distances at which an acceptable level of risk is achieved. They give rise to the Quantity – Distance (QD) rules and tables widely used for explosives licensing and ammunition storage.

3.6.2 Application of Quantity Distances

3.6.2.1 Definition of terms

Before considering the use of these rules and tables there are some terms that require definition:

- A Potential Explosives Site (PES) is any stock of explosives, however or wherever stored (building, stack, vehicle, railway wagon, berth, transit shed etc.), the explosion of which will affect an Exposed Site.

- An Exposed Site (ES) is any facility, service or civilian, exposed to and thus hazarded by the effects of an explosion or fire at a PES. These facilities include:
    - Any stock of explosives, however or wherever stored
    - Process Buildings and explosives workshops
    - Inhabited buildings and places of assembly
    - Public traffic routes, including roads, footpaths, railways, canals and civil aircraft facilities, etc.
    - Other Hazardous Installations, e.g. electrical sub-stations
- Net Explosive Quantity (NEQ). On the basis of assessment of the effects of such an explosives event (e.g. blast and fragment radii), and predictions as to which specified levels of risk obtain in terms of injury or damage, the MOD Explosives Storage and Transport Committee (ESTC) has developed tables of Net Explosive Quantity (NEQ) and associated recommended distances. These tables are known as Quantity Distance (QD) Tables and, together with other ESTC criteria for their use, form the foundation for MOD explosives licensing of Potential Explosion Sites (PES). The QD are based on trials and other data, but are susceptible to uncertainty owing to the variability of the nature of explosions and the incompleteness of the trials data. QD are subject to continuing refinement, as further data becomes available.
- The distances quoted in the QD Tables for HD 1.1 are applicable to quantities of TNT. Where explosives having a significantly more powerful or less powerful effect than TNT are being considered, a 'TNT equivalent' may be used to determine the appropriate QD. TNT equivalence can vary significantly depending on the parameters used to measure the equivalence. CIE (MOD) staff will advise on the appropriate equivalence to be used in any specific situation.

3.6.2.2 Expected Effects to Personnel and Facilities at Different QDs

The expected effects on people and facilities are described detail DSA 03.OME Part 2 and are reproduced at Annex C. The effects will depend on the hazard division or hazard type of the explosives in question.

For an explosion of HD1.1explosives the injury effects would be at:

- QD $8.0Q^{1/3}$ (Process Building Distance) Serious injuries or possible fatalities are likely from debris, firebrands, fragments, or building collapse. There is only a small chance of serious injury occurring due to direct blast effects.
- QD $14.8Q^{1/3}$ (Public Traffic Route Distance):
- QD $22.2Q^{1/3}$ (Inhabited Building Distance). Injuries are unlikely as a direct result of blast effects, but could occur due to glazing fragments and flying/falling debris.
- QD $44.4Q^{1/3}$ (Vulnerable Building Distance). Injuries are unlikely as a direct result of blast effects. Injuries that do occur will be caused principally by falling glass.

For an explosion of HD1.2 Explosives the injury effects would be:

- The total fragment/debris hazard at IBD would not be expected to exceed one potentially lethal fragment (>80 j) per 56 m^2 of ground area at the surface. It should be noted that the hazard is generated over a significant time period, generally in excess of one hour after the initial explosive event, and is not generated instantaneously as in the case of HD 1.1.
- For an explosion of HD1.3 Explosives the injury effects would be based on a thermal dose criterion of 62.8 kJ/m^2. It is anticipated that occupants of traditional UK types of inhabited buildings would not suffer injury unless standing in front of a window. Such personnel, and any personnel in the open, are likely to experience reddening of any exposed skin areas.

3.6.2.2.1 Building Damage Levels At Exposed Sites

The damage levels likely to occur to an ES (see 3.6.2.1) of conventional construction from an explosion of HD 1.1 at a PES (see 3.6.2.1) for different QDs are as follows:

- QD $2.4Q^{1/3}$ Buildings not designed to resist the blast loading will almost certainly suffer complete demolition.
- QD $8.0Q^{1/3}$ (PBD) Buildings not designed to resist the blast loading will probably suffer severe damage. Direct initiation of stored explosives is unlikely, but communication of the explosion as a result of fire could occur.
- QD $22.2Q^{1/3}$ (IBD) Buildings not designed to resist the blast loading should suffer only minor damage, mainly to glazing, lightweight cladding, etc.
- QD 44.4Q1/3 (Vulnerable Building Distance (VBD)) Buildings not designed to resist the blast loading are likely to suffer only superficial damage to large panes of glass and other lightweight cladding.

3.6.2.3 Separation Distances

The Explosives Act of 2014 does not use the QD terminology but instead uses the term “Separation Distance” and requires that “every person who stores explosives at a site must ensure that the relevant separation distance prescribed in Schedule 5 of the Act is maintained between a store and a building or other place to which that Schedule applies”. The Schedule specifies the different sorts of location which could be at risk in the event of an explosion. These are grouped into Classes of protected locations which in MOD parlance are regarded as exposed sites. A full description of the classes is provided in Schedule 5. Tables within Schedule 5 show the distances that these protected locations must be from a range of potential explosives sites containing different quantities of explosives as shown in Figure 3-1.

Table 1: Hazard Type 1 explosive in a brick-built mounded store

1 *Quantity of explosives (kg)*	*2* *Class A distance (m)*	*3* *Class B distance (m)*	*4* *Class C distance (m)*	*5* *Class D distance (m)*	*6* *Class E distance (m)*	*7* *Class F distance (m)*	*8* *Class G distance (m)*	*9* *Class H distance (m)*
0.1-25	33	50	100	100	100	50	9	18
25-30	33	50	100	100	100	50	9	18
30-40	34	51	103	103	103	51	9	18
40-50	35	53	106	106	106	53	9	18
50-60	37	55	110	110	110	55	10	22
60-70	37	56	111	114	114	57	10	22
70-80	38	57	113	118	118	59	11	22
80-90	38	58	115	121	121	61	11	22
90-100	39	59	118	125	125	63	11	22
100-150	43	64	128	142	142	71	13	27
150-200	46	70	139	156	156	78	14	27
200-250	50	75	150	169	169	85	16	30
250-300	54	80	161	170	170	85	16	30
300-350	57	86	172	172	172	86	18	33
350-400	61	91	183	183	183	92	18	33
400-450	64	97	193	193	193	97	19	36
450-500	68	102	204	204	204	102	19	36

Figure 3-1 Example of a Quantity-Distance table

It can be seen that for 55 kg of explosives in this brick built store a vulnerable building, dwelling or vulnerable building should be at least 204 metres away to remain safe. Less vulnerable specialist explosives buildings such as those in classes G and H can be located significantly closer to the potential explosives site.

3.6.2.4 Site Design and Building Construction

The QD and Separation Distance approach is essential in the design and construction of explosives facilities. It determines the construction of buildings that may be either or both PES and ESs. Their detailed construction will determine the level of protection they afford to people and any explosives present in the building and will also determine the nature of the hazard that they represent as a potential explosives site. DSA 03.OME Part 2 contains details of the construction of buildings associated with military explosives. Schedule 5 of the explosives act 2014 also illustrates how separation distances vary depending on the nature of the building containing the explosives and sort of explosives that they contain.

3.6.2.5 Other Uses of Quantity Distances

Quantity Distances have wider application to above ground explosives sites:

- Above Ground Storage for Marshalling Yards, Transit and Staging Facilities
- Military Explosives in Naval or Military Ports

- Storage and Loading/Unloading of Aircraft Explosives Held Forward on Airfields
- Underground Storage
- Mutually Hazardous and Other Non-Explosives Buildings and Facilities in Relation to Potential Explosion Sites
- Criteria for Disposal Grounds Co-located with Explosives Areas.

3.7 SAFEGUARDING

3.7.1 Introduction

3.7.1.1 Explosives Safeguarding

Explosives facilities are a potential hazard to persons and to property. Accordingly, in order to minimise these hazards should an explosion occur, it is necessary to site such facilities at prescribed Quantity Distances from buildings, roads, railways or places frequented by persons both within and without an enclosed explosives facility. These QDs frequently extend beyond the site boundary. To ensure that MOD explosives, and other essential defence installations, are not compromised by civil encroachment of private or public development within the prescribed quantity distances, maps limiting such development are lodged by Defence Infrastructure Organisation (DIO), via the Office of the Deputy Prime Minister (ODPM) and Department of Transport, Local Government and the Regions(DTLR), in England, the Scottish Executive in Scotland, and the Welsh Assembly in Wales, with the Local Planning Authority (LPA). This process is known as Explosives Safeguarding.

3.7.1.2 Explosive Safeguarding Maps

Under the arrangements described below, the lE's are responsible for the production of the Explosive Safeguarding Maps (ESMs).

3.7.1.2.1 Types of ESM

There are two types of ESM:

1. REGISTERED – Where part of the SG area falls outside the MOD boundary and the ESM is registered by DIO with the LPA.
2. UNREGISTERED - Where the SG area lies entirely within the MOD boundary, thereby only blighting MOD property so does not require registering with DIO or the LPA.

3.7.1.3 Safeguarding Direction Orders

From these ESMs DE (safeguarding) produce the Safeguarding Direction Orders (SDOs) which are issued, complete with the statutory direction to consult, to the LPAs which are responsible for development on land which adjoins those MOD sites. This is necessary to safeguard certain essential installations, of which explosives facilities form just a part (indeed, SDOs for

military airfields are in fact mostly concerned with the Safeguarding of the operational flying criteria). The initiation of changes to those elements of the map which deal with the prevention of civil encroachment to licensed explosives facilities are, in the MOD, the responsibility of the appropriate IE. DE issues the final editions of the Safeguarding Direction Order Maps and is directly and centrally responsible for the administration of Safeguarding on behalf of the MOD.

3.7.2 Safeguarding in Practice

3.7.2.1 Safeguarding legislation

The Town and Country Planning Act allows the MOD to safeguard areas by means of individual Directions which require planning authorities to notify DIO of planning applications for development within certain defined areas as shown on the Explosives Safeguarding Direction Order Maps(SDO). Statutory Safeguarding does not in itself impose restrictions on development. It does not go beyond placing on a LPA a statutory obligation to consult and to take into account any representations made by the MOD. The main features of the Safeguarding legislation are:

- Consultation with MOD by the LPA before planning consent is given
- Consultation requirements are illustrated on the SDO.

3.7.2.2 DO becoming valid

When MOD wishes to have a site safeguarded it informs DIO who issue a map in the form of a Direction Order (DO) to the relevant National Authorities. The DO becomes valid when National Authorities issue the DO to the relevant Local Planning Authority (LPA). The LPA are required to consult MOD, through DIO, before the LPA decides to approve development in the restricted areas denoted on the map.

3.7.2.3 DIO approval of development

When development is proposed within the restricted area MOD will be consulted and the proposal may be dealt with by DIO. Some cases will be referred to the relevant Inspector of Explosives and to other specialist advisors who will advise DIO. DIO then agrees to the development in full, in part or objects to the development. The decision is subject to appeal and may involve a public inquiry at which point MOD will need to present a robust case in support of its objection.

3.7.2.4 Safeguarding contractor sites

Safeguarding also applies to sites that are a strategic MOD asset operated by a Contractor under HSE explosives licensing where MOD capability would be affected if encroachment were allowed. The HSE licences granted are to be considered “Strategic” Licences and are solely for the purpose of establishing a MOD explosives safeguarded area. For sites where the HSE licence the facility

a “HSE safeguarding map” is required to be lodged with the LA. Consideration should be given to the area covered by this map and where possible the MOD safeguarding map should be made to fit this area.

3.7.2.5 Other safeguarding requirements

It is not only explosives that could present a risk to personnel around an MOD facility. Gun and rocket firing could present a significant source of risk. However such Directional Weapons Safety zones do not attract the same statutory protection as safeguarding. Nevertheless it could be a significant consideration in the development of areas within and around MOD installations. Maps that illustrate the danger areas are required to be produced at relevant sites and approved by the HOE and endorsed by the relevant IE inspector.

3.7.3 The Importance of Safeguarding

3.7.3.1 Failures of Safeguarding

The Safeguarding of explosive facilities is crucial to the continued operational effectiveness of a site and although the statutory system of consultation ensures that the majority of intended developments come to the notice of the MOD, the mechanism is not fool proof. The reasons for this are essentially threefold:

- Local authorities may occasionally, through error, omit to acquaint the MOD about local planning applications.
- The LPA overview maps cannot be amended quickly in order to reflect any changes made to the Safeguarded areas brought about by major changes in Explosives Licences through extensions to explosives facilities.
- Landowners may execute development without first seeking planning permission from the LPA.

3.7.3.2 Head of Establishment role in safeguarding

HoEs are to ensure that the procedures, which are intended to maintain the integrity of explosives facilities and to prevent encroachments of the Safeguarded Areas, are complied with in full. In particular, the monitoring process detailed is to include a regular physical inspection of the Safeguarded zones to check, in so far as is reasonably practical, that no encroachments have occurred.

3.8 REFERENCES

[1] UN Recommendations on the Transport of Dangerous Goods - Model Regulations Twentieth revised edition, United Nations (2017).

[2] European Agreement concerning the International Carriage of Dangerous Goods by Road, United Nations (2017).

[3] Industry guide and Code of Practice on the carriage of Dangerous Goods and use of Transportable Pressure Equipment Regulations 2009 (as amended) (CDG).

[4] Health and Safety Executive Web Communities, Explosives Group. Available at: Explosives Web Community (Accessed December 2017).

[5] European Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulation) January 2009. Available at: CLP (Accessed December 2017).

[6] Registration, Evaluation, Authorisation & restriction of Chemicals (REACH) Regulation. Available at REACH (Accessed December 2017).

Appendix A A Brief Description of the Purpose and Types of Tests Called for in the UN Classification Test Scheme

A.1 Test and criteria for acceptance into class 1

The tests for acceptance in UN Class 1 are grouped into four series of tests (further tests relate to the determination of the correct Hazard Division (HD)).

The numbering of these tests, and the tests to determine the correct HD, relates to the sequence of assessing results rather than the order in which the tests are conducted. Nevertheless it is important for the safety of experiments that certain preliminary tests using small quantities be conducted first, before proceeding to experiment with larger quantities. The result of such preliminary tests may also be used in the classification procedure.

The tests and sentencing criteria are fully detailed in the UN Manual of Tests and Criteria, to which reference should always be made. A brief description of the tests and their purpose is given below.

A.1.1 Acceptance tests

Test Series 1: These tests are applied to substances and designed to answer the question “Is it an explosive substance?” and these consist of three types of tests, as follows:

1. Type 1a. A shock test with a defined booster and confinement to determine the ability of the substance to propagate a detonation. JSP 482 Edition 4 Classification of Military Explosives For Storage and Transport Chap 4 Annex B Jan 2013 Page 2
2. Type 1b. A test to determine the effect of heating under confinement.
3. Type 1c. A test to determine the effect of ignition under confinement.

Test Series 2: These tests are applied to substances and designed to answer the question “Is the substance too insensitive for acceptance in Class 1?” Test Series 2 trials are essentially the same as those for Test Series 1. Series 2 tests and Series 1 tests have different pass/fail criteria, and consist of three types of tests as follows:

1. Type 2a. A shock test with defined initiation system and confinement to determine the sensitivity to shock.
2. Type 2b. A test to determine the effect of heating under confinement.
3. Type 2c. A test to determine the effect of ignition under confinement.

Test Series 3: These tests are applied to substances and designed to answer the question “Is the substance too hazardous for transport (in the form in which it is tested)?” This Test Series consists of four types of tests as follows:

1. Type 3a. Tests to determine the sensitiveness (see 20.2.1) to impact.

2. Type 3b. Tests to determine the sensitiveness to friction (including impacted friction).
3. Type 3c. Tests to determine the thermal stability.
4. Type 3d. Tests to determine the response to flame (i.e., the ease of deflagration to detonation transition in small quantities when unconfined).

Test Series 4: These tests are applied to packaged and unpackaged ammunition and to packaged/unpackaged explosives and designed to answer the question “Is the article, packaged article or packaged substance too hazardous for transport?” This Test Series consists of two types of tests as follows:

1. Type 4a. Tests to determine the thermal stability of packaged substances, packaged articles and unpackaged articles.
2. Type 4b. Tests to determine the effect of dropping the packaged substances, packaged articles or unpackaged articles from up to 12 metres. There is a special test for liquids.

A.2 Tests and criteria for assessing hazard divisions

After making sure that the substance or article is in Class 1, a further series of tests related to the determination of the correct HD (Tests Series 5, 6 and 7) is undertaken as appropriate. A brief description of the tests and their purpose is given below.

A.2.1 Tests to determine the Hazard Division

Test Series 5: These tests are applied to substances and designed to answer the question “Is it a very insensitive explosive substance with a mass explosion hazard?” Any candidate of HD 1.5 must pass all the following types of test:

1. Type 5a. Shock tests that determine the sensitivity to detonation by a standard detonator
2. Type 5b. Thermal tests that determine the tendency of transition from deflagration to detonation. .
3. Type 5c. Tests to determine if the substance, when in large quantities, explodes when subjected to a large fire. Classification of Military Explosives JSP 482 Edition 4 For Storage and Transport Jan 2013 Chap 4 Annex B Page 3
4. Type 5d. Tests to determine if the substance ignites when subjected to an incendiary spark (i.e., it is the intention to exclude easily ignitable substances, such as black powder, from HD 1.5).

Test Series 6: These tests are to determine the correct HD (from 1 to 4) to be applied to packaged and unpackaged ammunition and to packaged/unpackaged explosives. Test 6a and Test 6b are normally carried out at least three times unless explosion of the entire contents occurs earlier. Test 6c is normally performed once only. However, if the wood or other fuel used for the fire is all consumed leaving a significant quantity of unconsumed explosives

substance in the remains or in the vicinity of the hearth, consideration should be given to performing the test again using more fuel or a different method to increase the intensity and/or duration of the fire. Test 6d is normally carried out three times, in different package orientations, unless a decisive (negative) result is observed earlier. If the results of the recommended number of tests do not enable the Hazard Division to be determined, the number of tests is increased. The four types of test are as follows:

Type 6a (Single Package Test). Test on a single package for the purpose of determining:

- Whether initiation or ignition in the package causes burning or explosion and whether burning or explosion is propagated in the package,
- In what way the surroundings could be endangered by these effects.

Type 6b (Stack Test). Test on a stack of packages of ammunition or explosives, or unpackaged ammunition/explosives for the purpose of determining:

- Whether burning or explosion in the stack is propagated from one package to another, or from one unpackaged ammunition article to another,
- In what way the surroundings could be endangered in this event.

Type 6c (External fire (Bonfire) Stack Test). Test on a stack of packages of ammunition or explosives, or of unpackaged ammunition or explosives for the purpose of determining:

- How the packages or unpackaged ammunition/explosives in the stack behave when involved in an external fire simulating a realistic accident,
- Whether and in what way the surroundings are endangered by blast waves, heat radiation and/or fragment projection.

Type 6d (Unconfined package test). Test on an unconfined package of explosive articles to which special provision 347 of Chapter 3.3 of the Modal Regulations applies, to determine if there are hazardous effects outside the package arising from the accidental ignition or initiation of the contents.

Test Series 7: These tests are applied to articles to answer the question “Is it an extremely insensitive article?” Any candidate, including explosive substance(s), for HD 1.6 (articles, explosives, extremely insensitive (EEI)) must pass all applicable Test Series 7 tests:

- Type 7a. Shock test to determine the sensitivity of the explosive substance to detonation by a standard detonator.
- Type 7b. Shock test with a defined booster and confinement to determine the sensitivity of the explosive substance to shock. JSP 482 Edition 4 Classification of Military Explosives For Storage and Transport Chap 4 Annex B Jan 2013 Page 4
- Type 7c. Test to determine the sensitivity of the explosive substance to deteriorate under the effect of an impact.

- Type 7d. Test to determine the degree of reaction of the explosive substance to impact or penetration resulting from a given energy source.
- Type 7e. Test to determine the reaction of the explosive substance to an external fire when the material is confined.
- Type 7f. Test to determine the reaction of the explosive substance in an environment in which the temperature is gradually increased to 365_C.
- Type 7g. Test to determine the reaction to an external fire of an article that is in the condition as presented for transport.
- Type 7h. Test to determine the reaction of an article in an environment in which the temperature is gradually increased to 365 ^{o}C.
- Type 7j. Test to determine the reaction of an article to impact or penetration resulting from a given energy source.
- Type 7k. Test to determine if an article will detonate a similar item adjacent to it that is in the condition as presented for transport.

A substance intended for use as the explosive filling in an article of HD 1.6 should be tested in accordance with Test Series 3 and Test Series 7. Test Series 7 substance tests should be conducted on the substance in the form (i.e., composition, granulation, density, etc.) in which it is to be used in the article.

An article being considered for inclusion in HD 1.6 should not undergo Test Series 7 until after its explosives filling has undergone Test Type 7a to Test Type 7k to determine whether it is an extremely insensitive detonating substance (EIDS).

To determine whether the article with an EIDS filling is in HD 1.6, Test Type 7g to Type 7k need to be completed. These tests are applied to articles in the condition and form in which they are to be stored and transported, except that non-explosive components may be omitted or simulated if the competent National Authority is satisfied that this does not invalidate the results of the test.

Appendix B QRA Reports

B.1 Content and form of a QRA report:

1 Site Description

The purpose and outline arrangement of the site is described.

2 Management Standards

Management and technical standards are subject to regular technical inspections, often involving also an Explosives Auditor from Directorate of Safety, Environment and Fire Policy (DSEF Pol), to which ESTC reports. Any audit made by the Health and Safety Executive (HSE) is also noted.

3 Description of Method

Assessments may be made at a basic level (Level 1) or a higher level. Level 1 follows a standard mechanism; higher levels introduce more specialised methods where unusual problems have to be examined. The Level 1 .assessment method is based on an estimate for the frequency of initiation per Potential Explosion Site (PES) per year, taking a standard storage category for each store. In the case of a Process Building (PB), an additional frequency contribution is added. Further contributions to this basic frequency are made to include the probability of external hazards (aircraft crash, flood, lightning, and nearby hazardous installations). Finally, the probability of ignition by communication from neighbouring buildings is included. The total frequency of initiation is then combined with fatality predictions from a suite of consequence models (for blast, weapon fragments, building debris and thermal radiation) to produce probabilities of fatality. These are expressed in terms of individual and societal risk. The computations are performed using a programme (RISKWING) developed by AEA Technology. QRAs estimate the maximum risk generated by explosives areas, based on a range of assumptions. They also address the maximum quantities of explosives permitted by the Explosives Licence for each PES. A second assessment may be made based on the actual holdings on a particular day.

4 Exposed Sites

With the agreement of the local site management, a number of exposed sites (ES) are chosen for the assessment to represent the locations at highest risk, usually those recorded in the explosive limit licences. ES are usually both on the site and external to it. Details are entered into annexes. Also shown, for each ES, are the number of workers, residents and those exposed to transient risks, and the fraction of time they are likely to spend exposed, indoors and outdoors.

5 Potential Explosion Sites

Examples of PES are explosive store houses (ESH), process buildings (PB), hardened aircraft shelter (HAS), forward weapon store (FWS), road and rail

transfer points, road staging and rail marshalling areas, etc. Annexes show each PES by its number, type and length of building, NEQ and HD of the explosive for which it is licensed, the date of the licence, and the map co-ordinates.

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Confirmation is sought that storage rules are closely set out in the licences and operating procedures of the site under survey.

6 Site Co-ordinates

The site co-ordinates used in a RISKWING study are normally taken from Ordnance Survey maps, though they may be superimposed. They are taken into the ES and PES tables in the various annexes. The areas containing certain ES are divided into fine grids to give more accurate inter-building distances and facilitate the modelling.

7 Basic Initiation Frequency

Basic initiation frequencies are derived from the Level 1 method and entered for each PES in the PES annex. No account is taken of PES licensed only for HD 1.4, because of the very limited effects outside the building which are likely to follow from any accident. In buildings containing more than one HD, the highest is used for the assessment, the initiation frequencies being based on the greatest possible figure for munitions that might be held. Thus the worst credible event is assessed, even though in practice the management of storage always tends to reduce the frequency noticeably. The PBs, HAS, FWS, road and rail transfer points, road staging and rail marshalling areas, etc. are shown in the same way.

8 External Hazards - Contributions to Initiation Frequency

The following contributions are considered for addition to the basic initiation frequency, in line with an External Hazards Guidebook. The frequency contribution for each PES is entered in the PES annexes:

- Lightning. All PES where a lightning protection system (LPS) installed to BS 6651 is not fitted.
- Flooding. Any history of significant flooding at the site, or of stores being affected by it though water, sensitive stores will normally be fully protected by their packaging.
- Aircraft Crash. The probability of crash, by civil airline aircraft, light aircraft and small transports, military fixed wing aircraft (especially where the site is in a designated High Crash Concentration Zones (HCCZ)) and helicopters. Special factors, such as hot refuelling of helicopters on the site, are considered. Aircraft crash is normally the only external hazard to have a significant effect.
- Nearby Hazardous Installations. On a site, there may be storage tanks for heating oil and fuel for vehicles and machinery, and liquid petroleum

gas tanks. There may also be demolition and burning areas. Such installations are not normally regarded as constituting a significant hazard.

9 Additional Contributions to Initiation Frequency

The following are considered:

- Site Transport and Transfer Operations. The modelling programme makes standard allowances for frequency contributions arising from site transport and transfer operations. These apply at road and rail loading and transfer points, and need to be modified only if there are extraordinary conditions on the site.
- Malicious Destruction. The modelling programme also makes a standard allowance for frequency contributions arising from malicious destruction. This is also entered in the tables.
- Communication. A calculation is made of the probability of the communication of an initiation event between PES, each one in turn being regarded as donor and receptor. The input for the programme is based on the QD rules in Chapter 10.

10 Consequence Models

Once the total initiation frequency is known for each PES, based on all the above influences, the next step in the QRA process is to determine the fatality probability at each ES, given an event from each PES. This is done using the RISKWING programme. The RISKWING software has separate consequence models for assessing lethality from blast, weapon fragments, building debris and thermal radiation. Lethality can be determined for people in the open or inside domestic housing. For HD 1.1 and HD 1.2 stores, all consequences less thermal radiation are combined. For HD 1.3, thermal radiation is the only consequence model considered. The models are as follows:

- Blast. The relationship between quantity of explosives, separation distances and lethality is taken from two RAST reports. The lethality from blast applies only to HD 1.1 and HD 1.2 events. The lethality probability falls below 10- 9 (effectively zero) at a scaled distance (SD) of 6.8 for people outdoors and 55 for people indoors.
- Building Debris. The model for building debris has been derived for traversed PES of brick walled construction with a reinforced concrete roof. The method provides only a coarse estimate of fatality probabilities, but it can be taken as a maximum value. Special account has to be taken of debris from igloos, especially the front wall.
- Weapon Fragments. Fragment lethality is estimated for each PES licensed for HD 1.1 and HD 1.2. A selection of weapon type is made from the following, reflecting the worst long range consequence predicted for the contents of the PES:
    a. 155 mm L15 HE Shell
    b. 1000 lb Bomb
    c. 81 mm Mortar HE Bomb

d. 30 mm ADEN HE Round
e. Sea Dart SAM
f. Mk 24 Torpedo

For HD 1.2, the blast and debris effects are assessed on a notional NEQ of 50 kg rather than the licensed NEQ. This follows the assumption that HD 1.2 would detonate at intervals, in a series of initiations, rather than in mass. The 50 kg figure used allows for 10 consecutive explosions of 5 kg each, which it is assumed would give time for anyone in the immediate area to move to safety.

- Thermal Radiation. Where PES are licensed primarily for HD 1.3, an estimate has been made of the effects of thermal radiation, for which a procedure has been devised. These effects are clearly in a much lower order than blast and projection effects.

11 Results

B1.11.1 Assessment addresses the risks arising from the storage, handling and processing of explosives, particularly:

- The risks to workers operating at various points around the site, though not within the explosives areas, and taking into account the working hours during which they are actually exposed to risk.
- Chap 9 Annex D Jan 2013 Page 4 Explosives Licensing Arrangements JSP 482 Edition 4 Jan 2013 Chap 9 Annex D
- The risks to those workers regarded as ‘residents’ because of their permanent occupation of exposed sites, and also to the general public residing in houses around the sites.
- The risks to the transient general public on nearby railways, major roads and, in some cases, public rights of way.

12 Individual Risk

Responsibility for ensuring the Health and Safety of Service personnel, MOD civilian staff and members of the general public lies firmly with the line management who generate the hazard and the risks there from. The generator of the risk has to show that the risk not only is tolerable, but also has been reduced to a level which is ALARP. Under a procedure devised by ESTC and described in Chapter 9, the respective IEs are given guidance on how they may manage explosive storage and handling situations, including those which do not appear to meet ESTC recommendations for QDs as reflected in this publication. ESTC suggests that an IE could determine the range of risks of fatality which are generated by the high proportion of his explosives facilities which meet existing QD rules. Then, by assessing risks associated with a non-compliant situation, the IE could decide whether the problem generated a risk significantly greater than the normal range. If not, he may decide to issue a licence for the operation to proceed. He will remind the risk generator of his responsibility to ensure that the risks as ALARP. The IE may of course make his approval conditional on management constraints; regular review, time limits and so forth.

Even if risks are significantly higher than normal, he may conclude that they are ALARP and can be defended as tolerable within the guidelines laid down by the HSE. Chapter 9 states that he may proceed with issuing licences provided that CIE (MOD) is informed through ESTC, and that the situation is subject to regular review. Further guidance is offered for dealing with higher risks and those which affect the general public.

MOD does not have formally accepted criteria for tolerable risk, and each particular estimated risk has to be discussed in terms of criteria used by other bodies in similar situations. For example, HSE has published guidance on how to assess acceptable risk associated with the operation of nuclear power stations and the transport of dangerous substances. The approach followed in QRAs is recommended by HSE and involves the use of two threshold criteria. Above the upper threshold risk is considered intolerable and immediate steps must be taken to reduce or eliminate it. Below the lower threshold risks are accepted as tolerable and no further effort need be made to reduce them. In the intermediate region, the risk has to be demonstrated as ALARP. The IE is at liberty to identify conditions which enable him to defend the choice of different threshold values if he considers this both necessary and practicable.

QRA site assessments performed for each of the Services and results from across the MOD have shown that the risks generated by explosives storage facilities which meet ESTC QD recommendations can be defended as 'tolerable' using guidance issued by the Health and Safety Executive. Values used by HSE in their recommendations on the transport of dangerous goods are:

- 1 in 1000 per year - maximum tolerable risk of fatality for any identifiable group of workers
- 1 in 10 000 per year - maximum tolerable risk of fatality for the general public
- 1 in 1 000 000 per year - individual risk negligible for both workers and the general public

The estimated maximum values of individual fatality risks per year are shown, from all PES, for people at each exposed site. Comparison with the above figures will indicate whether the risks can be defended as tolerable. It should be noted that management action will normally reduce these risks further by, for example, restricting the routine movement of explosives to the smallest number of storehouses, or by restricting the storage of white phosphorous natures to specific ESH.

13 Societal Risk

Societal risk addresses the number of fatalities to be expected from an accident. This is done because of the perception that society in general tends to have a greater aversion to a single accident causing multiple casualties than to a number of separate accidents causing an equivalent number of deaths. Criteria for this have not been developed to the same extent as individual risk. HSE has estimated that the annual chance of an aircraft crash somewhere in

the UK killing more than 500 people is 1 in 1000 per year, and they have stated that a major societal risk in UK with a similar large number of casualties should be tolerable at a probability of 1 in 5000 per year. The calculation takes each PES in turn and determines the probability of an accident there having a lethal result at each ES. This probability is then summed for all the ES and multiplied by the population.

The QRA programme produces a graph indicating the estimated accident frequencies where between 0.1 and 1000 fatalities may be expected. The diagonal lines on the graphs indicate the seriousness of the risk and threshold values adopted by the HSE. Above the upper line, the risk must be regarded as intolerable, and below the bottom line broadly acceptable. Between the two lines, the risk can be regarded as tolerable but must be kept ALARP.

14 Assumptions

The risk estimates generated in a QRA are normally based on a number of assumptions:

1. For the permitted licence, all storehouses are full to the maximum NEQ allowed, with the worst case natures (highest frequency and most severe hazard division).
2. There are no materials stored in contravention of compatibility mixing rules.
3. Any processing operations are performed only in the permitted buildings.
4. Workers in buildings are protected only to a level expected in normal domestic housing.
5. Workers are generally at risk for a maximum of eight hours per working day (0.24 fractional exposure). The number of days in the year on which each specific exposed site is occupied varies considerably, however, and is taken into account.
6. The communication frequencies for the most vulnerable igloo and ESH may be applied to other similar PES.
7. The consequence models, though simplistic in several areas, represent maximum values and a worst case prediction. It follows that estimates of risk can be considered to be upper limits for a site operated as described and which meets MOD safety standards.

15 Conclusions

A QRA report can often conclude that the maximum risk of fatality to workers and residents from the storehouses, PBs and transport facilities, etc., on the site, can be defended as tolerable under the current Explosive Licences. This is normally so where the site is licensed under full QD rules, but tolerability of risk may also be established in circumstances where strict compliance with QD causes difficulties. Where the risk cannot be defended as tolerable, the deficiency will be identified. Care should be taken, in any event, to ensure that risks can be shown to be as low as is reasonably practicable.

16 Recommendations

Recommendations are made where required, especially when remedial action can be taken to address means of reducing risk to tolerable and ALARP.

Appendix C The Expected Injuries to Personnel at Specific QDs from Explosions.

The Effects at different QDs are:

C.1 QD $44.4Q^{1/3}$

Expected Effects – The expected effects are:

1. Unstrengthened normal structures are likely to suffer only superficial damage.
2. Certain types of vulnerable structures (particularly Type 4 structures – see Chapter 6 para 8.1.4(4)) may collapse and cause injuries or death by crushing and falling debris.
3. When large panes of glass or other non-load bearing frangible materials, e.g. external cladding panels, are exposed so as to face a PES, 50 % or more of these may be detached from the structure or broken by the blast.
4. Injuries and fatalities are very unlikely as a direct result of blast effects. Injuries that do occur will be caused principally by the impact on passers-by of falling, broken or detached panel or window materials. The risk of injury will often be reduced by minimising personnel exposure by, for example, placing gardens around the foot of buildings.

Personnel and Facilities Acceptable - This is the normal distance required for buildings of vulnerable construction and large facilities. Examples of such buildings are:

1. Large Facilities of Special Construction or Importance. Examples are:
    a. Large factories
    b. Multi-storey office or apartment buildings
    c. Public buildings and edifices of major value
    d. Large educational facilities
    e. Hospitals
    f. Major transport centres e.g. railway stations, airports, etc
    g. Major public utilities, e.g. water, gas and electric work
2. Facilities of Vulnerable Construction Used for Mass Meetings. Examples are:
    a. Assembly halls and fairs
    b. Exhibition areas
    c. Sports stadia
3. Built-up areas which are both large and intensely developed

C.2 QD $22.2Q^{1/3}$

General - The equivalent QD in respect of earth-covered buildings considered to be UK standard igloos are:

1. From the side: $19.0Q^{1/3}$
2. From the rear: $15.5Q^{1/3}$

Expected Effects - The expected effects are:

1. Unstrengthened buildings will suffer minor damage, particularly to parts such as windows, door frames and chimneys. Partial collapse may occur in buildings where structural integrity relies either on critical elements or the continuity of the structure.
2. Injuries and fatalities are very unlikely as a direct result of the blast effects. Injuries that do occur will be caused principally by glass breakage and flying/falling debris.

Personnel and Facilities Acceptable - This distance is known as the Inhabited Building Distance and is the minimum distance at which inhabited buildings not directly concerned with the functions of the explosives facility should be sited.

This QD is acceptable for the following types of ES:

1. Untraversed stacks of explosives
2. Structures in the administration area of the facility with a considerable number of occupants (see Chapter 10, Section 7), e.g. office buildings, non-explosives workshops, mess halls, changing areas with refreshment areas or showers.
3. Structures in the administration area of the facility which are important for the functioning of the installation, e.g., manned fire stations, manned heating plants, MT areas, unprotected water, gas and power supplies.
4. Inhabited buildings whether single buildings, communities or areas of scattered habitations.
5. Structures and facilities in which people assemble other than those at para 8.1.2, above.
6. Facilities serving the needs and safety of the general public such as water, gas and power supplies, radar installations and communications centres.
7. Important railways and public roads, e.g., main railway lines, motorways and major roads and navigable waterways.

C.3 QD $14.8Q^{1/3}$

General - The equivalent QD in respect of earth-covered buildings considered to be UK standard igloos are:

1. From the side: $14.0Q^{1/3}$
2. From the rear: $11.0\ Q^{1/3}$

Expected Effects – The expected effects are:

1. Unstrengthened buildings will suffer average damage costing in the range of 10 % of total replacement cost to repair.
2. Personnel under cover are afforded a high degree of protection from death or serious injury. Such injuries as do occur will be mainly caused by glass breakage and building debris.
3. Personnel in the open are not likely to be seriously injured by blast but some injuries are likely to be caused by fragments and debris depending

on the structure of the PES, the NEQ involved and fragmentation characteristics.

Personnel and Facilities Acceptable - This distance is known as the Public Traffic Route Distance and is the minimum distance at which routes used by significant numbers of people for purposes unconnected with the explosives facility must be sited.

This degree of protection is acceptable for the following:

1. Structures and facilities within an administration area concerned with the explosives facility with a limited number of occupants
2. Structures and facilities in which people assemble temporarily and which can be cleared quickly, e.g. sports fields, parking places, Small Arms ranges.
3. Railways, roads and navigable waterways of minor medium importance.

C.4 QD 9.6 $Q^{1/3}$

Expected Effects – The expected effects are:

1. Buildings that are unstrengthened can be expected to suffer damage to main structural members that will require repair. Repairs may cost more than 20 % of the replacement cost of the building. Strengthening of buildings to prevent damage and secondary hazards is feasible and not prohibitively expensive.
2. Cars may suffer some damage to metal portions of the roof and body by blast.
3. Windows may be broken; however, the glass should not cause serious injury to the occupants.
4. Aircraft will suffer some damage to appendages and sheet metal skin.
5. Cargo type ships will suffer minor damage from blast to deck houses and electronic gear.
6. Personnel may suffer temporary hearing loss, however, permanent ear damage is not likely. There are likely to be some injuries caused by fragments, debris, or translation of the individual(s) involved.

Personnel and Facilities Acceptable - This must be the least distance at which unprotected duty personnel (e.g. troops, military and civilian maintenance and security personnel and crews of ships) should be permitted when their duties are not closely and specifically related to the PES. This degree of protection is acceptable for the following:

1. Open air recreation/sporting facilities used only by military personnel where structures, or dependants and the general public, are not involved.
2. Training areas for unprotected military personnel.
3. All military aircraft when the PES is not for the immediate service of the aircraft.

C.5 QD 8.0QP1/3

General - The equivalent QD in respect of earth-covered buildings considered to be UK standard igloos are:

1. From the rear: $6.0Q^{1/3}$

Expected Effects – The expected effects are:

1. Buildings which are unstrengthened can be expected to suffer damage which is likely to cost above 30 % of the total replacement cost to repair.
2. Serious injuries to personnel, which may result in death, are likely to occur due to fragments, debris, firebrands or other objects.
3. There is some possibility of delayed communication of the explosion as a result of fires or equipment failure at the ES. Direct propagation of the explosion is not likely.
4. Cargo ships will suffer damage to decks and superstructure. In particular, doors and bulkheads on the weather deck are likely to be buckled by the overpressure.
5. Aircraft are expected to sustain considerable structural damage.

Personnel and Facilities Acceptable - This distance is the minimum permissible distance between a PES and a Process Building. This degree of protection is acceptable for the following personnel and facilities:

1. Process Buildings in which the number of personnel present is kept to a minimum essential for the task.
2. Packing and shipping/transit buildings in the Explosives Area.
3. Minor transmission and communication lines.

C.6 QD $3.6Q^{1/3}$

Expected Effects – The expected effects are:

1. Unstrengthened buildings will suffer structural damage approaching total demolition.
2. Severe injuries or death to occupants of the ES are to be expected from direct blast, building collapse, or translation.
3. Aircraft will be damaged, by both blast and fragments, to the extent that they will be beyond economical repair. If aircraft are loaded with explosives, delayed explosions are likely to result from subsequent fires.
4. A high degree of protection against direct propagation of an explosion is to be expected, provided direct attack by high velocity fragments is prevented, e.g. by a receptor traverse. Explosions may subsequently occur in adjacent PES from fire spread by lobbed debris or blast damage to an ES.

Personnel and Facilities Acceptable - This degree of protection is acceptable for the following personnel and facilities:

1. Temporary holding areas for vehicles containing explosives for Service production or maintenance facilities provided traverses are interposed both between the vehicle locations and other PES.

2. Unmanned auxiliary power facilities, transformers and other utilities that serve a PES and which are not vital and will not create a secondary hazard.

C.7 QD $2.4Q^{1/3}$

Expected Effects – Unstrengthened buildings will suffer complete demolition.

Personnel and Facilities Acceptable - This degree of protection is acceptable for the following personnel and facilities:

1. Personnel performing storage and shipping functions in explosives areas may operate for short periods at adjacent PES. In large explosives areas however, management controls must be in place to reduce the length of time that unrelated operations are exposed to one another at distances less than 9.6. $Q^{1/3}$

CHAPTER 4
EXPLOSION CHEMISTRY

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4 EXPLOSION CHEMISTRY

Author – J Akhavan (Cranfield University)

4.1 AWARENESS SUMMARY

All explosives when they function produce heat by chemical reaction, which in simple terms is the same chemistry used since mankind discovered fire, that is the chemistry of combustion. Fuels such as coal, wood and oil are burned for domestic and industrial heating and cooking and these fuels consist of carbon and hydrogen often called hydrocarbons. When hydrocarbons burn they require oxygen, which for the above uses comes from the air and the products of this chemistry are the gases carbon dioxide and water (a gas above 100 °C). If there is insufficient oxygen then carbon monoxide may be formed as well as or instead of carbon dioxide.

Carbon + Oxygen $\rightarrow$ Carbon Dioxide or Carbon Monoxide

Hydrogen + Oxygen $\rightarrow$ Water

Although it is not usually observed this burning chemistry produces both heat and gas as the gas products are invisible and are vented to atmosphere. Also, the rate of burning is relatively slow and so the gases do not cause any build-up of pressure. This is because the rate at which the oxygen in the air can react with the fuel is controlled, either by the low surface area of solid fuels such as lumps of coal or the controlled release of liquid fuels such as for oil fired boilers.

Chapter 1 (see 1.3.1) explains that an explosion is a rapid expansion of gas and this can be produced by chemical reaction if both heat and gas are produced at the required speed. Therefore the chemistry of combustion provides heat and gas but it must be at a much faster speed than conventional burning of fuels. This is achieved by providing an intimate mixture of the fuel (carbon and hydrogen) with a source of oxygen before the combustion starts. An example of this is the cause of a common accident when a gaseous fuel such as methane is released in to a closed space such as a building and mixes with air. When ignited the combustion chemistry can travel through the mixture at such a speed it causes an explosion usually destroying the building (see 9.4.1).

This concept can be applied to solids but now the fuel and source of oxygen must be solid materials and the more intimately mixed the quicker will be the chemical reaction. The first recorded explosive material, black powder or gunpowder, is a good example of a solid explosive, where in this case the fuel, carbon, is mixed with a chemical that can release oxygen, a solid called potassium nitrate known historically as saltpetre. Sulphur is also used in the mixture. Over 50% of the reaction products are solids and so do not contribute to gas production, although they do assist in the production of heat from the reaction.

Carbon + Sulphur + Potassium Nitrate $\rightarrow$ Carbon Dioxide + Nitrogen + Solids

As the components of this explosive are individual materials the manufacturer can alter the ratio of fuel to source of oxygen and so optimise the combustion to best effect. The manufacturing process developed to make the mixture as intimate as possible through milling, a hazardous activity when working with explosives.

A method by which the fuel elements carbon and hydrogen can be more intimately associated with a source of oxygen is to put all of these elements in the same molecule as shown in Figure 4-1.

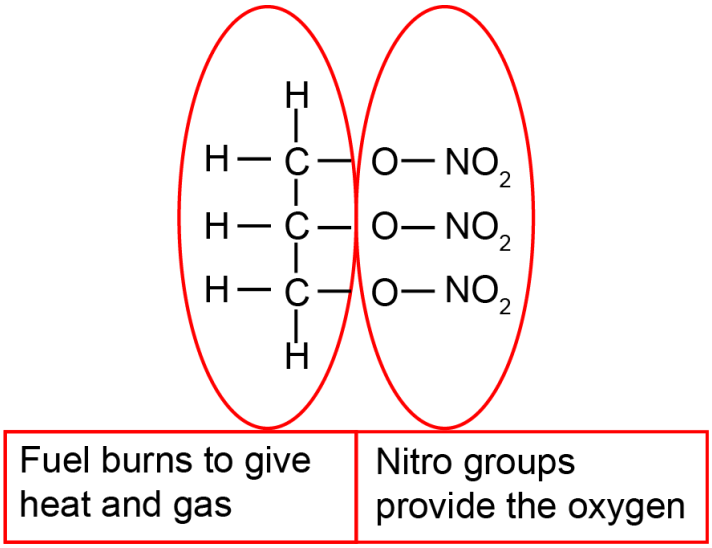


Figure 4-1 Nitroglycerine a molecular explosive

To understand just how much closer the fuel and oxygen atoms are in a molecule, if the carbon particles in a modern black powder were considered to be the size of England a molecule would be the size of a house.

Further examples of explosive mixtures and molecules can be found in the next section of the chapter including more detailed chemistry.

4.2 EXPLOSIVE MIXTURES AND MOLECULES

Chemical explosives can be divided into two groups, depending on their chemical nature; those that are classed as molecular explosives, and those that are explosive mixtures such as black powder.

4.2.1 Explosive Mixtures

Explosive mixtures can be gaseous, liquid or solid where the fuel and the oxidiser are mixed together. An example is when hydrogen gas is mixed with oxygen gas and initiated resulting in a fuel air explosion (FAE).

$$\tfrac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(g) \qquad \textbf{(4-1)}$$

Liquid fuel can also be mixed with a liquid oxidiser for example; the fuel unsymmetrical dimethylhydrazine is mixed with the oxidiser inhibited red fuming nitric acid and initiated to give gaseous products, as shown below.

$$5(CH_3)_2NNH_2(l) + 16HNO_3(l) \rightarrow 10CO_2(g) + 28H_2O(g) + 13N_2(g) \quad \textbf{(4-2)}$$

An example of a solid explosive mixture is black powder where the fuels carbon and sulphur are mixed with the oxidiser potassium nitrate. On initiation gaseous and solid products are formed. An example is given below.

$$10KNO_3(s) + 3S(s) + 8C(s) \rightarrow 2KCO_3(s) + 3K_2SO_4(s) + 6CO_2(g) + 5N_2(g) \quad \textbf{(4-3)}$$

Pyrotechnics are generally solid explosives mixtures. The reaction below is known as a thermite reaction.

$$Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s) \quad \textbf{(4-4)}$$

Another pyrotechnic mix is flash powder where aluminium powder is mixed with potassium perchlorate. The reaction is given below.

$$3KClO_4(s) + 8Al(s) \rightarrow 4Al_2O_3(s) + 3KCl(s) \quad \textbf{(4-5)}$$

All of these compositions require the fuel and the oxidiser being mixed together, where a poorly mixed composition results in a slow rate of burn compared to a mixture where the ingredients are in intimate contact.

4.2.2 Molecular Explosives

In order to improve the burn rate and hence the performance of explosives, molecular explosives have the fuel and oxidiser atoms on the same molecule as shown in Figure 4-2.

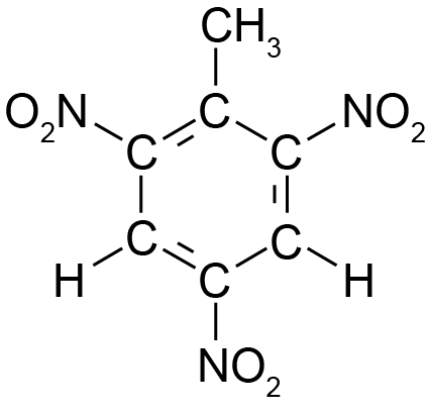


Figure 4-2 The molecular explosive trinitrotoluene (TNT)

Molecular explosives can be classified according to where the NO_2 groups are located in the molecule. There are three categories as shown in Figure 4-3.

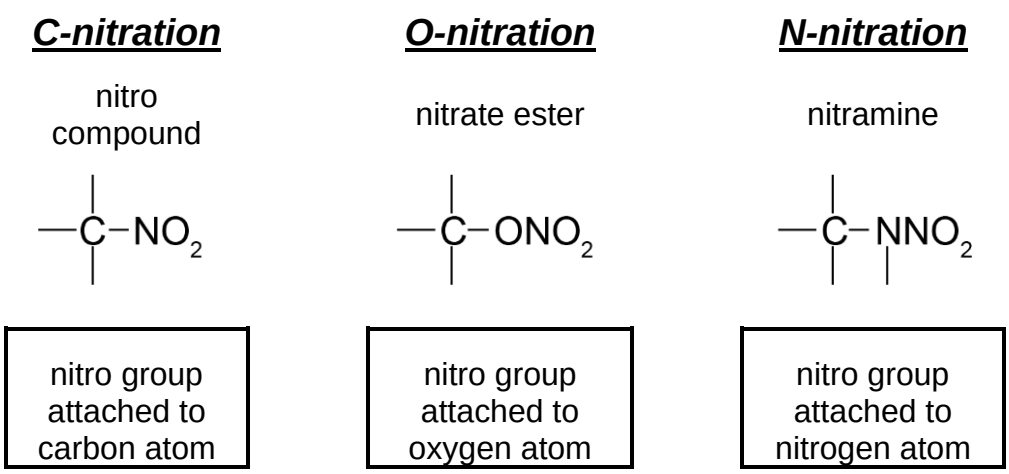


Figure 4-3 Classification of molecular explosives

Figure 4-4 gives an example of molecular explosives for the 3 categories.

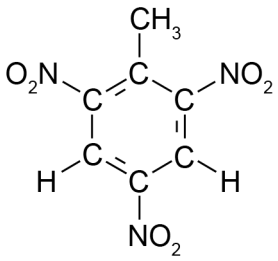
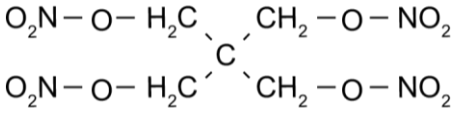
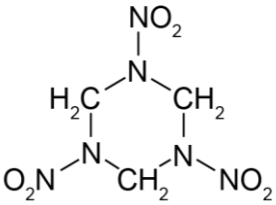
Nitro compound Trinitrotoluene (TNT)	
Nitrate ester Pentaerythrytoltetranitrate (PETN)	
Nitramine Cyclotrimethylene trinitramine (RDX)	

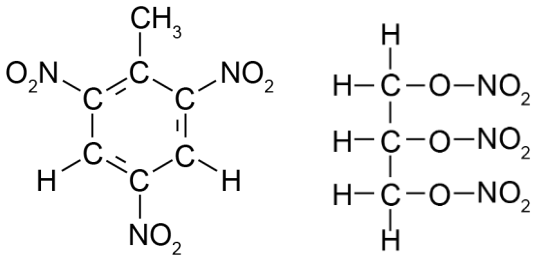
Figure 4-4 Examples of molecular explosives

4.3 CHEMICAL REACTIONS FOR THE EXPLOSIVE PROCESS

All molecular explosives when suitably initiated will undergo a chemical reaction. The products will depend upon the amount of oxygen available during the reaction. This supply of oxygen will depend in turn upon the quantity of oxidizing atoms which are present in the explosive molecule which can be quantified as the oxygen balance.

4.3.1 Oxygen Balance

This oxygen balance can be defined as the amount of oxygen, expressed in weight percent, liberated as a result of the complete conversion of the explosive material to CO_2, H_2O, SO_2, Al_2O_3 etc. If the amount of oxygen present in the explosive molecule is insufficient for the complete oxidation a negative oxygen balance will result. This can be seen in the molecule TNT Figure 4-5(a). Nitroglycerine, Figure 4-5(b), however has a high proportion of oxygen, more than required for complete oxidation of its fuel elements and therefore has a positive oxygen balance.



(a) (b)

Figure 4-5 (a) TNT and (b) Nitroglycerine

The oxygen balance Ω is calculated from an explosive containing the general formula $C_aH_bN_cO_d$ with molecular mass M as shown in Equation (4-6).

$$\Omega = \frac{[d - (2a) - (b/2)] \text{ x } 1600}{M} \qquad \textbf{(4-6)}$$

Using Equation (4-6) the oxygen balance for RDX ($C_3H_6N_6O_6$) is found to be -21.6 % as shown in the calculation below.

For RDX a=3, b=6, c=6 and d=6

Molecular mass is a sum of the atomic masses in the molecule, carbon = 12, hydrogen = 1, nitrogen = 14 and oxygen = 16:

$$\text{therefore } M = (3x12) + (6x1) + (6x14) + (6x16) = 222$$

$$\Omega = \left[\frac{6 - (2x3) - (6/2)}{222}\right] x\ 1600 = -21.6\ \%$$

The calculated oxygen balances for some explosive substances are presented in Table 4-1. It can be seen from Table 4-1 that explosive substances may have a positive or negative oxygen balance. If the oxygen balance is large and negative then there is not enough oxygen for carbon dioxide to be formed. Consequently carbon monoxide will be liberated or even elemental carbon.

The oxygen balance does not provide information on the energy changes which take place during an explosion. This information can be obtained by calculating the heat liberated during decomposition of explosive substances, known as the 'heat of explosion'. In order to calculate the heat of explosion, the decomposition products of the explosive must be determined, since the magnitude of the heat of explosion is dependent upon the thermodynamic state of its products. The decomposition process will be by detonation in the case of primary and secondary explosives and burning in the case of gun powders and propellants.

4.3.2 Product of Detonation

The detonation of RDX ($C_3H_6N_6O_6$) will result in the formation of its decomposition products. These may be carbon monoxide, carbon dioxide, carbon, water etc., as shown below.

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g), \text{ or} \quad \textbf{(4-7)}$$

$$C_3H_6N_6O_6(s) \rightarrow 3CO_2(g) + 3H_2(g) + 3N_2(g), \text{ or} \quad \textbf{(4-8)}$$

$$C_3H_6N_6O_6(s) \rightarrow CO(g) + 2CO_2(g) + 3H_2O(g) + 3N_2(g), \text{ or} \quad \textbf{(4-9)}$$

$$C_3H_6N_6O_6(s) \rightarrow 2CO_2(g) + C(s) + 2H_2O(g) + H_2(g) + 3N_2(g), \text{ etc} \quad \textbf{(4-10)}$$

In order to clarify this problem a set of rules were developed by Kistiakowsky and Wilson, known as the 'Kistiakowsky-Wilson' rules (K-W) rules. These rules should only be used for moderately oxygen deficient explosives with an oxygen balance greater than -40.0 % i.e. for oxygen rich explosives.

Table 4-1 Oxygen Balance of Some Explosives[1]

Explosive substance	Empirical formula	Oxygen balance % (w/w)
Ammonium nitrate	NH_4NO_3	+19.99
Nitroglycerine	$C_3H_5N_3O_9$	+3.52
Silver Azide	AgN_3	0.00
EGDN	$C_2H_4N_2O_6$	0.00
Lead Azide	PbN_6	0.00
PETN	$C_5H_8N_4O_{12}$	-10.12
CL-20	$C_6H_6N_{12}O_{12}$	-10.95
TNAZ	$C_3H_4N_4O_6$	-16.66
Mercury Fulminate	$HgC_2N_2O_2$	-16.86
Lead Styphnate	$PbC_6H_3N_3O_9$	-18.79
FOX-12	$C_2H_7N_7O_5$	-19.13
FOX-7	$C_2H_4N_4O_4$	-21.61
RDX	$C_3H_6N_6O_6$	-21.61
HMX	$C_4H_8N_8O_8$	-21.61
Nitrocellulose (14.14 % N)	$C_6H_7O_{11}N_3$	-24.24
Nitroguanidine	$CH_4N_4O_2$	-30.75
Picric acid	$C_6H_3N_3O_7$	-45.39
Tetryl	$C_7H_5N_5O_8$	-47.36
NTO	$C_2H_2N_4O_3$	-49.18
TATB	$C_6H_6N_6O_6$	-55.78
Tetrazene	$C_2H_8N_{10}O$	-59.52
HNS	$C_{14}H_6N_6O_{12}$	-67.52
TNT	$C_7H_5N_3O_6$	-73.96

4.3.3 Kistiakowsky-Wilson Rules

The Kistiakowsky-Wilson rules (K-W) rules are presented below in order of priority.

1. Carbon atoms are converted to carbon monoxide
2. If any oxygen remains then hydrogen is then oxidized to water
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4. All the nitrogen is converted to nitrogen gas N_2

Using these rules the decomposition products of RDX ($C_3H_6N_6O_6$) can be determined.

1. Carbon atoms are converted to carbon monoxide
   $3C \rightarrow 3CO$
2. If any oxygen remains then hydrogen is then oxidized to water
   $6H \rightarrow 3H_2O$
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
   No more oxygen
4. All the nitrogen is converted to nitrogen gas N_2
   $6N \rightarrow 3N_2$

Therefore the overall reaction for the decomposition of RDX is:

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g) \quad \textbf{(4-11)}$$

For explosive materials which have a lower oxygen balance than -40 the modified Kistiakowsky-Wilson rules must be employed.

4.3.4 Modified Kistiakowsky-Wilson Rules

The modified Kistiakowsky-Wilson rules (mod. K-W) rules are presented below in order of priority.

1. Hydrogen atoms are converted to water
2. If any oxygen remains then carbon is converted to carbon monoxide
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4. All the nitrogen is converted to nitrogen gas N_2

Using the modified Kistiakowsky-Wilson rules the decomposition products for TNT ($C_7H_5N_3O_6$) can be determined.

1. Hydrogen atoms are converted to water
   $5H \rightarrow 2½H_2O$
2. If any oxygen remains then carbon is converted to carbon monoxide
   $3½C \rightarrow 3½CO$
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide

No more oxygen

4. All the nitrogen is converted to nitrogen gas N_2
   $3N \rightarrow 1½N_2$
5. The remaining carbon remains as elemental carbon
   $3½C \rightarrow 3½C$

Therefore the overall reaction for the decomposition of TNT is:

$$C_7H_5N_3O_6(s) \rightarrow 3½CO(g) + 3½C(s) + 2½H_2O(g) + 1½N_2(g) \quad \textbf{(4-12)}$$

The reaction for the decomposition of explosive substances can therefore be determined using either the Kistiakowsky-Wilson (K-W) rules or the modified Kistiakowsky-Wilson (mod. K-W) rules.

Table 4-2 and

Table 4-3 present equations for the decomposition for some explosive materials using the K-W rules and the modified K-W rules respectively.

The K-W and modified K-W rules will only provide an insight to the decomposition products, they do not give any information as to the energy released on decomposition but are essential when calculating the heat of explosion. They are simple to apply and do give fairly good approximations.

Table 4-2 Reactions for Decomposition Products Using the K-W Rules(1)

Explosive substance	Reaction for decomposition products
Nitroglycerine	$C_3H_5N_3O_9(l) \rightarrow 3CO_2(g) + 2½H_2O(g) + ½O(g) + 1½N_2(g)$
EGDN	$C_2H_4N_2O_6(s) \rightarrow 2CO_2(g) + 2H_2O(g) + N_2(g)$
PETN	$C_5H_8N_4O_{12}(s) \rightarrow 2CO(g) + 3CO_2(g) + 4H_2O(g) + 2N_2(g)$
CL-20	$C_6H_6N_{12}O_{12}(s) \rightarrow 3CO(g) + 3CO_2(g) + 3H_2O(g) + 6N_2(g)$
TNAZ	$C_3H_4N_4O_6(s) \rightarrow 2CO(g) + CO_2(g) + 2H_2O(g) + 2N_2(g)$
FOX-12	$C_2H_7N_7O_5(s) \rightarrow 2CO(g) + 3H_2O(g) + ½H_2(g) + 3½N_2(g)$
FOX-7	$C_2H_4N_4O_4(s) \rightarrow 2CO(g) + 2H_2O(g) + 2N_2(g)$
RDX	$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g)$
HMX	$C_4H_8N_8O_8(s) \rightarrow 4CO(g) + 4H_2O(g) + 4N_2(g)$
Nitrocellulose (14.14 % N)	$C_6H_7O_{11}N_3(s) \rightarrow$ $4½CO(g) + 1½CO_2(g) + 3½H_2O(g) + 1½N_2(g)$
Nitroguanidine	$CH_4N_4O_2(s) \rightarrow CO(g) + H_2O(g) + H_2(g) + 2N_2(g)$

Table 4-3 Reactions for Decomposition Products Using Modified K-W Rules(1)

Explosive substance	Reaction for decomposition products
Picric acid	$C_6H_3N_3O_7(s) \rightarrow 5½CO(g) + ½C(s) + 1½H_2O(g) + 1½N_2(g)$
Tetryl	$C_7H_5N_5O_8(s) \rightarrow 5½CO(g) + 1½C(s) + 2½H_2O(g) + 2½N_2(g)$
NTO	$C_2H_2N_4O_3(s) \rightarrow 2CO(g) + H_2O(g) + 2N_2(g)$
TATB	$C_6H_6N_6O_6(s) \rightarrow 3CO(g) + 3C(s) + 3H_2O(g) + 3N_2(g)$
Tetrazene	$C_2H_8N_{10}O(s) \rightarrow ½H_2O(g) + 2C(s) + 3½H_2(g) + 5N_2(g)$
HNS	$C_{14}H_6N_6O_{12}(s) \rightarrow 9CO(g) + 5C(s) + 3H_2O(g) + 3N_2(g)$
TNT	$C_7H_5N_3O_6(s) \rightarrow 3½CO(g) + 3½C(s) + 2½H_2O(g) + 1½N_2(g)$

4.4 HEAT OF EXPLOSION AND GAS PRODUCTION

4.4.1 Heat of Formation

The heats of formation of a reaction can be described as the heat released or absorbed during the formation of a pure substance from its elements, at constant pressure and usually denoted by ΔH_f. For explosive substances which do not contain sufficient oxygen in its molecule for complete oxidation ie TNT, products such as CO, carbon and H_2 are formed. The energy liberated during the formation of these products is known as the 'heat of explosion'. If these products are then isolated and allowed to burn in excess oxygen to form substances like CO_2, H_2O etc., the heat evolved added to the heat of explosion would be equal to the 'heat of combustion'. Consequently the value for the heat of combustion is higher than the value for the heat of explosion for explosive substances which have insufficient oxygen for complete oxidation. For explosive substances with positive oxygen balances i.e. nitroglycerine, there is generally no difference between the values for the heat of explosion and the heat of combustion.

The value for the heats of formation can be negative or positive. If the value is negative, heat is liberated during the reaction and the reaction is exothermic, whereas if the value is positive heat is absorbed during the reaction and the reaction is endothermic. For reactions involving explosive components the reaction is always exothermic. In an exothermic reaction the energy evolved may appear in many forms, but for practical purposes it is usually obtained in the form of heat. The energy liberated when explosives deflagrate is called the 'heat of deflagration', whereas the energy liberated by detonating explosives is called the 'heat of detonation' in kJ mol^{-1} or the 'heat of explosion' in kJ kg^{-1}.

In a chemical reaction involving explosives, molecules of an explosive are first raised to a higher energy level through input of the 'heats of atomization' to

break their interatomic bonds. Then the atoms rearrange themselves into new molecules, releasing a larger quantity of heat and dropping to an energy level lower than the original as shown in Figure 4.6.

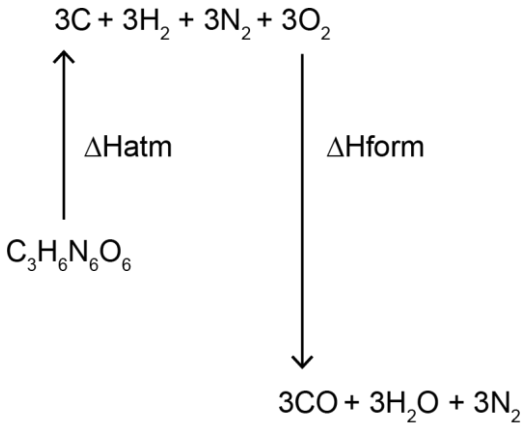


Figure 4-6 Energy diagram for RDX and its reaction products

The thermodynamic path presented in Figure 4.1 will most likely not be the same as the 'kinetic path'. For instance, the reaction may take place in several stages involving complex systems of reaction chains etc. Nevertheless, the energy evolved depends only on the initial and final states and not on the intermediate ones. Once the reaction is completed, the net heat evolved is exactly the same as if the reactant molecules were first dissociated into their atoms, and then reacted directly to form the final products (Hess's Law).

4.4.2 Heat of Explosion

When an explosive is initiated either to burning or detonation, its energy is released in the form of heat. The liberation of heat under adiabatic conditions is called the 'heat of explosion' notated by the letter *Q*. The heat of explosion provides information about the work capacity of the explosive, where the propellants and secondary explosives generally have high values of *Q*. For propellants burning in the chamber of a gun, and secondary explosives in detonating devices, the heat of explosion is conventionally expressed in terms of constant volume conditions Q_v. For rocket propellants burning in the combustion chamber of a rocket motor under conditions of free expansion to the atmosphere, it is conventional to employ constant pressure conditions. In this case, the heat of explosion is expressed as Q_p.

Under constant volume conditions Q_v can be calculated from the standard internal energies of formation for the products $\Delta U_f^{\ominus}{}_{(\text{products})}$ and the standard internal energies of formation for the explosive components $\Delta U_f^{\ominus}{}_{(\text{explosive components})}$ as shown in Equation (4-13).

$$Q_v = \Sigma \Delta U_f^{\ominus}{}_{(\text{products})} - \Sigma \Delta U_f^{\ominus}{}_{(\text{explosive components})} \quad \textbf{(4-13)}$$

A similar equation is given for the heat of explosion under constant pressure conditions as shown in Equation (4-14), where $\Delta H_f^{\ominus}$ represents the corresponding standard enthalpies of formation.

$$Q_p = \Sigma \Delta H_{f(\text{products})}^{\ominus} - \Sigma \Delta H_{f(\text{explosive components})}^{\ominus} \quad \textbf{(4-14)}$$

In considering the thermochemistry of solid and liquid explosives, it is usually adequate, for practical purposes, to treat the state functions ΔH and ΔU as approximately the same. Consequently heats, or enthalpy terms tend to be used for both constant pressure and constant volume conditions.

Therefore the heat of explosion Q can be calculated from the difference between the sum of the energies for the formation of the explosive components and the sum of the energies for the formation of the explosion products, as shown in Equation (4-15).

$$Q = \Delta H_{(\text{reaction})} = \Sigma \Delta H_{f(\text{products})} - \Sigma \Delta H_{f(\text{explosive components})} \quad \textbf{(4-15)}$$

The calculated values do not exactly agree with those obtained experimentally since the conditions of loading density, temperature, pressure etc, are not taken into consideration.

The value for Q in kJ kg^{-1} is generally derived from the heat of detonation ΔH_d kJ mol^{-1}. The heat of detonation ΔH_d for RDX can be illustrated using Hess's law as shown in Figure 4-7.

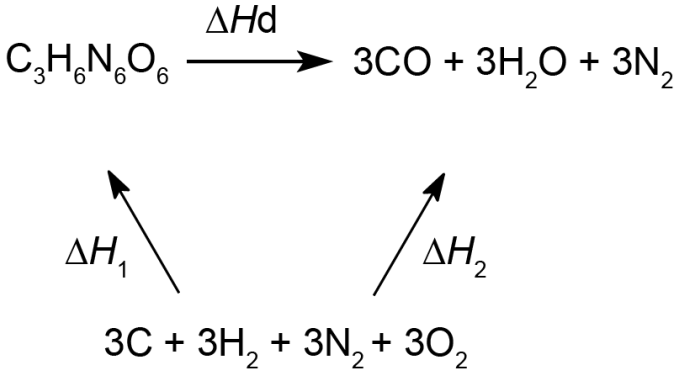


Figure 4-7 Enthalpy of detonation for RDX using Hess's law

Using the diagram in Figure 4-7 the heat of detonation for RDX can be calculated as shown below.

Heat of formation of RDX = ΔH_f(RDX) =+70.29 kJ mol^{-1}
Heat of formation of carbon monoxide = ΔH_f(CO) = -110.525 kJ mol^{-1}
Heat of formation of water in the vapour phase = $\Delta H_f(H_2O_{(g)})$= -241.830 kJ mol^{-1}
Therefore $\Delta H_1 = \Delta H_f$(RDX) = +70.29 kJ mol^{-1}

$\Delta H_2 = [3 \times \Delta H_f(CO)] + [3 \times \Delta H_f(H_2O_{(g)})]$
$= [3 \times (-110.525)] + [3 \times (-241.830)]$

= -1057.065 kJ mol^{-1}

$\Delta H_d = \Delta H_2 - \Delta H_1$
= - 1057.065 - (+70.29)
= -1127.355 kJ mol^{-1}

The heat of detonation for RDX is -1127.355 kJ mol^{-1}. This value can be converted to the heat of explosion Q as shown in Equation (4-16), where M is the molecule mass of RDX (222.117):

$$\boldsymbol{Q = \frac{\triangle H_d \, x \, 1000}{M} = \frac{-1127.355 \, x1000}{222.117} = -5075.5 \, kJ \, kg^{-1}} \qquad \textbf{(4-16)}$$

Table 4-4 presents calculated heat of explosions together with their calculated heat of detonation for some primary and secondary explosive substances. The negative sign for the heat of explosion is generally omitted since it only denotes an exothermic reaction. From this table it can be seen that secondary explosives generate far more heat during an explosion than primary explosives.

4.4.3 Gas Production

The volume of gas produced during an explosion will provide information on the amount of work done by the explosive. In order to measure the volume of gas generated standard conditions must be established, because the volume of gas will vary according to the temperature at which the measurement is taken. These standard conditions also enable comparisons to be made between one explosive and another. The standard International Union of Pure and Applied Chemistry (IUPAC) conditions set the temperature at 0 °C or 273 K, and the pressure at 1 atm. These conditions are known as 'Standard, Temperature and Pressure', (STP). Under these standard conditions one mole of gas will occupy 22.4 dm^3, which is known as the molar gas volume. The volume of gas V produced from an explosive during detonation can be calculated from its equation of decomposition, an example of which is shown below for RDX.

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g) \qquad \textbf{(4-17)}$$

The production of water will be turned into steam as the temperature of explosion will be very high, therefore water will be regarded as a gaseous product. From the equation above it can be seen that 9 moles of gas are produced from one mole of RDX. Therefore 9 moles of gas will occupy 201.6 dm^3 and one kilogram of RDX will produce 907.6 dm^3 kg^{-1} of gas at STP as shown in the calculation below:

1 mole of gas at STP will occupy 22.4 dm^3
9 moles of gas will occupy 22.4 x 9 = 201.6 dm^3
Therefore 1 mole of RDX produces 201.6 dm^3 of gas
1 kilogram of RDX produces

$$V = \frac{201.6}{222.117}\ x1000 = 907.6\ dm^3\ kg^{-1}$$

where the molecular mass of RDX is 222.117.

Table 4-5 presents the calculated volumes of gases produced by some explosive substances at STP.

Table 4-4 Heat of Explosion and Heat of Detonation for Some Primary and Secondary Explosives(1)

Explosive substance	Empirical formula	ΔH_d/kJ mol^{-1}	Q_v/kJ kg^{-1}
Primary explosives			
Mercury fulminate	$HgC_2N_2O_2$	-500.00	1756.70
Lead styphnate	$PbC_6H_3N_3O_9$	-868.00	1853.49
Lead azide	PbN_6	-469.00	1610.36
Tetrazene	$C_2H_8N_{10}O$	-310.04	1647.79
Secondary explosives			
Nitroglycerine	$C_3H_5N_3O_9$	-1414.40	6228.46
Nitrocellulose (14.14%N)	$C_6H_7O_{11}N_3$	-1281.37	4312.84
EGDN	$C_2H_4N_2O_6$	-1021.31	6716.30
PETN	$C_5H_8N_4O_{12}$	-1838.37	5815.08
RDX	$C_3H_6N_6O_6$	-1127.36	5075.50
HMX	$C_4H_8N_8O_8$	-1484.44	5012.30
Nitroguanidine	$CH_4N_4O_2$	-260.31	2501.36
Picric acid	$C_6H_3N_3O_7$	-756.28	3301.02
Tetryl	$C_7H_5N_5O_8$	-1246.35	4340.50
TATB	$C_6H_6N_6O_6$	-902.89	3497.52
NTO	$C_2H_2N_4O_3$	-362.08	2783.90
TNAZ	$C_3H_4N_4O_6$	-1131.86	5891.01
CL-20	$C_6H_6N_{12}O_{12}$	-2609.59	5955.43
FOX-12	$C_2H_7N_7O_5$	-591.54	2828.70
FOX-7	$C_2H_4N_4O_4$	-574.71	3881.13
HNS	$C_{14}H_6N_6O_{12}$	-1798.46	3994.48
TNT	$C_7H_5N_3O_6$	-929.34	4091.63

Table 4-5 Calculated Volume of Gas Produced by Some Explosives at STP(1)

Explosive substance	**Decomposition products**	***V*/dm^3 kg^{-1}**
Nitroglycerine	$3CO_2(g) + 2½H_2O(g) + ½O(g) + 1½N_2(g)$	739.80
Nitrocellulose (14.14%N)	$4½CO(g) + 1½CO_2(g) + 3½H_2O(g) + 1½N_2(g)$	821.79
EGDN	$2CO_2(g) + 2H_2O(g) + N_2(g)$	736.53
PETN	$2CO(g) + 3CO_2(g) + 4H_2O(g) + 2N_2(g)$	779.41
RDX	$3CO(g) + 3H_2O(g) + 3N_2(g)$	907.63
HMX	$4CO(g) + 4H_2O(g) + 4N_2(g)$	908.12
Nitroguanidine	$CO(g) + H_2O(g) + H_2(g) + 2N_2(g)$	1076.22
Picric acid	$5½CO(g) + ½C(s) + 1½H_2O(g) + 1½N_2(g)$	831.06
Tetryl	$5½CO(g) + 1½C(s) + 2½H_2O(g) + 2½N_2(g)$	819.90
TATB	$3CO(g) + 3C(s) + 3H_2O(g) + 3N_2(g)$	780.94
NTO	$2CO(g) + H_2O(g) + 2N_2(g)$	861.13
TNAZ	$2CO(g) + CO_2(g) + 2H_2O(g) + 2N_2(g)$	816.29
CL-20	$3CO(g) + 3CO_2(g) + 3H_2O(g) + 6N_2(g)$	766.80
FOX-12	$2CO(g) + 3H_2O(g) + ½H_2(g) + 3½N_2(g)$	964.04
FOX-7	$2CO(g) + 2H_2O(g) + 2N_2(g)$	907.63
HNS	$9CO(g) + 5C(s) + 3H_2O(g) + 3N_2(g)$	746.28
TNT	$3½CO(g) + 3½C(s) + 2½H_2O(g) + 1½N_2(g)$	739.65

4.5 EXPLOSIVE POWER AND TNT EQUIVALANCE

4.5.1 Explosive Power

In an explosive reaction heat and gases are liberated. The volume of gas *V* and the heat of explosion *Q* can both be calculated independently but these values can be combined to give the value for the explosive power as shown in Equation (4-18).

$$Explosive\ Power = Q\ x\ V \quad \textbf{(4-18)}$$

4.5.2 Power Index

The value for the explosive power can be compared to the explosive power of a standard explosive (picric acid) resulting in the power index, as shown in Equation (4-19), where $Q_{picric\ acid}$ and $V_{picric\ acid}$ are 3301.02 kJ kg^{-1} and 831.06 $dm^3\ kg^{-1}$ respectively.

$$Power\ Index = \frac{Q\ x\ V}{Q_{picric\ acid}\ x\ V_{picric\ acid}}\ x\ 100 \quad \textbf{(4-19)}$$

4.5.3 TNT Equivalence

The value for explosive power can also be compared to the explosive power of TNT resulting in the TNT equivalence value as shown in Equation (4-20). The term "TNT equivalence" is a normalisation technique for equating properties of an explosive to TNT, the standard. There are many ways to calculate "TNT equivalence" and the term is often misused because the property in question and basis for the equivalence are not defined.

$$TNT\ equivalence = \frac{Q\ x\ V}{Q_{\ TNT}\ x\ V_{TNT}} \quad \textbf{(4-20)}$$

The explosive power, power index and TNT equivalence of some primary and secondary explosives are presented in

Table 4-6. As expected the values for the power, power index and TNT equivalence of secondary explosives are much higher than the values for primary explosives.

4.6 TEMPERATURE OF DETONATION

When an explosive detonates the reaction is extremely fast and, initially, the gases do not have time to expand to any great extent. The heat liberated by the explosion will raise the temperature of the gases which will in turn cause them to expand and work on the surroundings to give a 'lift and heave effect'. The effect of this heat energy on the gas can be used to calculate the temperature of explosion.

The temperature of explosion T_e is the maximum temperature which the explosion products can attain under adiabatic conditions. It is assumed that the explosive at an initial temperature T_i is converted to gaseous products which are also at the initial temperature T_i. The temperature of these gaseous products is then raised to T_e by the heat of explosion Q. Therefore the value of T_e will depend on the value of $\underline{Q}$ and on the separate molar heat capacities of the gaseous products as shown in Equation (4-21), where C_v is the molar heat capacities of the products at constant volume and Σ represents the summation of the heat capacity integrals corresponding to the separate components of the gas mixture.

$$Q = \Sigma \int_{T_i}^{T_e} C_v . dT \qquad \textbf{(4-21)}$$

The rise in temperature of the gases is calculated by dividing the heat generated $\underline{Q}$ by the mean molar heat capacity of the gases at constant volume ΣC_v as shown in Equation (4-22), where T_i is the initial temperature.

$$T_e = \frac{\underline{Q}}{\Sigma C_v} + T_i \qquad \textbf{(4-22)}$$

Table 4-6 The Calculated Explosive Power, Power Index and TNT Equivalence of Some Explosives(1)

Explosive substance	Qv/ kJ kg^{-1}	V/ dm^3 kg^{-1}	Explosive Power*	Power index/%	TNT Equiv.
Primary explosives					
Mercury fulminate	1756.70	215	37.77	13.77	0.12
Lead styphnate	1853.49	301	55.79	20.34	0.19
Lead azide	1610.36	218	35.11	12.80	0.16
Secondary explosives					
Nitroglycerine	6228.46	739.80	460.78	167.97	1.52
Nitrocellulose (14.14%N)	4312.84	821.79	354.42	129.19	1.17
EGDN	6716.30	736.53	494.68	180.32	1.63
PETN	5815.08	779.41	453.23	165.21	1.50
RDX	5075.50	907.63	460.67	167.92	1.52
HMX	5012.30	907.63	454.99	165.85	1.50
Nitroguanidine	2501.36	1076.22	269.20	98.13	0.89
Picric acid	3301.02	831.06	274.33	100.00	0.91
Tetryl	4340.50	819.90	355.88	129.73	1.18
TATB	3497.52	780.94	273.13	99.56	0.90
NTO	2783.90	861.13	239.73	87.39	0.79
TNAZ	5891.01	816.29	480.88	175.29	1.59
CL-20	5955.43	766.80	456.66	166.46	1.51
FOX-12	2828.70	964.04	272.70	99.41	0.90
FOX-7	3881.13	907.63	352.26	128.41	1.16
HNS	3994.48	746.28	298.10	108.66	0.98
TNT	4091.63	739.65	302.64	110.32	1.00

*Q x V $x10^4$/kJ dm^3 kg^{-2}

Table 4-7 Mean Molar Heat Capacities at Constant Volume (C_v) J mol^{-1} K^{-1}(1)

Temp (K)	CO_2	CO	H_2O	H_2	N_2
2000	45.371	25.037	34.459	22.782	24.698
2100	45.744	25.204	34.945	22.966	24.866
2200	46.087	25.359	35.413	23.146	25.025
2300	46.409	25.506	35.865	23.322	25.175
2400	46.710	25.640	36.292	23.493	25.317
2500	46.991	25.769	36.706	23.665	25.451
2600	47.258	25.895	37.104	23.832	25.581
2700	47.509	26.012	37.485	23.995	25.703
2800	47.744	26.121	37.849	24.154	25.820
2900	47.965	26.221	38.200	24.309	25.928
3000	48.175	26.317	38.535	24.260	26.029
3100	48.375	26.409	38.861	24.606	26.129
3200	48.568	26.502	39.171	24.748	26.225
3300	48.748	26.589	39.472	24.886	26.317
3400	48.924	26.669	39.761	25.025	26.401
3500	49.091	26.744	40.037	25.158	26.481
3600	49.250	26.819	40.305	25.248	26.560
3700	49.401	26.891	40.560	25.405	26.635
3800	49.546	26.962	40.974	25.527	26.707
3900	49.690	27.029	41.045	25.644	26.778
4000	49.823	27.091	41.271	25.757	26.845
4500	50.430	27.372	42.300	26.296	27.154
5000	50.949	27.623	43.137	26.769	27.397

The mean molar heat capacities of the gaseous products vary with temperature in a non-linear manner. Some gaseous products at various temperatures are presented in

Table 4-7.

Using this information the heat liberated by an explosion at various temperatures can be calculated. T_e can then be determined from a graphical representation of T_e versus Q, as shown in the example below.

The heat (energy) liberated Q during an explosion of RDX was calculated earlier to be 1127.36 kJ mol^{-1}. This heat is then used to raise the temperature of 1 mole of the gaseous products from their initial temperature T_i to their final temperature T_e. Let us assume that the temperature of explosion T_e equals 3500 K and the initial temperature equals 300 K. The heat liberated by the explosion of RDX at a temperature of 3500 K is calculated from the mean molar heat capacities (C_v) of the gaseous products at 3500K as shown below.
Mean molar heat capacities (C_v) at 3500 K, using

Table 4-7 are:

$CO = 26.744\ J\ mol^{-1}\ K^{-1}$
$H_2O = 40.037\ J\ mol^{-1}\ K^{-1}$
$N_2 = 26.481\ J\ mol^{-1}\ K^{-1}$

Heat liberated by the explosion RDX at 3500K = $Q_{3500K} = (\Sigma Cv) \times (T_e - T_i)$

$Q_{3500K} = [(3x26.744) + (3x40.037) + (3x26.481)] \times (3500-300)$
$Q_{3500K} = 895315\ J\ mol^{-1}$
$Q_{3500K} = 895.3\ kJ\ mol^{-1}$

The calculated value of Q_{3500K} is 895.3 kJ mol^{-1} which is too low since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. Therefore the temperature of explosion must be higher. Let us now assume that T_e equals 4500K, the heat liberated by the explosion of RDX at this higher temperature is calculated to be 1220.0 kJ mol^{-1} as shown below.

Mean molar heat capacities (C_v) at 4500 K are:

$CO = 27.372\ J\ mol^{-1}\ K^{-1}$
$H_2O = 42.300\ J\ mol^{-1}\ K^{-1}$
$N_2 = 27.154\ J\ mol^{-1}\ K^{-1}$

$Q_{4500K} = [(3x27.372) + (3x42.300) + (3x27.154)] \times (4500-300)$
$Q_{4500K} = 1220007.6\ J\ mol^{-1}$
$Q_{4500K} = 1220.0\ kJ\ mol^{-1}$

This value of Q_{4500K} is too high since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. By calculating the values of Q at various temperatures of T_e a graph can be drawn and the correct value for T_e can be obtained as shown in Figure 4-8. From this the value for the temperature of explosion for RDX is found to be ~4215 K.

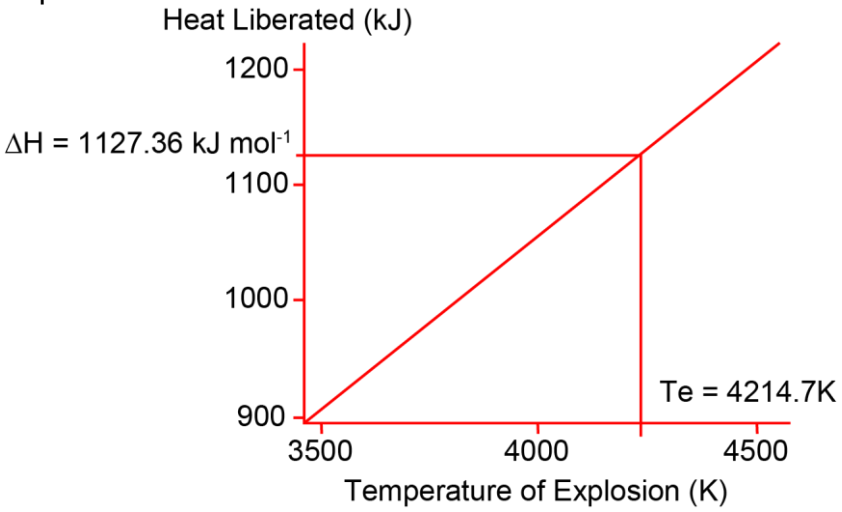


Figure 4-8 Calculated values of heat liberated at various temperatures of explosion using C_v for RDX[1]

These calculations were based on mean molar heat capacities at a constant volume (C_v). However the enthalpies of formation and therefore heats of explosion were based on values at constant pressure. It is possible to convert the mean molar heat capacities at a constant volume (C_v) to the mean molar heat capacities at a constant pressure (C_p) using Equation (4-23)[2] where R is the gas constant (8.3145 J mol^{-1} K^{-1}).

$$C_p = C_v + R \qquad \textbf{(4-23)}$$

The calculated C_p values are presented in Table 4-8 and the recalculated values for T_e using this Table are shown below.

Mean molar heat capacities (C_p) at 3500 K:

CO = 35.058 J mol^{-1} K^{-1}
H_2O = 48.351 J mol^{-1} K^{-1}
N_2 = 34.795 J mol^{-1} K^{-1}

Heat liberated by the explosion RDX at 3500K = Q_{3500K} = (ΣC_p) x (T_e - T_i)

Q_{3500K} = [(3x35.058) + (3x48.351) + (3x34.795)] x (3500-300)
Q_{3500K} = 1134758 J mol^{-1}
Q_{3500K} = 1134.8 kJ mol^{-1}

The calculated value of Q_{3500K} is 1134.8 kJ mol^{-1} which is too high since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. Therefore the temperature of explosion must be lower when using C_p values. Now assume that T_e equals 3000K, then the heat liberated by the explosion of RDX at this lower temperature is calculated to be 938.2 kJ mol^{-1} as shown below.

Mean molar heat capacities (C_p) at 3000 K

CO = 34.631 J mol^{-1} K^{-1}
H_2O = 46.849 J mol^{-1} K^{-1}
N_2 = 34.343 J mol^{-1} K^{-1}

Q_{3000K} = [(3x34.631) + (3x46.849) + (3x34.343)] x (3000-300)
Q_{3000K} = 938166.3 J mol^{-1}
Q_{3000K} = 938.2 kJ mol^{-1}

This value of Q_{3000K} is too low since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. The value for T_e can now be measured from the graph in Figure 4-9, which gives a value of 3481 K.

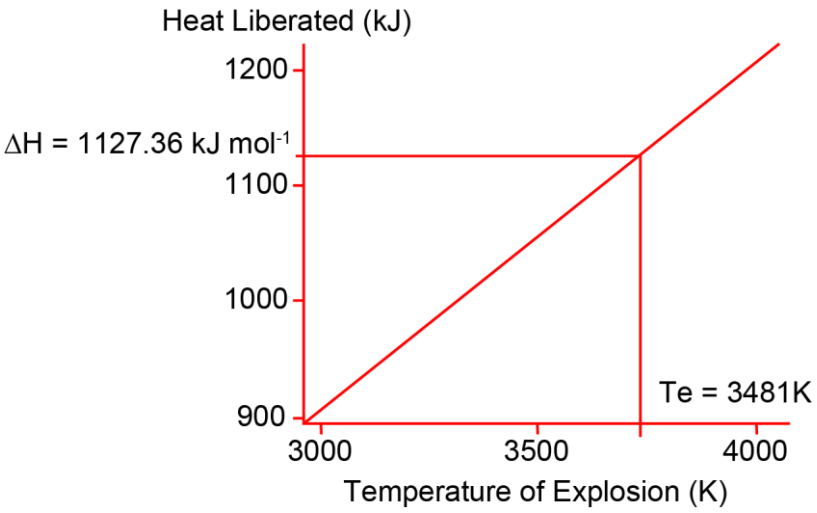


Figure 4-9 Calculated values of heat liberated at various temperatures of explosion for RDX using C_p

Therefore, when using C_p instead of C_v to calculate the temperature of explosion, a lower T_e value is obtained because the values for the mean molar heat capacities C_p is higher compared to C_v.

Table 4-8 Mean Molar Heat Capacities at Constant Pressure (C_p) J mol^{-1} K^{-1}

Temp (K)	CO_2	CO	H_2O	H_2	N_2
2000	53.685	33.351	42.773	31.096	33.012
2100	54.058	33.518	43.259	31.28	33.18
2200	54.401	33.673	43.727	31.46	33.339
2300	54.723	33.82	44.179	31.636	33.489
2400	55.024	33.954	44.606	31.807	33.631
2500	55.305	34.083	45.02	31.979	33.765
2600	55.572	34.209	45.418	32.146	33.895
2700	55.823	34.326	45.799	32.309	34.017
2800	56.058	34.435	46.163	32.468	34.134
2900	56.279	34.535	46.514	32.623	34.242
3000	56.489	34.631	46.849	32.574	34.343
3100	56.689	34.723	47.175	32.92	34.443
3200	56.882	34.816	47.485	33.062	34.539
3300	57.062	34.903	47.786	33.2	34.631
3400	57.238	34.983	48.075	33.339	34.715
3500	57.405	35.058	48.351	33.472	34.795
3600	57.564	35.133	48.619	33.562	34.874
3700	57.715	35.205	48.874	33.719	34.949
3800	57.86	35.276	49.288	33.841	35.021
3900	58.004	35.343	49.359	33.958	35.092
4000	58.137	35.405	49.585	34.071	35.159
4500	58.744	35.686	50.614	34.61	35.468
5000	59.263	35.937	51.451	35.083	35.711

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CHAPTER 5
INITIATION OF EXPLOSIVES

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5 INITIATION OF EXPLOSIVES

Authors – S G Murray (Cranfield University) and Dr W Proud (Imperial College London)

5.1 AWARENESS SUMMARY

In the practical application of explosives there is a requirement to start the explosive event by a reliable method of initiation. This could be initiation to a burning reaction, for example for gun propellants, rocket propellants or pyrotechnics, or initiation to detonation for high explosive charges. In either case energy must be imparted to the explosive such that the chemical reaction of explosive molecules or explosive mixture is caused to occur at such a rate it becomes self-propagating, that is it continues through the explosive charge. All of the methods described below that are capable of causing ignition or detonation of a charge will cause the explosive to be raised in temperature since the chemical reaction of explosion will increase its rate rapidly as temperature increases as shown in Figure 5-1. The methods of energy input are deliberate for practical initiation system; however, they also will be relevant to the potential accidental initiation of explosives.

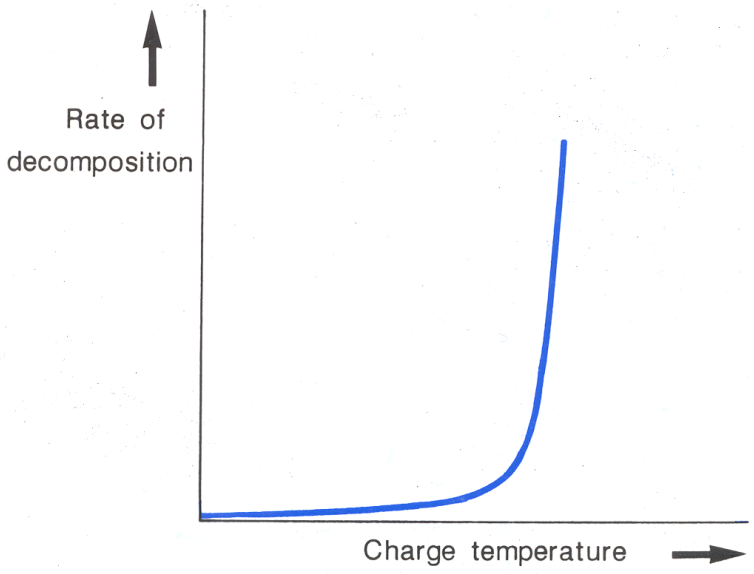


Figure 5-1 Rate of explosive reaction vs temperature

5.1.1 Initiation to Burning

5.1.1.1 Direct heat

If an explosive is heated, for example on a metal plate, at some point it will achieve a temperature at which ignition will occur. This would not be practical in a munition but is relevant to safe handling of explosives. Raising the temperature of a small sample of explosive at 5 °C per minute until ignition is

seen provides a Temperature of Ignition (T of I) (see 20.10.2.3) for that explosive (Table 5-1). If an explosive is heated much more slowly, then this value can reduce by several 10s of degrees.

Table 5-1 Some Temperature of Ignition Values for Common Explosives

Explosive	Temperature of Ignition* (°C)
Nitrocellulose	187
Nitroglycerine	188
RDX	204
PETN	205
TNT	240
HMX	273

* Heated at 5 °C per minute

5.1.1.2 Flame

This is an obvious method of producing high temperatures and is used often for igniferous ignition, e.g. for igniting propellant. The source of the flame is either a pyrotechnic or primary explosive and temperatures well in excess of 10,000 °C can be produced. The explosive to be ignited is raised in temperature by heat conduction from hot gas products and often hot particles. The flash of flame must have sufficient time to raise the explosive to its ignition temperature.

5.1.1.3 Percussion

If an explosive material is struck and compressed it is possible for hot spots to be created in the explosive by adiabatic compression. That is if a trapped pocket of air is rapidly compressed it is raised in temperature. This is the mechanism used in small arms percussion caps (Figure 5-2) (see 6.2.2.4) where the hammer of the weapon hits the cap causing an indentation, which compresses the cap composition.

This is an example of hot spot formation (see 5.3) within the explosive that is being ignited. These hot spots create centres of ignition that grow and coalesce to ignite the whole charge. If the cap composition is pressed too much in production then a significant number of the small air pockets are lost as the density increases. This can cause failures of percussion caps known as ‘dead pressing’ where the round fails to fire when hit by the hammer.

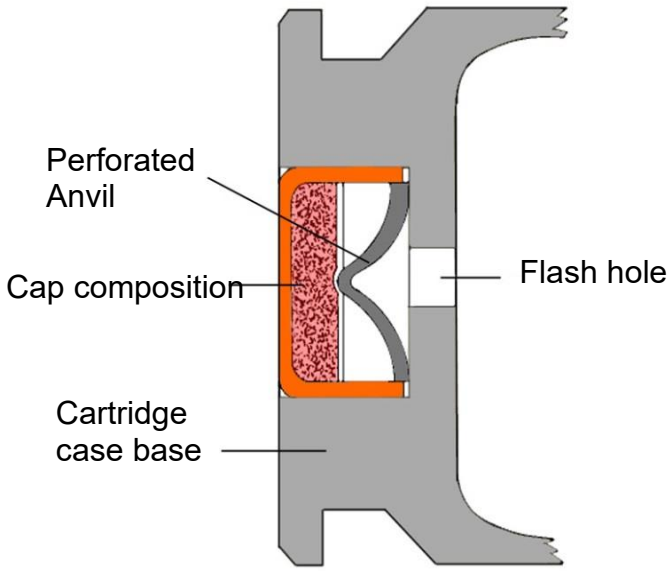


Figure 5-2 Small arms percussion cap assembly

5.1.1.4 Friction

The ability of friction to create increases in temperature is a well-known phenomenon. From a safety perspective this is important if bare explosive could experience friction such as walking on spilled explosive. For gritty explosives such as pyrotechnics this is a particular risk as they are generally powdered materials either in final form or during manufacture.

A practical use of friction as a method of ignition is the striking of match fuze and also the stab igniter (

Figure 5-3) will have a large element of friction in the mechanism causing ignition. As the striker needle enters the stab sensitive composition friction heating will occur between the composition and the sides of the angled needle point. There may also be an element of compression.

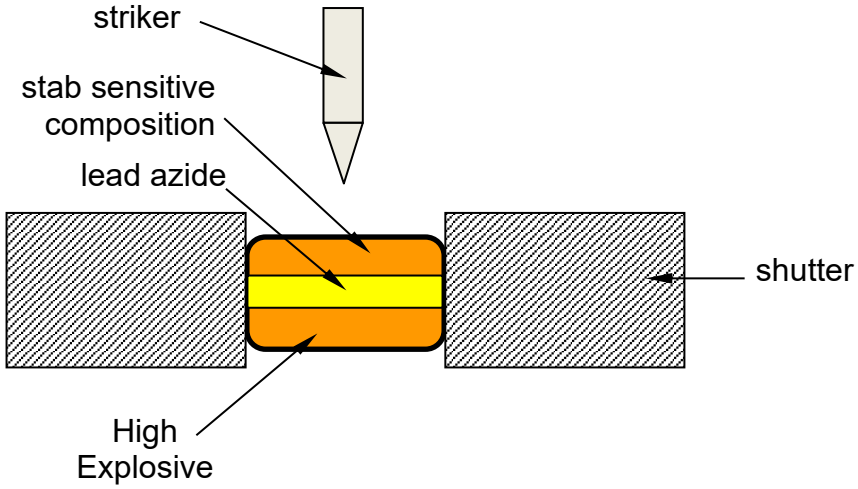


Figure 5-3 Stab initiation system

5.1.1.5 Electrical bridgewire

Passing a current through a wire that has resistance will cause it to heat. A common method to produce a flash of flame that can then be used as a source of ignition is the electric match-head. A bridgewire embedded in a primary explosive ignites when a current is passed through the wire, the ignition mechanism is simply the large temperature produced in the electrically heated wire (see 6.2.2.9).

5.1.1.6 Static discharge

The most potent static discharge is lightning, which has a core temperature of around 15,000 °C, which clearly has the potential to initiate explosion reactions. Much lower energy static discharge also has the potential to ignite explosives. The discharge spark is in essence a highly localised source of energy, which creates a hot spot.

5.1.1.7 Conducting composition

Some primary explosive compositions contain graphite powder and when pressed in to a pellet will have conducting pathways created by particles of this conducting material. If a current is passed through the pellet there will be high resistance at points where the particles touch causing hot spots to be created and thus ignition of the explosive (see 6.2.2.8).

5.1.2 Initiation to Detonation

5.1.2.1 Burning to detonation

Certain primary explosives such as lead and silver azides on ignition will immediately increase their rate of decomposition until burning transitions to a shock wave, which is to detonation. This is the most common method of creating a detonation in munitions. As the initial flame front moves through the

explosive it creates an ever increasing pressure and temperature ahead of it until the velocity exceeds the speed of sound at which point it detonates through the rest of the explosive.

Lead and silver azide will undergo this transition even unconfined and in small quantities such as tens of milligrams. Many explosives if confined can also undergo burning to detonation, which poses a hazard from munitions containing explosive in heavy metal casing such as artillery and mortar ammunition.

5.1.2.2 Donor-acceptor shock to detonation

An explosive charge that is undergoing detonation can, when in close proximity, detonate another charge. Factors that affect the success of this shock transfer are:

- Detonation shock pressure of the donor charge
- Sensitivity of the acceptor charge
- Any barrier between the two charges

As the shockwave from the donor enters the acceptor it will create an intense pressure wave that can create hot spots through compression of voids as for percussion initiation but in a more extreme manner. Other mechanisms such as shear forces add to the heat deposition and this forms a shockwave in the acceptor explosive. The intensity of the pressure wave entering the donor will depend on the detonation pressure of the donor explosive and anything that could reduce it such as a barrier, which can be a solid or indeed just air.

Figure 5-4 shows how the intensity of a detonation shockwave is affected by a barrier and by the sensitivity of the acceptor. When the stable shockwave in the donor enters a barrier it immediately begins to fall in pressure. As it enters the acceptor it begins to create energy release in the acceptor that then begins to produce a stable shockwave in the acceptor until it reaches the stable velocity of detonation and therefore stable detonation pressure.

If the acceptor has low sensitivity the shock pressure may fall significantly before it begins to accelerate to the stable condition. The thicker the barrier the lower the shock pressure entering the acceptor for a given donor shock pressure.

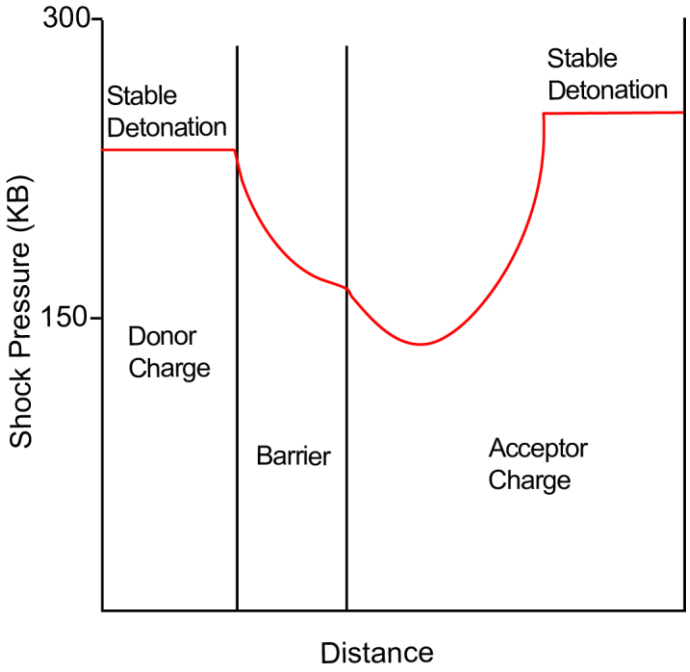


Figure 5-4 Shock pressure within a donor/barrier/acceptor

5.1.2.3 High velocity impact

Usually high velocity impact such as fragments and bullets do not directly shock an explosive to detonation. When a munition detonates in a bullet or fragment impact test the explosive content first initiates to burning but under heavy confinement of the munition casing detonates through deflagration (burning) to detonation transition. This occurs so rapidly the munition appears to detonate on impact.

In an Exploding Foil Initiator (EFI) type detonator, high velocity impact can be designed to create a detonation. A bridgewire sandwiched between two pieces of thin plastic is subject to a very large current delivered in less than a microsecond. This causes the bridgewire to explode firing a small fragment of the plastic at very high velocity in to a secondary booster type explosive with a sensitivity that allows the impact to form hot spot energy deposition and cause a shock wave to be created (see 6.3.4.8).

5.1.2.4 Exploding bridgewire (EBW) detonator

As with the EFI, in an EBW a bridgewire is subject to the same electrical conditions with the wire embedded in a secondary booster type explosive. The bridgewire explodes with such violence it creates a shockwave in the booster explosive that transitions it to a self-sustaining shockwave in the explosive (see 6.3.4.7).

5.2 INITIATION THEORY

5.2.1 The Effect of Temperature on Energy Distribution

One of the successes of quantum mechanics is in the definition of temperature. All materials possess energy in their structure, even at absolute zero a small amount of energy is retained in atoms and molecules. This energy resides in the electrons in their atomic orbitals around the nucleus, kinetic energy, whole linear motion (translation) of the particle, as well as vibration of chemical bonds, rotation of parts of the molecule around chemical bonds and the full body rotation of the molecule. In solids and liquids these atoms and molecules collide with neighbours with incredible regularity, 10^{13} collisions per second being common. Each collision allows for energy to be transferred between particles – one particle gaining energy the other losing it. In a system at a fixed temperature there will be a distribution of energy within the atoms and molecules, some particles possessing high energy, some low energy and the vast majority in the middle. Given the large number of collisions in the system the exact energy within a given particle will move up and down with time. The system is in a dynamic equilibrium.

The exact form of the energy-particle distribution depends on a large number of variables such as the mass of the constituent atoms, the number and strength of the bonds, internal symmetry of the molecule, the number of energy states which exist with the same energy level etc. This is the field of computational quantum mechanics.

If extra energy is added to the system the temperature increases the molecular level effect the frequency and violence of the collisions, vibrations and rotation increases. This causes a redistribution of energy between the molecules and within the molecules until a new dynamic equilibrium is reached. Figure 5-5 gives a schematic of the change caused by heating.

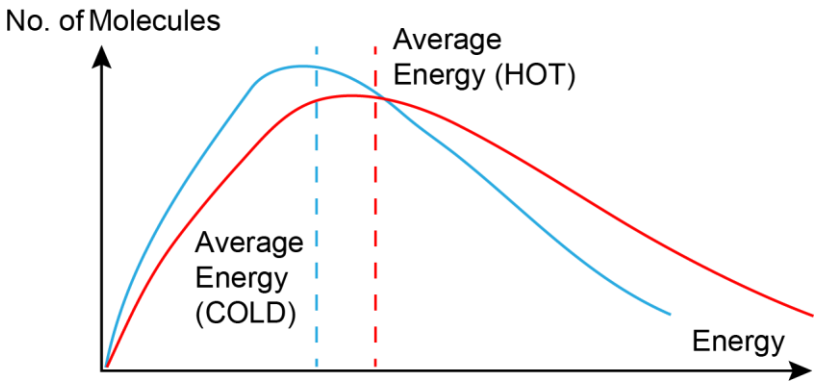


Figure 5-5 The effect of temperature on energy population

5.2.2 Bond-Breaking and Chemical Kinetics

If sufficient energy is accumulated in a molecule by collision, absorption of light/gamma rays/ cosmic rays, impact by high-speed particles etc. then it is possible that a bond can break. In many cases it is likely that the separated entities produced by the bond breakage recombine almost immediately. However, in some cases the separated entities form strong bonds with other atoms and molecules in the vicinity or undergo further fragmentation. This forms the basis of chemical kinetics.

Most chemical reactions start with an endothermic step, this means that energy has to be added to the molecule causing the initial bond breakage., Immediately after separation, the fragments are in a very high energy state. The fragments can lose energy by collision, the particles will lose a lot more energy by forming new bonds or by rearranging and fragmenting further. The energy released by this to other molecules can cause those molecules to fragment and so lead to a succession of chemical reactions. Reactions which give out energy are called exothermic and it is the balance between the endothermic and the exothermic reactions which determines the overall energy output. Figure 5-6 gives a schematic of the energy release for an exothermic reaction.

The easiest way to concentrate energy into a molecule is by heating it. If once, chemical reaction has started, sufficient energy is released this can cause the system to be self-heating. Effectively a positive feedback mechanism, building up the energy release rate to the phenomenal levels seen in explosives.

The energy required to take a molecule from its normal, standard temperature and pressure (298 K and 1 atmosphere) to the state where its weakest bond breaks is called the activation energy (E_{act}). The energy difference between the initial material and the final products is the energy that is available for doing other work. In most explosives this means a conversion from a solid or a liquid to a hot, high pressure gas which violently pushes against, fracturing and moving the surrounding material. Figure 5-6 gives a schematic idea of the energy thresholds and energy output.

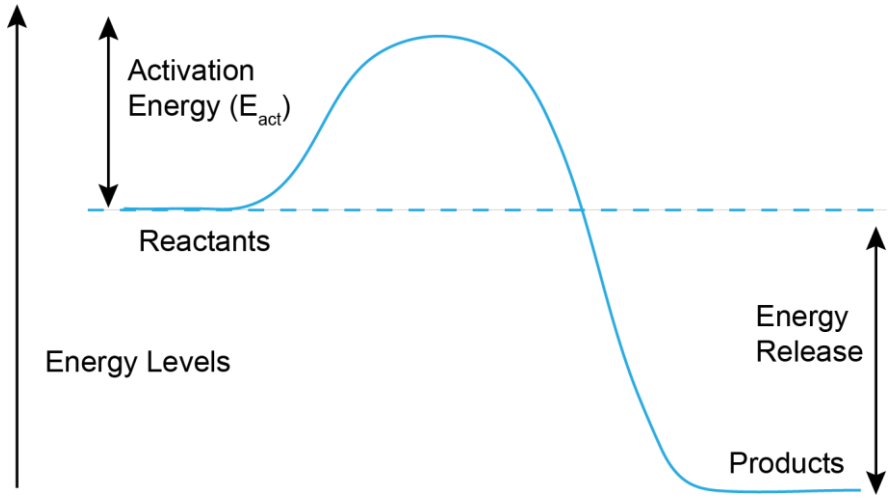


Figure 5-6 Energy balance from reaction in an exothermic chemical system

5.2.3 Boltzmann and Arrhenius

There are two fundamental equations used to understand this area of work. These were developed by Boltzmann and Arrhenius. Boltzmann considered the relative populations of a high energy state compared to a low energy state. The resulting equation has the form shown in Equation (5-1.

$$\frac{Nh}{Nl} = e^{(-\delta E/RT)} \qquad (5\text{-}1)$$

Where *Nh* is the number in the high energy state and *Nl* is the number in the low energy state, δE is the energy difference between the two levels per mole of material, *R* is the gas constant and T is the temperature measured in Kelvin (K). Sometimes in Physics based texts the term *R* is replaced by *k*, the Boltzmann constant, in which case δE is energy per atom or molecule not per mole of reactant.

In this basic form the population of the lowest energy state is always higher than more energetic states. However, due to symmetry considerations, there may be several bonds which are equivalent, e.g. methane has 4 identical C-H bonds for example. The number of states with the same energy level is called the degeneracy and this often means that while there is one low energy state, there may be hundreds of higher energy states available resulting, at room temperature, in most molecules being at energy levels above the lowest energy state.

Arrhenius looked closely at chemical kinetics and discovered that, for a fixed reaction pathway, that the rate constant, a measure of the speed of transformation, was temperature dependant. While a complete exposition of this is beyond this text, it is useful to examine the dependencies within the Arrhenius equation (Equation (5-2)).

$$k(T) = A\, e^{(-Eact/RT)} \qquad (5\text{-}2)$$

Where k(T) is the rate constant at a temperature T, a value that links concentration to overall transformation rate. The term *A* is called the pre-exponential term. This encapsulates the frequency of impact of molecules against one another and the efficacy of that impact. Molecules have a structure and so the exact position of the impact on the structure is important. Overall the value of A varies from the low, $<10^{-6}$, showing that the overwhelmingly large number of impacts have no effect. Whereas some biological enzyme reactions have values so high it implies virtually every impact between the reactants results in reaction. The exponential term looks very similar to the Boltzmann relation. This not surprising, as the δE term is represented here as the activation energy i.e. the amount of energy that has to be concentred in the molecules to take it from the average state to the bond-breaking peak of the energy level diagram. T is the absolute temperature of the system. Processes with lower activation energy tend to occur more regularly than those with high activation energy, the higher the temperature the larger the number of molecules nearer the high-energy state.

For primary explosives e.g. Lead Azide, the activation energy is of the order 105 kj/mol and the value of A is 10^{11}. For secondary explosives the activation energies are generally larger, of the order 222 kJ/mol (for TNT) and collision factors are of the order 10^{22}. As the activation energy represents the energy needed to cause breakdown of the material this means that primary explosives require less stimulation to cause reaction. This agrees with the general fashion of rating primary as sensitive and secondary as less sensitive but this time in a quantitative fashion.

5.2.4 Frank-Kamenetskii Thermal Explosion Theory

In the 1930's the soviet scientist Frank-Kamenetskii investigated the thermal stability of energetic materials in a quantitative fashion. This work led to thermal explosion theory, which can be seen as a pre-cursor to hot-spot theory particularly with respect to energy balance.

Consider a solution of explosive in a solvent in an oven. It is relatively easy to vary the concentration of the explosive and strength of the heating i.e. the oven can be set to heat to a different temperature for each experiment. As the explosive heats up some of it will decompose into smaller molecules, releasing energy. This energy release will cause the solvent close to the decomposing energetic molecule to heat up. If there is a second explosive molecule near the decomposing molecule, this second energetic molecule will heat up and become more likely to decompose and so an escalation of temperature can occur locally then spreading to lead to increased and sustained reaction. However, if there are only a few or no energetic molecules in the vicinity of the decomposing energetic molecule then the energy released will spread into the general background level of the solvent molecules and effectively have no long

term effect. The important factor is the balance between heating caused by reaction and cooling based on the temperature of the surrounding solvent. This effect can be assessed in a more quantitative fashion by examining Figure 5-7 below.

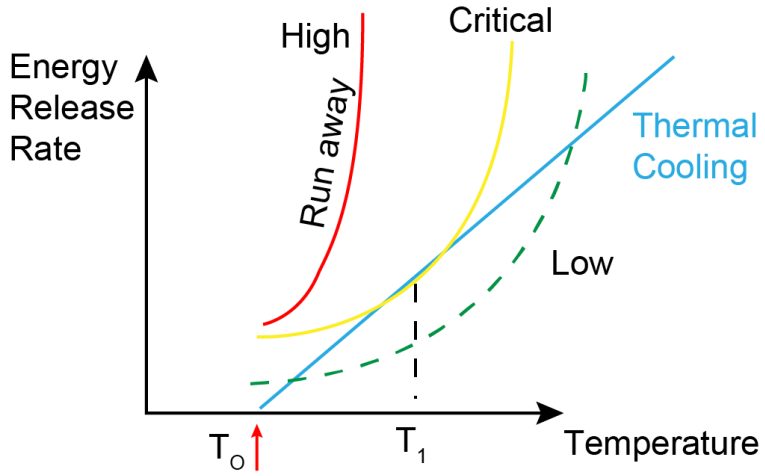


Figure 5-7 Energy balance for a heated explosive solution

In Figure 5-7 the three curves correspond to different concentrations of explosive, high, critical and low in an oven set a temperature T_0. These curves represent the energy output caused by the different concentration of explosive. The blue line represents thermal cooling. Newton developed a law of cooling which, simply stated, said that energy loss was directly proportional to the temperature difference between the hot body and the surrounding environment.

In the case of the high concentration of explosive it can be seen that the energy release rate is always above that of the thermal cooling line. This implies that the explosive solution will rapidly heat up and will 'run away' generally to an explosion. At the other extreme we have the low concentration, the green line, as it is heated and releases energy it raises the temperature. However, the cooling processes are very strong compared to the energy release. This means that at the point where the solid green curve meets the blue cooling line the rate of energy release is balanced by thermal cooling, so the system sits at a temperature slightly above T_0. The system neither heats nor cools from this temperature until the concentration of explosive, through decomposition, is reduced at which point the solution cools back towards T_0. The dotted green curve indicates where the temperature would have risen, in the absence of cooling.

For the critical concentration, decomposition causes the temperature to rise and as the temperature goes up so does the cooling rate. At this critical concentration a temperature is reached where the heating and the cooling are exactly balanced. Here the system is in a delicate balance, a slight increase in the energy release rate and the system will run away. The insight of Frank-Kamenetskii was to understand that not only were the rates of energy production and loss the same, but that the rates of change of energy production

and energy loss were the same. Having the two sets of equations one balancing the heat loss with heat production and the other the rate of change of those quantities allowed calculation of the time it would require for an explosive to heat to run away at a given oven temperature as shown in Equation**(5-3)**. The resulting calculations gave the results shown in Figure 5-7.

$$\tau = \frac{c_v R(T)^2}{AQ\,E} e^{E_{act}/RT} \qquad \textbf{(5-3)}$$

Where τ is the time to run away (or explosion), c_v is the heat capacity of the solution, basically the energy need to raise the temperature by 1 degree Celsius, A is the pre-exponential rate constant, Q is the amount of energy released from the reaction, T is the temperature of the oven, E_{act} is the activation energy. Looking at the form of this equation it is clear that a large value of activation energy means a long time to explosion, a large energy output means a shorter time, a large heat capacity means a longer time. By performing a series of experiments varying the temperature of the oven and measuring the time to explosion then values of A and E_{act} can be determined. This is useful as it allows insight into how much energy is required to cause extended reaction.

5.2.5 Thermal Values

In general, it is relatively easy to find tables of the thermal values of explosives in the literature. Safety databases will give values for flash point, spontaneous reaction etc. These values often seem to be very exact. However, as the discussion above shows the rate and extent of reaction is dependent on temperature and the molecules are distributed over a range of energies at any given temperature. This leads to a general approximation which works for a wide range of reactions ‘increasing the temperature by 10 ^{o}C doubles the reaction rate’.

Therefore, when reading data such as flash point or a phase change in a material there is a kinetic element to the value. Heating something slowly allowing time for reaction to build up may have equally aggressive consequences at a temperature below a stated value compared to plunging the explosive directly into a bath of material above the flash point. This can be thought of as a Frank-Kamenetskii style experiment: time to explosion depend on the heating rate.

As a consequence, when dealing with explosives the values for flash point or ignition point should be taken as a limit not to be approached and certainly violent explosion may occur of a munition is stored at a temperature below the flash point, for a long period of time.

5.3 HOT-SPOT FORMATION

In parallel with the work of Frank-Kamenetskii research was being conducted into friction and lubrication and calculations performed on the impact phenomena of explosives. The energy deposited in the explosive sample was shown to be sufficient to raise the temperature by a few degrees or a few tens of degrees, very much lower energies than the levels required for a thermal explosion.

This resulted in the idea of hot-spots, areas in the material where energy was concentrated and exceeded the ignition threshold[1,2]. These areas were associated with heterogeneities in the structure of the explosive e.g. a bubble in liquids, a crack in an explosive crystal or the presence of a hard grit particle in a mixture. If the hot-spot was of sufficient size and concentrated sufficient energy, a so-called critical hot-spot, then it would grow, ultimately leading to ignition in the explosive. Many mechanisms were investigated of which six mechanisms were found to be capable of producing hot-spots of a critical size, these mechanisms are; bubble collapse, friction, shear band formation, fracture, visco-plastic work and electrical discharge. It must be remembered that while heterogeneities such as voids will cause energy to concentrate, not every heterogeneity will produce a critical hot-spot. Hot-spots which are too small or not sufficiently hot, will lose energy to the surroundings quickly and be thermally quenched: these are the sub-critical hot-spots. Research done by Bowden and Yoffe[1] was pivotal in this and they showed that the size, temperature and duration required to form a hotspot was of the order: size 0.1 - 10 µm, time duration 10 µs - 1 ms, temperature 700+ K.

In all cases the difference between critical and sub-critical hot-spots needs to be drawn. In the case of a critical hot-spot the reaction site is of sufficient size that the heat loss via thermal conduction is lower than the energy produced by the chemical reactions. Thus the temperature and reaction zones increase and extend into the bulk material. Sub-critical hot-spots are those for which, while chemical reaction may break out, the heat loss from the region is higher than the production rate from the reactions and thus the reaction is quenched.

In liquids, the conditions for critical hot spot formation have been extensively studied[3-8] and the size, duration and temperature required have been reasonably well-quantified. One advantage of a liquid or a single crystal of explosive is the inherent homogeneity of the system and relative ease of visualisation of the reaction front. However, many explosive systems are heterogeneous and energy concentration relies on interplay between the components.

Calculations[9] and experiments[10] on single cracks growing in individual energetic crystals show that the energy released from the crack tip is not sufficient on its own to cause sustained reaction. However, friction, caused by rubbing of the fracture surfaces against one another after crack growth, is an important mechanism in the production of hot-spots. These mechanisms are important in propellants as well as detonative systems[11].

5.3.1 Drop Weight Studies (Fracture, Friction and Pore Collapse)

A standard technique for sensitivity studies, the drop-weight is a system that allows long, low-level pressure pulses to be applied to small samples. In combination with high-speed photography, photodiodes and stress transducers it is a powerful system for both qualitative and quantitative analysis of material response. The standard way of analyzing the output of a drop weight assumes the weight behaves as a rigid body and hence that one can simply apply Newton's laws of motion. This is used in determining the calibration of the drop weight force, by directly relating the measured force both to the deceleration of the weight also to position.

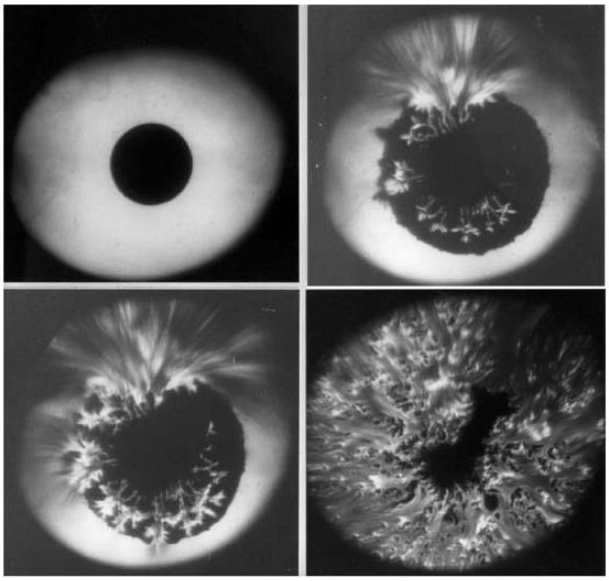


Figure 5-8 Ignition under impact of a thermite composition (Courtesy of Imperial College London)

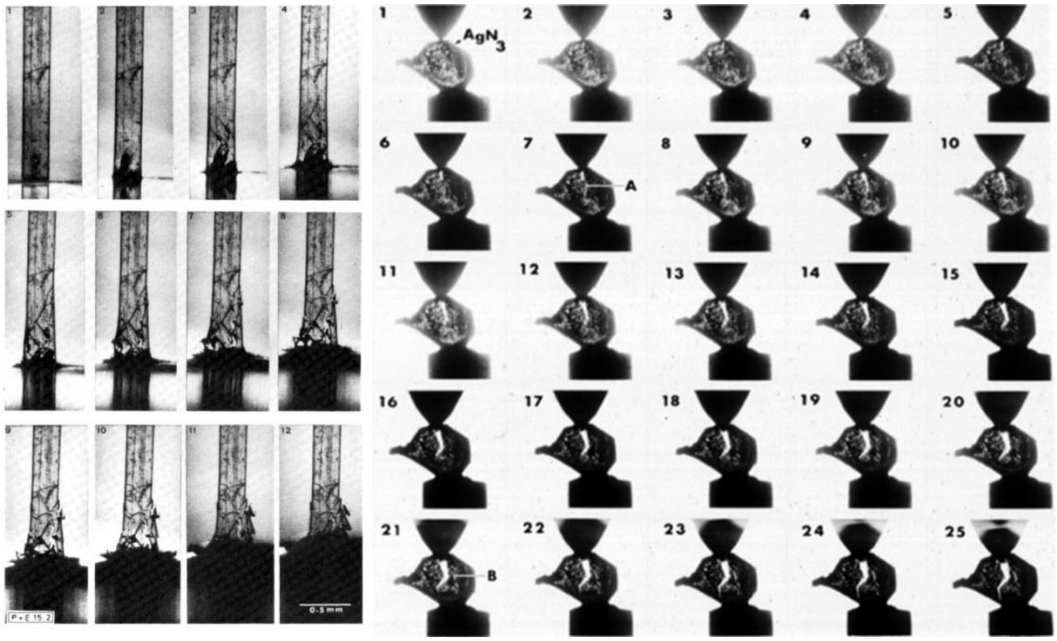
An example of a 'classic' high-speed photographic sequences obtained using this apparatus is given in Figure 5-8. Using transparent anvils images are taken along the impact axis. The top left image shows the disc of explosive before impact. The top right image shows the expansion, fragmentation and fracture of the sample. In the bottom left image there is an outbreak of reaction at the top of the sample, indicated by the jetting of hot, product gases. In the final image there is reaction throughout the sample. The time difference between these images was 10 ms. By varying the density of the sample, the grain size the contributions of the collapse of pores within the sample, the friction of grains against one another, and fracture of the grains can be studied.

5.3.2 The Relative Importance of Fracture

Fracture is often considered to be a principle cause of ignition. This can be the case but caution must be used. Figure 5-9(a) shows the effect of explosively loading a single crystal of silver azide, a sensitive primary explosive. The images were taken with an interframe time of 5 microseconds. The images

show a crystal of silver azide, resting on a barrier of thin metal sheet which appears as a shadow line near the bottom of the image. A second crystal of silver azide is underneath and is initiated. The function of the metal sheet is to stop hot reaction products from causing thermal explosion. Throughout the sequence it can be seen that the silver azide crystal shatters but does not otherwise react. In Figure 5-9(b) a single silver azide crystal is between the jaws of a loading device which crushes downwards into the crystal, breaking it. Although the fracture is moving at a high speed, again there is no reaction.

These results may seem counter intuitive, however, when the energy involved is calculated it is shown that the fracture energy released by an explosive crystal shattering is 40 mJ m^{-2}, which is not enough to cause much of a temperature rise. However, a tough polymer such as Perspex (polymethylmethacrylate) has a fracture energy of 250 J $m^{-2,}$ which is sufficient to cause critical hot-spots. This is important as if soft, rubbery polymer-bonded explosives are taken below their glass transition temperature then the strong, brittle polymer state will allow fracture to cause ignition.



(a) **(b)**

Figure 5-9 (a) fracture of a silver azide crystal by explosion, no reaction seen (b) fracture of a single crystal by knife edges, fast fracture but no ignition (Courtesy of Imperial College London)

5.3.3 Shear Bands

One mechanism which was not mentioned in the early studies is that of shear band formation. Here the impact on pressed powder pellets causes further compaction. However, this is followed by localised heating and fracture. These bands are formed when the area which is deforming becomes hot due to the

concentration of mechanical stress, which softens the material in that area. This soft material becomes easier to distort and so deformation and motion and further heating occur along this surface. A similar process is found in some metals and if the process is very quick with limited heat flow into the surrounding metal they are referred to as adiabatic shear bands.

Figure 5-10 shows a drop weight sequence for impact on to PETN. Initially the sample is opaque, however, during the impact the sample spreads and friction between the crystals leads to surface melting and fusing of the crystals. This makes the sample become relatively transparent. A reaction breaks out in the sample with the lines of reaction indicated by arrows on the frame marked as 0 µs. Reaction then builds along these lines in the later frames.

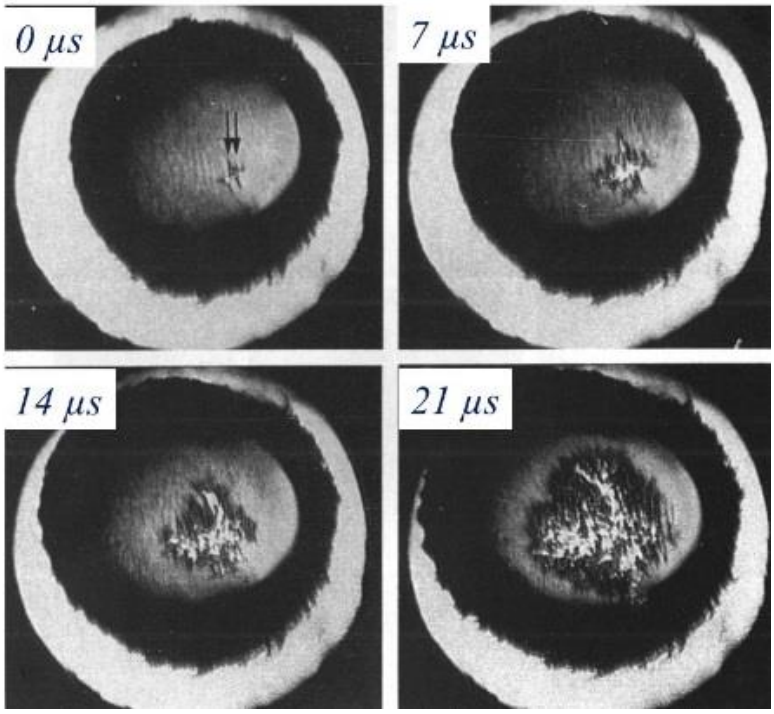


Figure 5-10 Impact on to a PETN sample (Courtesy of Imperial College London)

Figure 5-11 shows the results from using thermally sensitive film on the base of a sample of HMX that has been impacted. This was recovered after the impact and shows a series of lines indicating localized heating and evidence of shear band formation.



Figure 5-11 Shear bands seen on thermally sensitive paper recovered from a drop-weight impact on HMX sample (Courtesy of Imperial College London)

Figure 5-12 shows the initiation of a silver azide crystal under a shear load. Here, unlike in Figure 5-9(a), the crystal is loaded by the right hand side being pulled upwards and the other side being pulled downwards, without the crystal being allowed to rotate. Two fractures form in the crystal as indicated by the arrows in frame 3 and reaction builds up and spreads from those sheared surfaces.

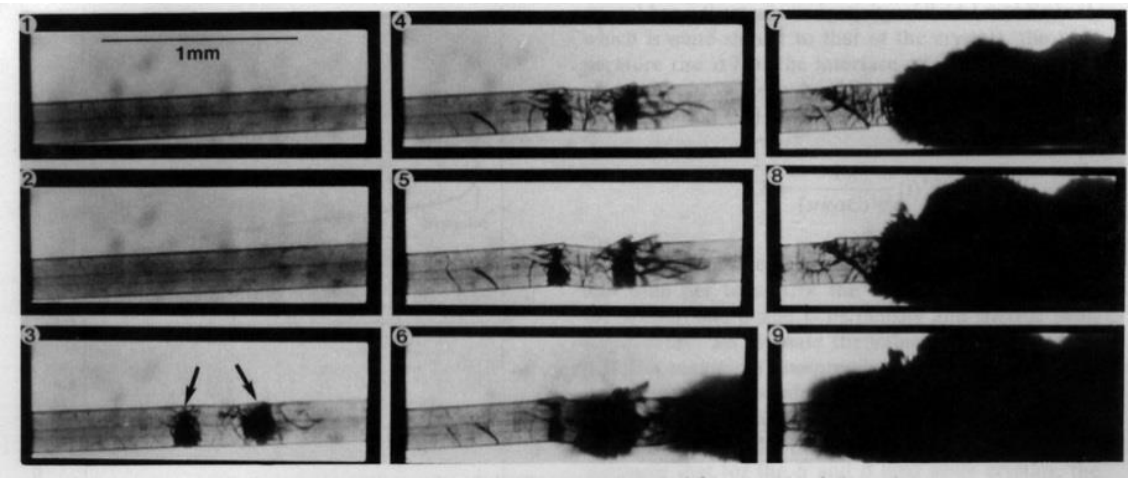


Figure 5-12 Silver Azide crystal showing initiation under shear loading (Courtesy of Imperial College London)

5.3.4 The Effect of Pressing Density

While five principal mechanisms of hot-spot formation have been identified the relative importance of these processes in a given sample is more difficult to quantify. The presence of additives, such as pressing agents, tends to reduce the effect of frictional heating, while PBXs with hard polymers tend to be susceptible to fracture.

One factor that clearly affects initiation mechanisms, particularly for powdered explosives and pyrotechnic compositions, is the pressing density. Figure 5-13 shows the level of light coming from samples of Ammonium Nitrate which have been struck by a high velocity copper plate. The level of light indicates the extent of reaction. As can be seen, the sample with 44% by volume of voids shows rapid build up to reaction. Those with 24, 17 and 11% void show much less light output. The extent of reaction drops with pressing density.

This result can be explained by considering the mechanisms. There are fewer pores in the sample at higher density and so pore collapse is reduced. Similarly, as the packing density is higher it is more difficult for crystal to move relative to one another, so friction is reduced. Pressing will also tend to break the crystals into smaller pieces so most crystals will have already have fractured slowly, so not allowing heating to be significant. Impact on these pre-fractured crystals does not allow for new surface to rub and shear against one another. Overall the incidence of heterogeneities favourable to hot-spot formation is reduced. This reduction in sensitivity is called ‘dead-pressing’.

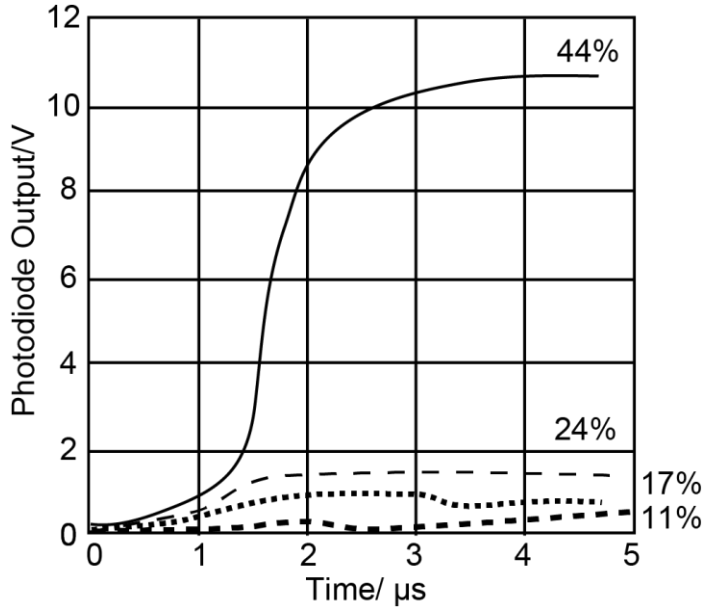


Figure 5-13 The effect of density on reaction breakout. The output of light from an impact on ammonium nitrate is shown. The lines correspond to the % volume of voids and pores in the sample

5.3.5 Bubble Collapse and Visco-Plastic Work

One of the most studied of the hot-spot mechanisms is that of bubble collapse[5-8]. This is understandable as it is easier to image voids in liquids compared to solids. The image in Figure 5-14 shows frames from a sequence showing the effect of a shock wave going across a single 3 mm void in a sheet of gelatin. It can be seen that the collapse is asymmetric with one side being forced across the bubble to strike the far side. There are a number of thermal processes occurring here. Firstly, there is the compression of gas in the void. This gives a flash of intense light as the temperature of the gas can reach several thousand degrees centigrade. While this sounds impressive, it must be remembered that the amount of gas in the cavity is limited and the total energy this represents can be quite small. A second mechanism is the local visco-plastic work going into the liquid around the cavity as it collapses. This can be significant and cause local heating. In this case the liquid becomes less viscous as it heats and so this may concentrate energy up to the point where the liquid becomes relatively inviscid. Finally, there is the energy of the impact of one side of the bubble against the other. This can be substantial, and lead to intense localized heating.

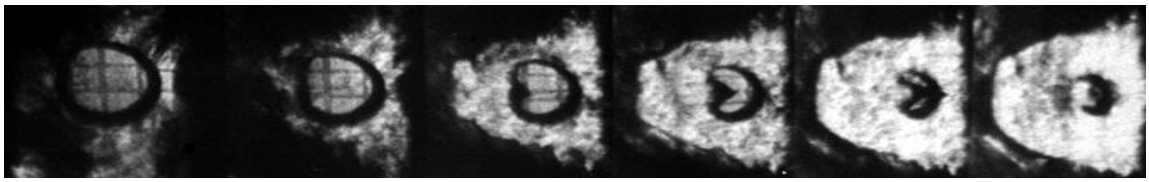


Figure 5-14 The collapse of a cavity in gelatine under shock wave loading (Courtesy of Imperial College London)

After the impact there will be turbulent mixing of the liquid and gas, thus stimulating further reaction. Overall, the combination of these three phenomena produces opportunity for a critical hot-spot to form.

5.3.6 Electrostatic Discharge

Electrostatic discharge can be an issue in dealing with some explosives and is widely recognized as an issue for pyrotechnics. This is an issue in some industries where static discharge in the presence of materials such as flour, dispersed in the air, can produce a fuel-air explosion (see 9.4.1).

A non-conductive object can be charged by rubbing through a process known as triboelectrification. Typical examples of this occurring involve the removal of covers or packaging and manufacturing processes involving the relative movement of liquids and solids including particulates. The rate of charge generation will usually increase as the speed of the process increases. Corona discharge through the air provides the only charge limiting factor in continuous processes where no ground leakage paths exist. This allows very high potentials to be generated in processes such as the movement of a helicopter rotor through snowy air. The capacitance of an electrically isolated conductive object is typically dependent on factors such as its geometrical relationship to

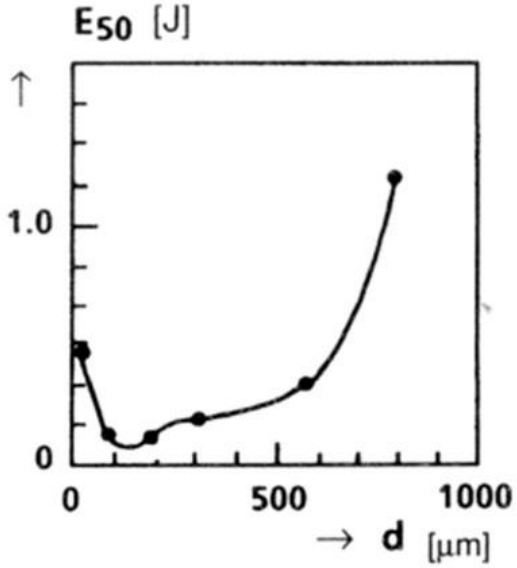
ground and its size. Overall, electrically isolated conductors are particularly hazardous due to their ability to retain charge and release it all in a single incendive discharge.

From an electrostatic perspective the human body is regarded as a conductive object. The average human capacitance is around 150–500pF, which can charge to potentials of 5 to 25kV on an electrically isolated person. In the worst case, i.e., greatest energy, this means an isolated person could release a 156mJ spark. While this energy level is unlikely, a typical spark from an ungrounded person would be of the order of at least tens of millijoules. This quantity of energy could be generated from a simple action such as rising from a chair.

The incidence of electrostatic discharge increases during cold weather. This trend is difficult to quantify, but as the temperature falls so does the moisture the air can retain. This problem will be exaggerated within a warm room as the relative humidity will be lower for the same absolute humidity; essentially reducing the tendency of the air to produce a conductive film of moisture on clothing, casings, ground, etc. As a consequence, the resistivity of these surfaces will increase. This effect is exaggerated when dealing with the hydrophilic surfaces of natural materials, e.g., cotton and wood.

For materials such as lead azide[12] the semi-conductor characteristics of the material are cited as important in allowing current flow. The amount of energy absorbed by the material can be thought of as the simple current squared multiplied by resistance. PETN has been identified as a secondary material sensitive to spark initiation. This was shown to ignite at a voltage of 70 kV when the material was at 50% Theoretical Maximum Density (TMD).

For some materials like HMX the sensitiveness (see 20.2.1) is dependent on grain size as shown in Figure 5-15. The sensitiveness increases as the grain size increases from 10 to 150 µm, remains fairly constant from 150 - 500 µm and finally rapidly decreases



above 500 µm[13]. This variation is attributed to sharp grains with small contact areas at the low grain sizes. At intermediate sizes the grains have truncated shapes and while the number of contact points is smaller they tend to be larger in area. At the higher grain size, the thermal conductivity of the system becomes important, tending to quench the hot-spots (see 5.3) by thermal cooling[14].

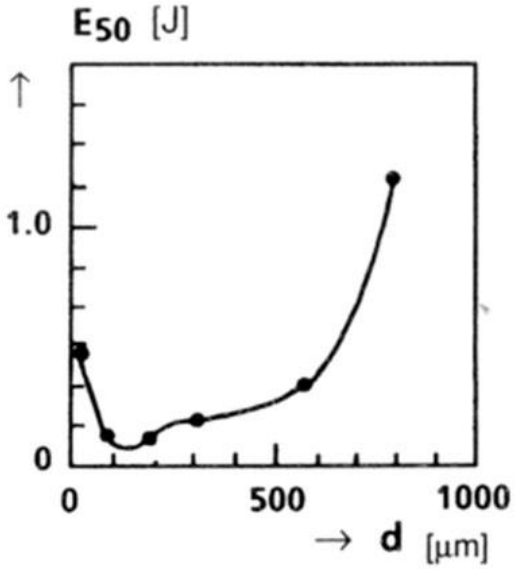


Figure 5-15 The sensitivity of HMX to electrostatic discharge with grain size

5.3.7 Hot-Spot Growth and Quenching

In Figure 5-16 the images of an impact of a flyer plate at 700 m s^{-1} on an 0.4mm thick bed of ammonium nitrate grains (150 – 210 µm) are shown causing hot-spots to be produced[15]. The exposure time of each image was 30 ns and the interframe time was zero. The increase and then decrease in light intensity from the hot-spots can clearly be seen in the sequence. Figure 5-17 shows the first two frames in detail where 2 areas are highlighted showing an area where hot-spots are growing an coalescing and another where the hot-spots are reducing and quenching. Other regions where the hot-spots are more widely spaced, towards the centre of the image, have died out. This appears to represent a distinction between critical and sub-critical hot-spots. Those hot-spots which are in proximity to one another link together possibly as a result of pressure pulses travelling between the hot-spots as a result of the production of product gases. Hot-spots which are more widely spaced tend to be quenched. In the third frame of Figure 5-16 the reaction front has spread to cover about 55% of the impact area. In the later frames the reaction moves away from the central zone where the ammonium nitrate has been consumed.

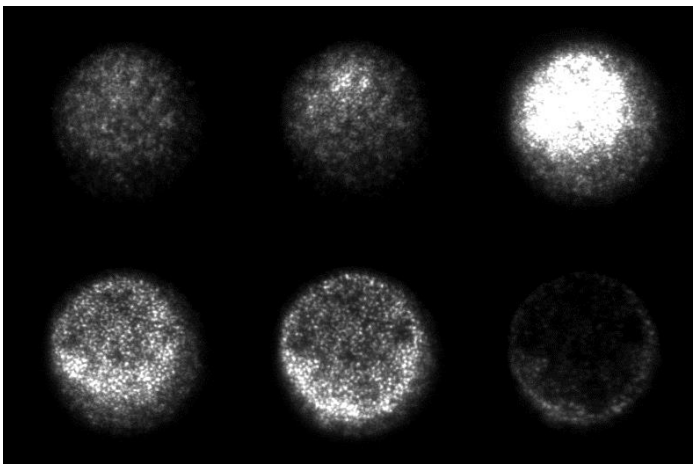


Figure 5-16 Hot-spot formation growth and quenching in ammonium nitrate struck by a flyer plate. Frames are in the order top left to top right, bottom top to bottom right. Diameter of the reaction zone viewed is approximately 8 mm (Courtesy of Imperial College London)

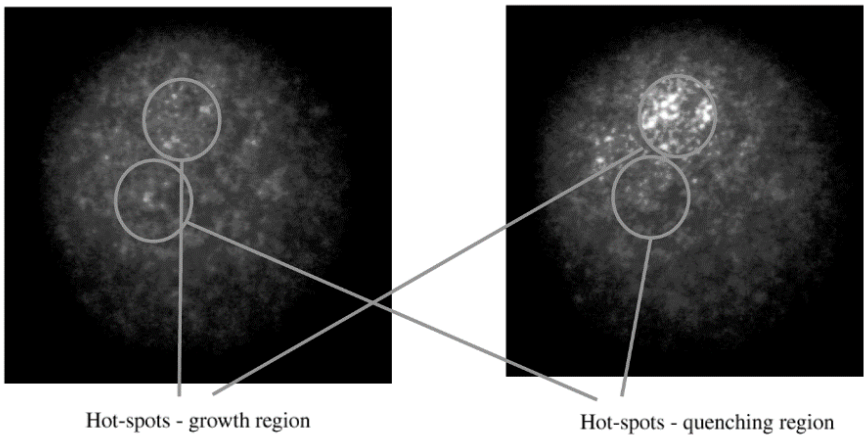


Figure 5-17 The first two frames of the sequence in Figure 5-16 (Courtesy of Imperial College London)

5.4 DEFLAGRATION TO DETONATION TRANSITION

One widely accepted mechanism for transition between deflagration and detonation (DDT) was described by McAfee et al[16-18]. Here, the critical hot spots lead to deflagration; this is associated with conductive burning at a rate of order 0.01 m s^{-1} though the energetic material. There is also a faster convective burning, caused by product gases forcing open channels either pre-existing in powder compacts or produced by impact. It has also been seen that slow cook-off can allow such channels to develop over timescales of hours. This convective burning happens at velocities of order 10 m s^{-1}. The pressure associated with the convection wave also caused the material immediately in

front of it to become compacted, represented by the compaction waves shown in Figure 5-18, this slows the rate of gas percolation, but allows pressure, temperature and pressure to increase rapidly. This confined burning presses against the surrounding material forming a dense plug of material that is pushed into unreacted material. This plug forms a considerable number of compressed hot-spots in the unreacted material which cause a rapid pressure build up and a shock to detonation transition (SDT). SDT is discussed in more depth in the next section. This transition has been studied experimentally[19].

The transit time between the deflagration and detonation depends on the density of the explosive, the degree of confinement and nature of explosive, so is highly variable and subject to the precise local conditions. The timescales for DDT is of milliseconds. A faster process which occurs for high-velocity impacts and stress is shock to detonation transition which occurs in microseconds. Shock to detonation also occurs when a detonating explosive is placed in contact with or in very close proximity to another explosive charge.

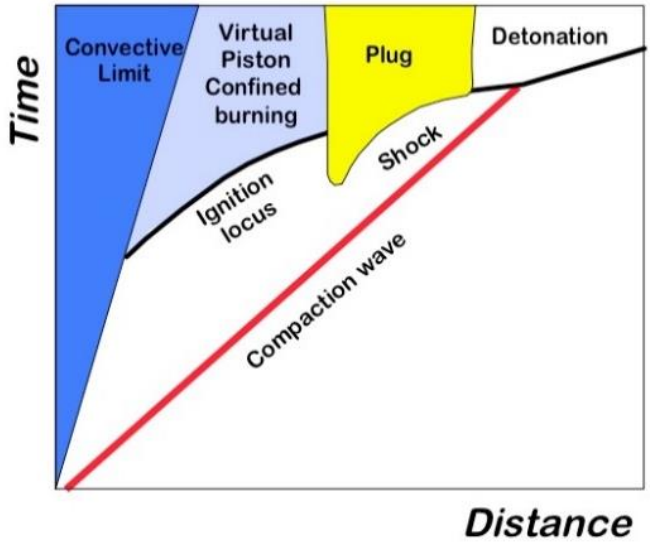
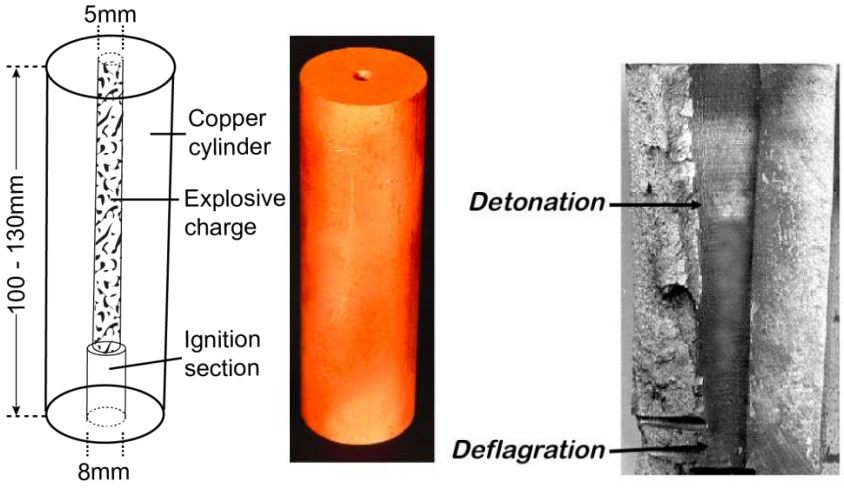


Figure 5-18 Schematic of overall process proposed by McAfee et al., along the centre line of a stick of explosive. Distance is the distance along the column from the ignition point

5.4.1 Deflagration to Detonation Studies

Amongst the simplest experiments are those, which heavily confine an explosive within a metal cylinder or square section bar in a 5mm diameter centrally drilled channel. The postmortem experiments use a cylinder of copper as shown in Figure 5-19(a). The result is seen in Figure 5-19(b) where physical evidence of the detonation can be seen.



(a) (b)

Figure 5-19 (a) Cylinder for use in post-mortem type experiments (b) visual evidence of the location where detonation begins (Courtesy of Imperial College London)

With the square steel bar a 1 mm wide polycarbonate window is laid along the length of the bar, which allows the event to be photographed with a streak camera. The window is thin enough that the level of confinement afforded by the steel is not overly compromised. This arrangement is shown in Figure 5-20.

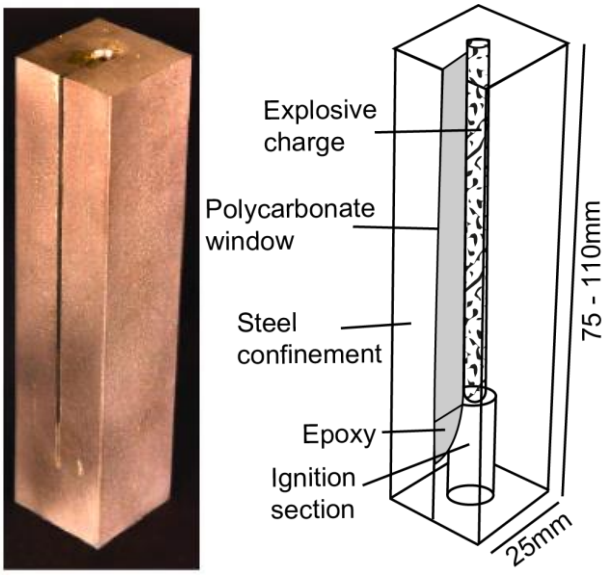


Figure 5-20 Square section bar showing the 1mm wide polycarbonate window (Courtesy of Imperial College London)

The type of data recorded from these experiments[20-22] is shown in Figure 5-21. The streak camera image shows convective burning B, the step from

deflagration to detonation D and the movement of the waves including a detonation wave F.

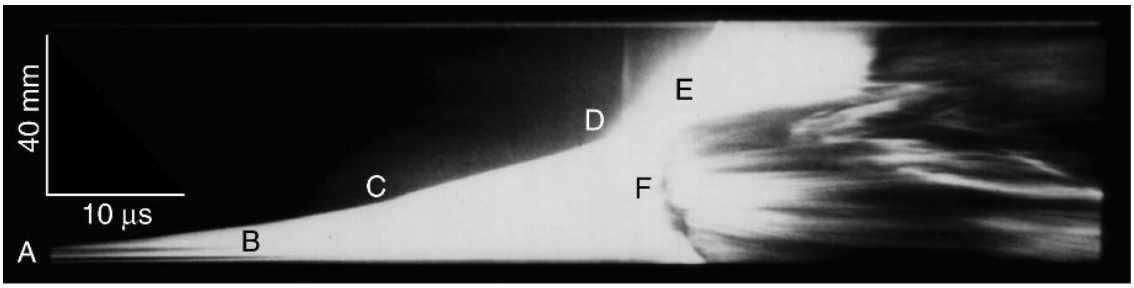


Figure 5-21 DDT event in ultrafine PETN[20] (Courtesy of Imperial College London)

5.5 SHOCK TO DETONATION TRANSITION

Shock to detonation transition (SDT) occurs in high-stress, shock wave environments. The process is effectively a thermal heating process. Shock waves are associated with rapid compression, high pressures and temperature rise. After a shock wave has passed over the material due to, for example, an impact or shock from another detonating explosive, the region around the impact zone is subjected to a temperature rise which allows reaction to start via the shock heating. Again this can be considered as the formation of a considerable number of hot-spots which each send out pressure waves which can coalesce to produce a large pressure pulse. Effectively, thermal explosion occurs after an induction time depending on local conditions. When the detonation wave breaks out it runs through material already compressed and heated by the initial shock thus causing super-detonation, detonation at a higher velocity than that normally associated with the material. Eventually the reactive shock overtakes the original shock to produce overdriven detonation in the lower density material. Ultimately, this settles to the 'normal' detonation velocity over some relaxation time and distance. This is shown in Figure 5-22.

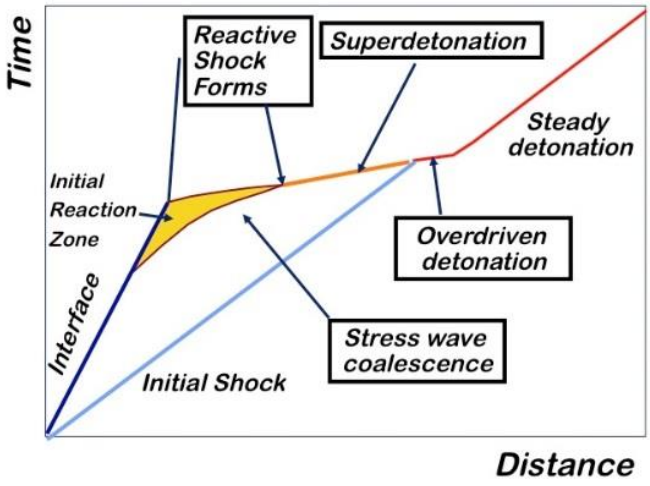


Figure 5-22 The process of Shock to Detonation Transition (SDT)

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CHAPTER 6
INITIATION SYSTEMS

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6 INITIATION SYSTEMS

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6.1 AWARENESS SUMMARY

6.1.1 Explosive Trains

Modern ammunition is required to be virtually 100 % reliable, because of the expensive and possibly dire consequences of a malfunction. Even more importantly, it is required to be 100 % safe to the user, in view of the high cost of accidents to personnel and equipment and because of the general lowering of morale which would result from lack of confidence in Service materiel. Munitions designers meet these requirements of safety and reliability by the use of an explosive train.

An explosive train is a sequential arrangement of explosive components with the fundamentals being an easily initiated primary explosive (initiator), a booster sensitive enough to be reliably initiated by the modest output of the initiator but also providing much higher output to initiate the relatively insensitive main charge. Figure 6-1 shows examples of both igniferous and detonating explosive trains (see 6.1.3). The burning train shows the initiation of gun propellant charge, the booster being fine grain propellant or black powder in a primer tube. The detonating train for a high explosive shell has an initiator that has a detonation shock output that detonates the booster, which in turn detonates the main charge. For detonating trains that use a sensitive primary explosive a physical arming mechanism is required to prevent inadvertent initiation of the main charge if the primary explosive is accidentally initiated such as if the munition is dropped.

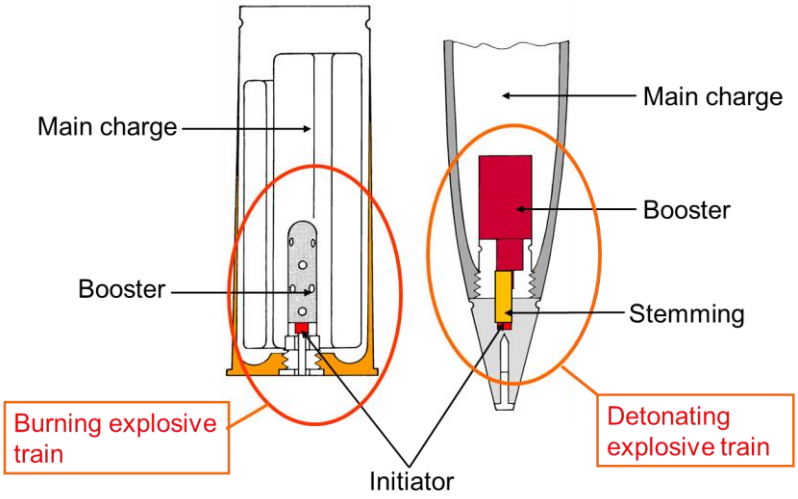


Figure 6-1 Examples of burning (gun propellant) and detonating (HE shell) explosive trains

6.1.2 In-line and Out-of-line Detonating Explosive Trains

To protect against accidental detonation of a main high explosive charge in a munition the concept of a safety and arming mechanism is employed with an out-of-line explosive train. In virtually all cases this involves the physical movement of the initiator held in a shutter that either slides or rotates to bring the initiator in line with the booster. Figure 6-2 demonstrates this concept where the primary explosive (initiator) cannot be struck by the striker while in this, the out-of-line, position. For this to arm the shutter must move and bring the initiator in line with both the striker and the booster charge. Where possible the munition should experience two independent stimuli that will then allow the shutter to move. As an example, an artillery shell fuze must experience both the g-force of launch (set-back) and rotational acceleration (spin) together before it will arm.

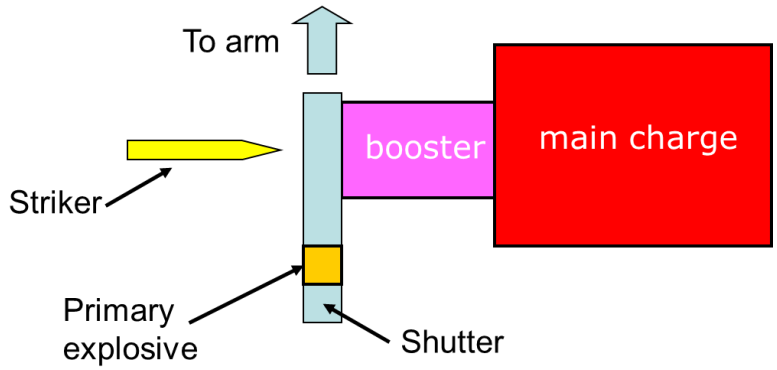


Figure 6-2 Safety and arming in the out-of-line position (not to scale)

An in-line detonating explosive train is one where all of the explosive components including the initiator are in a configuration such that if the initiator fires the explosive train will detonate. For this to provide the necessary safety against accidental detonation of the booster and main charge the initiator must not contain sensitive primary explosive. To achieve this, Exploding Bridgewire (see 6.3.4.7) and Exploding Foil Initiator (see 6.3.4.8) type detonators are employed. These contain only secondary explosive and are initiated to detonation by an electrical pulse that cannot be produced accidentally. Even then it is usual to have a safety and arming mechanism within the firing circuit for additional safety.

6.1.3 Igniferous and Disruptive Trains

All explosives burn or detonate, but undesirable forms of both processes can occur including transitions from one process to another. Explosive trains are designed to ensure that the main charge is effectively initiated to one mode or the other without risk of anomalous or inferior performance. A train intended to cause the deflagration of a propellant charge, or the combustion of a pyrotechnic charge, is called an igniferous train. Igniferous means, literally, 'fire-carrying'. A train intended to bring about detonation in a high explosive (HE) main charge is called a disruptive train. An igniferous train consists entirely of

components which burn, though some of them do so with explosive violence. A disruptive train, on the other hand, commences in nearly every case with an ignition and converts to detonation at some subsequent point in the train. This fact, however, may not be immediately obvious, even to the user of the system; the system may be so miniaturised and its effect so rapid and violent that the process appears outwardly to be entirely detonative, e.g. the UK Service L1A2 and L2A2 Demolition, detonators.

The first component of the train is designed to be triggered by some external influence a positive human action, the acceleration of the launch, an impact against a target, a change of ambient pressure or an electronic timing device. This releases a mechanical, electrical or chemical effect to act on the explosive filling of the first component of the train. This component is known as an initiator. Once the initiator functions, it acts on the next component of the train and so on until the main explosive payload is initiated by either a burning or shock stimulus.

In military explosive trains the common means of initiation are percussion, stabbing, electrical energy or friction. Friction devices are not common in British service but are widely used in foreign ammunition. The output of the initiator may be one of two general types. The first is a flash or longer-lasting flame, perhaps accompanied by a pressure pulse and/or hot particles. The other type is a detonation shock wave, usually accompanied by high-velocity metal fragments.

Each component of the train is so designed that it is reliably sensitive to the means of input and has adequate output to activate the next component. In disruptive explosive chains once detonation has been achieved then the next component must be shock sensitive enough to 'accept' the shock output from the previous 'donor' component. With igniferous explosive chains it is essential to ensure that each component is chosen to reliably accept the stimulus (e.g. hot particle or hot gas) from the previous component otherwise failure of the train will occur at the interfaces of the components. Once the ignition stimulus has been transferred to the next component in the chain reliable propagation will only continue if the heat generated by the reaction zone is sufficient to raise the next layer of unreacted composition to its ignition temperature and compensate for any radial heat losses.

The number of components in the train is the minimum consistent with the reliable and effective initiation of the main charge, whether it is HE, propellant or pyrotechnic. The number of components in and the complexity of explosive trains can vary greatly with the type of munitions. For example, hand grenades have relatively simple trains whereas modern guided weapons have very complex explosive trains which also involve simultaneous initiation of several components at different locations on the weapon system.

Another important principle of explosive trains is that the first one or two components of the train, which are intrinsically very sensitive to one or more types of stimulus, are designed in a minimum size. Succeeding components are

larger, of greater output but less sensitive. The reasons for the small size of initiators are:

1. They can be more easily shielded from external causes of accidental initiation.
2. The consequences of accidental initiations in manufacture, assembly and use are minimised.
3. The initiators can be conveniently incorporated in fail-safe mechanical devices whereby they are physically separated not only from the means of their own initiation but also from the next component.
4. Primary explosives are expensive.

Examples of igniferous (smoke grenade and propelling charge) and disruptive (warhead) explosive trains are shown below (Figure 6-3). The examples for the smoke grenade and warhead show how it is usual to have additional elements in the explosive train. The delay composition in the smoke grenade controls timing between the initiator and the booster priming composition and the stemming in the warhead transfers the detonation produced by the stab detonator to the booster. One of the main safety features of the disruptive explosive train shown below would be to incorporate the stab detonator in a fail-safe mechanical device (see 6.1.2). The high explosive and pyrotechnic compositions used in these trains are covered in the specific chapters on these types of explosive. The initiatory components in these trains contain several primary explosives and these compositions and their components are discussed in the next sections of this chapter.

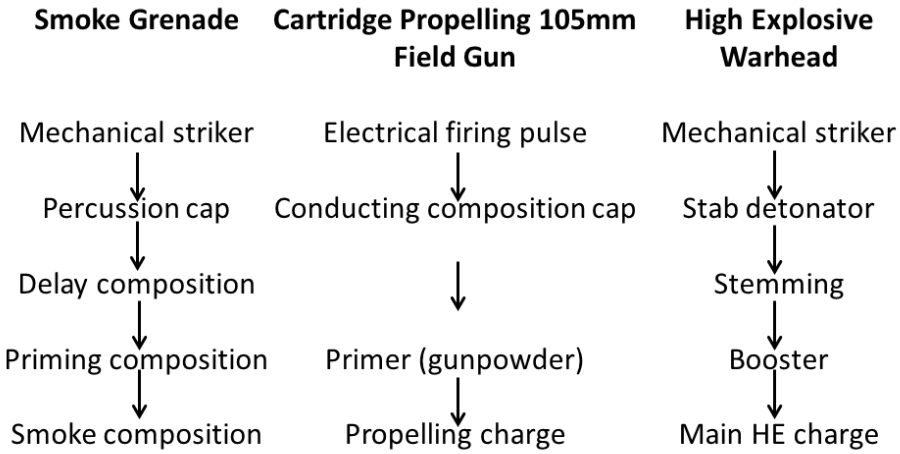


Figure 6-3 Examples of explosive trains

6.1.4 Initiators

The first component in a military explosive train is an initiator. Initiators are divided into two types, namely igniters and detonators. Igniters, or more strictly their fillings, burn when initiated by an appropriate stimulus. They produce a

flash or longer-lasting flame and thereby impart an igniferous effect to the next component.

Detonators themselves undergo detonation, though not necessarily instantaneously upon initiation, and impart a detonation shock wave to the next component in the train. All disruptive trains contain a detonator, or an equivalent component, at some point in the system.

Disruptive trains are less easy to define than igniferous ones, for several reasons. Firstly, in many cases it is necessary that the train does not function at detonation speed throughout its entire length. In many explosive trains there are requirements for pyrotechnic delays to burn between the time of initiation of the train and the required time of detonation of the main charge. Secondly, a detonation process is usually set up by burning to detonation.

This process may take place within the first component, and be completed within tens of microseconds of the initiating stimulus. Alternatively, the burning process may be designed to occupy a much longer time, perhaps seconds, before converting to detonation. Irrespective of the time which elapses between the first initiation of the train and its conversion to detonation, and irrespective of the number of igniferous stages before the conversion takes place, the component which brings about the conversion to detonation is always the detonator. A detonator can often be considered as a device for causing deflagration to detonation transition (DDT) in an explosive train, although there are detonator types where the detonation is created by very high pressure impact in EBWs and EFIs.

In general, therefore, disruptive trains commence either with an almost instantaneous detonation process brought about by a detonator, or with a burning process of appreciable duration started by an igniter and converted at a later stage to detonation via a detonator. The combination of an igniter and detonator, with or without igniferous components interposed, is common in military explosive trains.

6.1.5 Igniters and Detonators

The initiating stimuli applied to igniters can be either mechanical or electrical. The mechanical stimuli are stabbing and percussion. Electrical stimuli are provided by the use of hot-wire devices, sparking systems or the high resistance of conductive explosives. Some igniters are referred to as caps, a cap being defined in 1986 by the Ordnance Board as `a small metal container fitted with a flame-producing explosive composition'. Although this definition covers numerous types of igniter, only the percussion and conducting explosive types are usually referred to as caps. These have in common the fact that they are often obturating (gas-sealing) components in gas-producing systems, but otherwise the differentiation between caps and other kinds of igniter is not clear.

Because detonators, unlike igniters, are not always the first component in a train, the stimuli by which they are designated are not completely identical to those used in igniter nomenclature. The mechanical method is by stabbing,

there being few requirements for percussion detonators. Electrical stimuli are provided by; for example, hot-wire devices, high-resistance conducting explosive compositions, exploding bridgewire (EBW) (see 6.3.4.7) and exploding foil initiator (EFI) (see 6.3.4.8) detonators. Detonators can also be initiated by the output of igniters or delay columns, as in the case of flash-receptive detonators.

6.1.5.1 Mechanically initiated explosive devices

Mechanically initiated igniters and detonators respond to some type of mechanical force such as percussion to activate an explosive contained in the device.

6.1.5.2 Electrically initiated explosive devices

Electro-explosive devices (EEDs) are pyrotechnic or explosive containing devices designed to be initiated by electrical means. EEDs are termed as igniters if they have an igniferous output or detonators for a detonative output and can be classified as either low voltage or high voltage types. They may be classed as single or double pole devices. Double pole devices can be initiated either by discharge directly between the poles (pin to pin discharge) or by discharge between the pins and the case via the explosive filling (pin to case discharge).

Electric detonators/igniters are often referred to as electro-explosive devices (EEDs), these include hot-wire detonators/igniters, Semi-Conductor Bridge (SCB) devices, Exploding Bridge Wire (EBW) devices and Exploding Foil Initiators (EFIs). All of these devices require the application of voltage stored in a discharging device until the voltage reaches a level that will cause the violent destruction of some component to release the energy into the explosive.

Low voltage igniters and detonators include, hot-wire, fusehead, conducting composition and Semi-Conductor Bridge (SCB) devices whilst high voltage detonators include Exploding Bridge Wire (EBW) and Exploding Foil Initiator. Both low and high voltage devices are detailed in Sections 6.2.2 (igniters) and 6.3.4 (detonators).

6.2 IGNITERS

6.2.1 Primary Explosives Used in Initiators

In contrast to conventional explosives which are materials capable of very rapid reaction, attended by the sudden liberation of a large amount of heat energy and the simultaneous formation of a large volume of gas, primary explosives are energetic materials that possess exceptionally high initiation sensitiveness (see 20.2.1) to impact, friction, electrostatic discharge, heat, and shock. The assessment of a boundary between primary and secondary explosives is a matter on which there could be considerable argument depending on the criteria

considered, but it is convenient for this purpose to take mechanical sensitiveness as the principal criteria and to classify any material with a Figure of Insensitiveness (F of I) (see 20.10.2.1) below 30 as a primary explosive, for example, lead azide (15–25), lead styphnate (18) and VH2/VH4 compositions (10).

Primary explosives are further classified according to the rate of explosive decomposition. Initiators with low rates of explosive decomposition (igniferous/deflagrating) decompose by normal chemical reactions to produce high temperatures and flames and these are used to ignite primers, propellants or pyrotechnics. Examples of igniferous/deflagrating primary explosives are the lead styphnate based percussion primer cap compositions, VH2 and VH4. Materials which detonate produce a shock wave, supersonic in the medium of the explosive which decomposes the substance instantaneously as it passes through the substance liberating energy to maintain the shock wave. The shock wave produced by the primary explosive is used to initiate the detonation of booster or main charge high explosives. Examples of detonative primary explosives are lead azide and silver azide.

The selection of an explosive for use in an igniter or detonator depends on the type of initiating stimulus to be applied, the nature of the output required and on considerations of safety, reliability and cost. The explosives used are mostly of the primary type, that is, those which are readily ignited by a small mechanical, electrical or other thermal stimulus. For use in initiators, the main requirements for primary explosives are:

1. Sufficiently sensitive to explode reliably under the designed stimulus and yet be sufficiently stable to permit manufacture, filling and normal handling in service to be carried out safely.
2. High output of flash for igniters or rapid burning to detonation for detonators.
3. Consistency of reaction time.
4. A long storage life, entailing good chemical and thermal stability and also compatibility with the materials of which initiators are commonly made.

Primary explosives may be single compounds or mixtures (compositions) of several ingredients. The number of single chemical compounds having the above requirements and which can be made easily and cheaply is fairly small with British service initiators relying mainly on the following primary explosive compounds, either in the pure state or in mixtures:

- Lead styphnate (lead 2,4,6-trinitroresorcinate)
- Barium styphnate (barium 2,4,6-trinitroresorcinate)
- Lead dinitroresorcinate (lead 2,4-dinitroresorcinate)
- Lead mononitroresorcinate
- Lead trinitrophloroglucinate
- Lead azide

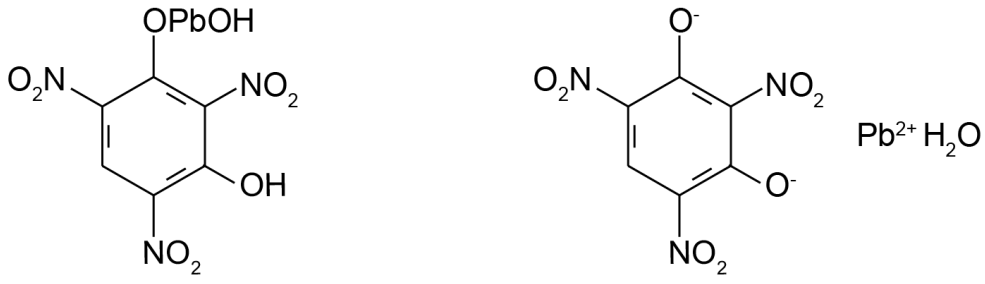
- Silver azide
- Tetrazene
- Potassium picrate

Of these compounds, the azides are essentially disruptive in nature and are used only in detonators. The others are less violent and more versatile. Other compounds used include potassium chlorate and barium nitrate, which are not explosive in the unmixed state but are useful oxidants in explosive mixtures, also antimony sulphide and calcium silicide which are fuels in such mixtures. Many of the primary explosive compounds used in British service initiators are allotted code numbers from the RD1300 series, which historically were the responsibility of the Propellants, Explosives and Rocket Motor Establishment (PERME), Waltham Abbey. Another set of code numbers is the RD1600 series (mixtures), which for many years was the responsibility of the Royal Armament Research Development Establishment (RARDE), Fort Halstead. In both cases the initials derive from the former Research Department, the forerunner of both PERME and RARDE. Following privatisation of the Royal Ordnance in 1987, Royal Ordnance Plc and latterly BAE Systems owned the rights to the RD formulations and in many instances adopted their own designations. The main igniferous and detonative primary explosive compounds and mixtures used in initiators and the devices employed are detailed in the following sections.

The methods of manufacture of primary explosives are detailed in Chapter 10.

6.2.1.1 Lead styphnate

Lead styphnate (lead 2,4,6-trinitroresorcinate) the lead salt of styphnic acid (2,4,6-trinitroresorcinol) has been of particular use as an initiator material. There are two forms of the salt; the Basic salt (β-form) where the crystals tend to be needle like in appearance and give rise to a powdery product and the Normal salt (α-form) which contains one molecule of water of crystallisation, the single crystal is rhombic varying from granular to prism form with a tendency to widely varying aggregation according to the conditions of its formation. The formulae for the basic and normal salts are shown in Figure 6-4.



Monobasic lead styphnate

Normal lead styphnate
(lead 2,4,6-trinitroresorecinate monohydrate)

Figure 6-4 Basic and normal lead styphnate

Lead styphnate is very sensitive to mechanical shock, friction, heat (flash) and static electricity and when dry, it can be readily ignited by static discharges from the human body. The longer and narrower the crystals, the more susceptible the material is to static electricity.

Lead styphnate is manufactured in the form of microscopic orange-brown crystals which are insoluble in water and in most organic solvents. The crystal density is 3.09 g cm^{-3}. At this density the velocity of detonation is 5200 m s^{-1}, at a density of 2.6 g cm^{-3} it is 4900 ms^{-1} and at a density of 0.93 g cm^{-3} it is 2100 m s^{-1}. Lead styphnate has an ignition temperature of 260 °C and is readily ignited by flame and particularly so by electric sparks. Its F of I (see 20.10.2.1) is 20. It should be noted that in addition to F of I used to characterise the sensitiveness (see 20.2.1) of a material, the friction, thermal and electrostatic sensitiveness shall also be considered. Like all heavy metal derivative explosives, lead styphnate has a low heat of explosion (Q=1885 J g^{-1}) and low power index as RD1303, (lead block = 41). It is not sufficiently brisant to be used alone in detonators, but is used for such in admixture for example with lead azide and aluminium powder in ASA (Lead **A**zide/Lead **S**typhnate/**A**luminium) mixture used in the flash sensitive demolition detonators, L1A2 and L2A2. In mixtures, lead styphnate is widely used in igniters of various kinds, including percussion caps. When mixed with graphite, lead styphnate forms a “conducting composition” (CC) which is used in a number of CC igniters.

There are several different forms of lead styphnate used in British service, namely; RD1302, α–normal monohydrate which has been superseded by RD1303 which is similar to RD1302 but has a special crystal size and habit and is less susceptible to ESD. RD1303 is used as an ingredient for percussion cap composition VH4 and is mixed with powdered graphite for use in electric cap and igniter compositions. RD1346 is a free flowing form of β-monobasic lead styphnate and is used as an ingredient for priming compositions, bridgewire compositions and fast delay compositions. RD1349, β-monobasic lead styphnate is similar to RD1346 but has a modified particle size and shape to RD1336 and is used as an ingredient of priming compositions and fusehead compositions. RD1367 an α–normal lead styphnate is manufactured using a commercial process which is more economic for the manufacture of percussion cap composition, VH2. It should be noted that as all normal lead styphnate salts contain one molecule of water of crystallisation, they are unsuitable for use in stores which may be subjected to temperatures above 130 °C. For this purpose, use is made of monobasic lead styphnate.

6.2.1.1.1 Properties of lead styphnates

The properties of lead styphnate, RD1303, RD1346, RD1349 and RD1367 as defined in UK Military Explosive Safety Certificates No’s SC1523 (RD1303, RD1367) and Safety Certificate No SC1529 (RD1346 and RD1349) and relevant UK Defence Standards are detailed in Appendix A Table A-1

6.2.1.2 Barium styphnate

Normal barium styphnate (2,4,6-trinitroresorcinate), the barium salt of 2,4,6-trinitroresorcinol (styphnic acid) contains one molecule of water of crystallisation. It is made for British service in four different crystalline forms, RD1320, RD1320A, RD1320B and RD1340. All forms are relatively insensitive having F of Is (see 20.10.2.1) of approximately 40 - 50 and are difficult to ignite by electric spark. RD1320 is used in fuze delay compositions, RD1320A is used as a gas producer in Igniter Electric Bridgewire (IEBW) igniters, RD1320B is used as a priming composition in electric bridgewire applications. RD1340 is used as an ingredient in composition RD1652 (RD1340/potassium chlorate/antimony sulphide) an igniferous composition used in flash sensitive cap composition, an ingredient for delay compositions and an ingredient for stab sensitive and igniferous detonator and cap compositions. It should be noted that all barium styphnate salts are incompatible with sulphur, sulphides, lead and lead compounds

The formula for normal barium styphnate (barium 2,4,6-trinitroressorcinate monohydrate) is shown in Figure 6-5.

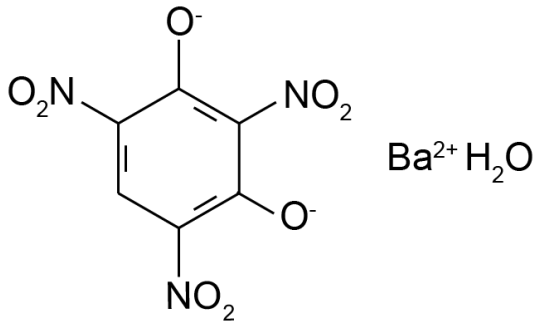


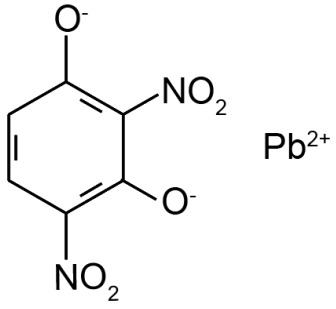
Figure 6-5 Normal barium styphnate

6.2.1.2.1 Properties of barium styphnate

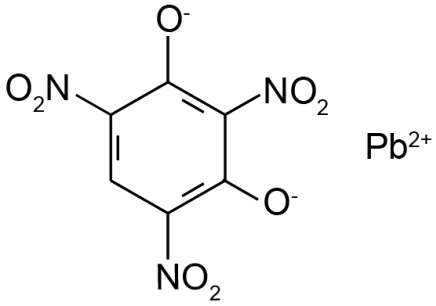
The properties of barium styphnate, RD1320, RD1320A, RD1320B and RD1340 as defined in UK Military Explosive Safety Certificate Nos SC1596A (RD1320, RD1320A, RD1320B) and Safety Certificate No SC1597 (RD1340) and relevant UK Defence Standards are detailed in Appendix A Table A-2.

6.2.1.3 Lead dinitroresorcinate

Lead dinitroresorcinate (LDNR) has one less nitro-group than lead styphnate, and therefore has a lower oxygen balance and is a less violent explosive, but it is more sensitive to impact. Two structural isomers of the compound have been manufactured, usually referred to as 2,4-LDNR (RD1337) and 4,6-LDNR (RD1308) respectively. Their formulae are shown in Figure 6-6.



Lead 2,4-dinitroresorcinate
(2,4-LDNR)



Lead 2,4-dinitroresorcinate
(4,6-LDNR)

Figure 6-6 Structural isomers of lead dinitroresorcinate

The first to enter British service was 4,6-LDNR, which in monobasic form is known as RD1308 and contains carboxymethylcellulose as a granulating agent. It was used unsuccessfully in World War II as a delay for small-calibre shells but now has little or no use in military applications. Improvements to manufacturing processes resulted in the production of RD1353 which has found use as a priming and delay composition used in some bridgewire igniters, for example in composition RD1655, an igniferous, flash sensitive composition. Further refinements produced a low lead type material, RD1358 which has been used in fusehead compositions and as a gas producer.

The 2,4-isomer of LDNR was also first used in British service in World War II, originally to replace RD1308.The first version was called RD1305, and this was followed by an improvement to the manufacturing process to give a better product called RD1337, otherwise known as 'R Composition'. RD1337 is now the most important version of LDNR. It is easily and reliably initiated by percussion (F of I = 10), stabbing or by flash. It is used in admixture with barium nitrate and tetrazene in composition RD1651, commonly known as “L mixture”, which is the most common filling in British service stab igniters and is also used as a priming layer in flash-receptive detonators such as RZY detonators. It conforms to the requirements of high-temperature stability since it contains no water of crystallisation.

6.2.1.4 Properties of lead dinitroresorcinate

The properties of lead dinitroresorcinate, RD1308 and RD1337 as defined in UK Military Explosive Safety Certificate No’s SC832 and SC1530 (RD1308 and RD1337 respectively) and relevant UK Defence Standards are detailed in Appendix A Table A-3.

6.2.1.5 Lead trinitrophloroglucinate

Lead trinitrophloroglucinate has the formula shown in Figure 6-7. Its explosive properties are similar to those of lead styphnate and it performs better at low temperatures. Moreover, it has the advantage over normal lead styphnate of

containing no water of crystallisation and so is more resistant to high temperature conditions. It is known as RD1359 and has been used in applications where its advantages outweigh its high cost.

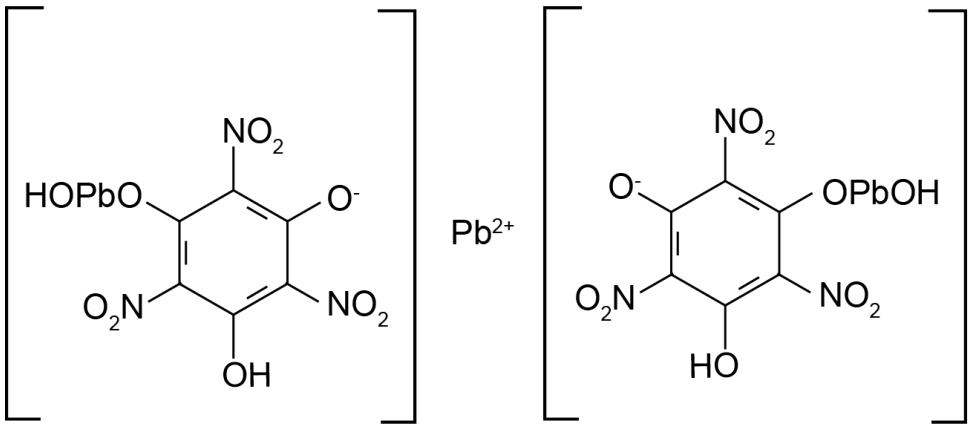


Figure 6-7 Lead trinitrophloroglucinate

6.2.1.6 Tetrazene

Tetrazene is an organic primary explosive which, unlike those described in the foregoing paragraphs, contains no metallic elements. It is not used alone, or as a major ingredient on a weight basis, but it is an excellent sensitiser for both igniferous and disruptive mixtures, such as in VH2 and VH4 mixtures used in primer percussion caps. Tetrazene has the chemical name 1-amino-1(1H-tetrazol-5-yl)-azo-guanidine monohydrate. Its chemical formula is shown in Figure 6-8.

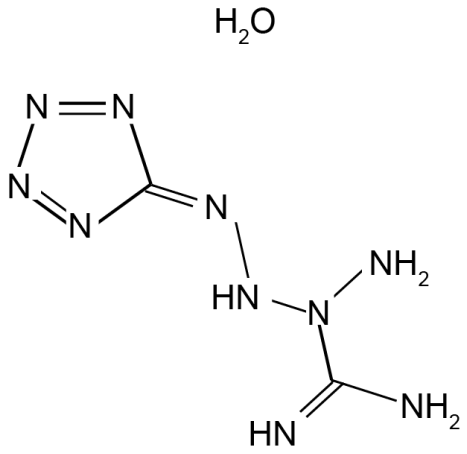


Figure 6-8 Tetrazene

It is a white or pale yellow fluffy crystalline material which can be in one of two polymorphic forms. It is not readily soluble in any common solvent and so cannot, in practice, be either purified or physically modified by recrystallisation.

Tetrazene was first used in the British service about the time of World War II. As manufactured by the original method it was an extremely difficult substance to process, but an improved method was developed which provided tetrazene of micro granular, free-flowing form and of better stability, this was designated RD1357A. Its bulk density is 0.6 g cm^{-3} and this can be increased to 1.05 g cm^{-3} by pressing at 6.9 MPa. The latter fact is, however, not relevant since tetrazene is not used alone.

The F of I (see 20.10.2.1) of tetrazene is 10, denoting a highly sensitive material. It has remarkable properties as a sensitiser of other primary explosive compounds and mixtures. When added to lead azide in quite small proportions, between 2 % w/w and 5 % w/w, it reduces the F of I considerably, but larger additions do not further increase the sensitisation. Tetrazene is also used in small proportions to sensitise stab or percussion igniter compositions based on lead styphnate or on lead dinitroresorcinate (LDNR). The omission of tetrazene in percussion cap compositions often results in unreliable ignition and in some instances failure of the caps to function.

It is believed that the sensitising effect of tetrazene in mixtures is due to the abrasion, upon stabbing or percussion, of the soft tetrazene crystals by the harder crystals of the other constituents, e.g. lead azide or barium nitrate, calcium silicide, antimony sulphide etc. This friction produces 'hot spots' too which tetrazene, with its low ignition temperature of 160 °C, is particularly susceptible. The ignition of the tetrazene then initiates the whole mixture.

Tetrazene has low thermal and hydrolytic stability and will readily decompose at around 90 °C and is destroyed by the addition of boiling water. As a result of this research has been undertaken by Pacific Scientific Energetic Material Co, USA in conjunction with the Office of Naval Research, USA, to find tetrazene replacements with enhanced stability(1).

6.2.1.6.1 Properties of tetrazene

The properties of tetrazene, RD1357A as defined in UK Military Explosive Safety Certificate No’s SC802 and relevant UK Defence Standards are detailed in Appendix A Table A-4.

6.2.1.7 UK manufactured igniferous primary explosives

Examples of igniferous primary explosive compounds and compositions presently manufactured in the UK along with their use in military stores are detailed briefly in Table 6-1.

Table 6-1 Igniferous Primary Explosive Compounds/Composition and Their Use

Primary Explosive	Designation	Use
Lead Styphnate	RD1303	Composition RD1303/Graphite
	RD1349	Fuseheads, IEBW213
	RD1367	Composition ASA
Barium Styphnate	RD1320	Protractor DR2037
	RD1320A	IEBW222
	RD1340	Composition RD1652
Lead 2,4 dinitroresorcinate (LDNR)	RD1337	Composition RD1651
Potassium Picrate	RD1369M	Cap Electric 30 mm (Aden)
Tetrazene	RD1357A	Composition RD1651

6.2.2 Types of Igniter

6.2.2.1 Igniferous mixtures

It is not always possible to find a material, which meets all the requirements for a particular service use. It is therefore, often necessary to prepare mixtures of several ingredients tailored to meet the specific service requirement. Lead styphnate and LDNR, in their various chemical and crystalline forms, are used in igniters, either unmixed or mixed with other ingredients to modify their sensitivity and/or their igniferous output. These mixtures commonly contain an inorganic salt as oxidant and other materials which act as fuels or sensitisers or both. Some commonly used ingredients for initiator mixtures and their function are given in Table 6-2.

Table 6-2 Examples of Ingredients for Initiator Mixtures

Function	Ingredient
Explosive	lead styphnate, lead 2,4-dinitroresorcinate (LDNR)
Oxidant	nitrates, perchlorates, peroxides
Sensitisers	tetrazene, sulphur, ground glass
Heat Producers	calcium silicide, aluminium
Conducting Materials	graphite

A common igniferous composition of this type is RD1651, otherwise known as L Mixture consisting of the following ingredients:

- 2,4-LDNR, (RD1337) 50 % w/w
- Barium nitrate 45 % w/w

- Tetrazene 5 % w/w

This mixture is easily and reliably initiated by percussion (F of I = 15), stabbing or by flash, and can therefore, be used as either the first, or as a subsequent filling in an igniferous explosive train. Its output of flash is highly effective. It has excellent thermal stability and has a predicted Service life of 20 years. L Mixture is the most common filling in British service stab igniters. It is also used in numerous flash-receptive detonators. Other igniferous compositions, approximately formulated on similar lines include; RD1652, RD1655 and RD1658. Details of the compositions, F of I's (see 20.10.2.1) and examples of their UK service use are detailed in Table 6-3.

Some igniferous compositions are used in stores which are ultimately self-destroying and therefore the chemical nature of the products of combustion is not important, even if, like the solid chlorides deposited by chlorate and perchlorate compositions, those products are corrosive to metals. In cap compositions for the ignition of propellants in small arms, however, it is essential that the products are not corrosive to the bore of the weapon. The percussion caps used in the Service for this purpose, still contain the complex mixtures patented by von Herz in the 1920s and which are designated by his initials plus a number. Examples are the VH2 and VH4 compositions, detailed in

Table 6-4.

Table 6-3 Igniferous Primary Explosive Compositions

Primary Explosive Composition	Designation	Use	F of I
Barium Styphnate (RD1340) Potassium Chlorate Antimony Sulphide	RD1652	TVE L4A2, LMDE N2/N12, CERU 200/400 Range	20
Aluminium Lead Styphnate (RD1367) Lead Azide (Dextrinated)	ASA	Demolition detonators L1A2/L2A2	15
Lead Styphnate (RD1303) Graphite	RD1303 Graphite	TVE L4A2, CC Cap Electric (30 mm Aden)	35
Lead 2, 4 DNR (RD1337) Barium Nitrate Tetrazene	RD1651 (L Mixture)	Detonator 6.5 grn LZY, Stab Igniter 2.1 grn L (1 grain (grn) = 64.799 mg)	15
Potassium Picrate Potassium Perchlorate	RD1658	Cap Electric 2.3 grn (30 mm Aden)	30

Aluminium		(1 grain (grn) = 64.799 mg)	

Table 6-4 Igniferous Primary Explosive Percussion Cap Compositions

Composition Designation	Ingredients (w/w)	F of I	Use
VH2	Lead styphnate (RD1367) 38 % Barium nitrate 39 % Tetrazene 2 % Antimony sulphide 5 % Calcium silicide 11 % Lead dioxide 5 %	10	Percussion caps (7.62 mm, 5.56 mm SAA) Artillery Primers Grenade Fuzes Thermal Batteries
VH4	Lead styphnate (RD1303) 27 % Barium nitrate 44 % Tetrazene 2 % Antimony sulphide 27 %	10	Mortar Bomb Primary Cartridges, PYTHON

VH2 and VH4 compositions are largely non corrosive and are used extensively as percussion cap compositions used in a wide range of small arms ammunition (SAA) including both 7.62 mm and 5.56 mm SAA respectively. Many USA primers also contain secondary explosives such as PETN which is added to increase explosive output whilst powdered aluminium may also be added to increase flame temperature. The compositions are manufactured by dry mixing of the composition ingredients. A safer and more convenient ‘Eleyprime’ process was developed during the 1970s. This process involved the mixing of non-explosive precursor chemicals and filling them into SAA caps. The reaction to produce the active explosives was initiated in the cap itself by adding a drop of water. However, this process was not adopted for the manufacture of British SAA caps, although the process is presently used for the manufacture of “rimfire” type caps used in commercial shot gun cartridges. As a result, the process of the dry mixing of ingredients adopted for the manufacture of compositions VH2 and VH4 continues to be used today. The manufacture of ‘Eleyprime’ is detailed briefly in Chapter 10.

Primer percussion L21A1 containing a percussion cap “SINOXID” composition is the trademark used for traditional primer compositions of DYNAMIT NOBEL

AG which consist of identical ingredients as VH2 composition however, ingredient ratios are not known.

6.2.2.2 Composite igniters

The number of single compounds suitable for use alone in igniters is very small, because of the requirement that the compound must not burn to detonation within the confinement of the initiator. Only lead styphnate, LDNR and to a lesser extent barium styphnate and lead trinitrophloroglucinate, are candidates for use in an unmixed state. There are two ways of enlarging the range of possible fillings. One is by employing mixtures which modify the properties of the base ingredient. Some examples of this, as applied to lead and barium styphnate and LDNR, have been described earlier. The other way is to combine two complementary fillings in one initiator, pressed in separate but contiguous layers.

One layer supplies the required sensitivity and the other provides the required output. A third layer may also be present. The principle is applied both to igniters and detonators, and they are called `composite' types.

The contents of Service composite initiator igniters are denoted by a simple code which combines the recognised abbreviations (shown below) or other designations of the layered fillings:

L	=	L Mixture (RD1651)
P	=	Gunpowder G20
R	=	R Composition (RD 337)
SR112	=	tetranitrocarbazole (40 % w/w), potassium nitrate (60 % w/w)

An example of this nomenclature is the L/SR 112 igniter. If the letters are single the solidus is omitted, e.g. LP.

6.2.2.3 Stab igniters

Stab igniters are used to initiate flash-receptive detonators or pyrotechnic delay trains. A typical stab igniter is shown in Figure 6-9.

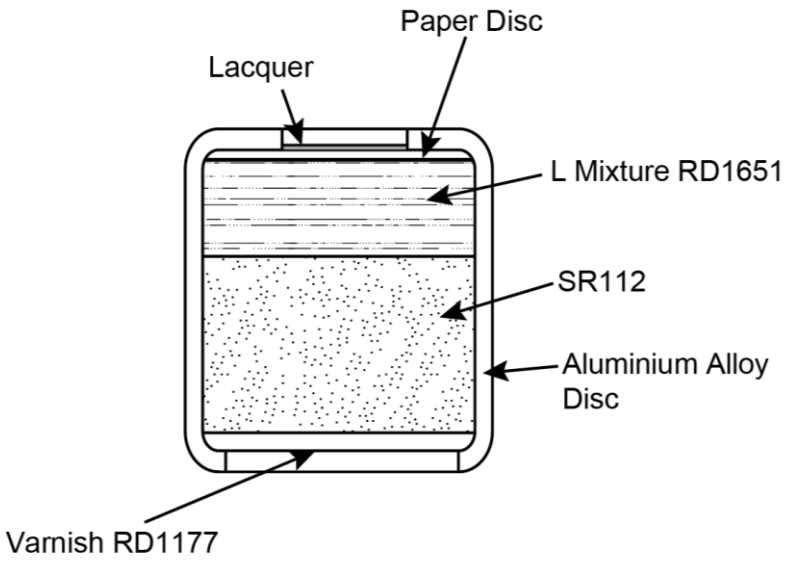


Figure 6-9 Typical stab igniter 1.5 grn L/SR 112

They are employed mainly in fuzes for shell, bombs and some pyrotechnic marker smoke stores and consist of a cup made of copper, aluminium or aluminium alloy and the filling which must be compatible with the material used. The cup is small, typically 4 mm - 5 mm in length and diameter, with a hole at both ends. The input hole is closed with a paper disc and lacquered. The output hole is closed with a thin metal disc and similarly sealed. The total filling weight varies between 0.55 grain (0.036 g) and 4.1 grain (0.27 g). Most Service stab igniters have filling weights of less than 2.0 grains (0.13 g).

If the flash component of the output is the main requirement a stab igniter is usually filled with L Mixture only. Alternatively, if the flash output needs prolonging for up to, say, 20 milliseconds a pyrotechnic layer is pressed in as a base charge and topped with L Mixture. Typical base charges are SR112 and gunpowder G20, giving fillings designated L/SR112 and LP respectively.

Stab igniters are initiated by the action of a steel striker needle, which is tapered at about 30° from parallel and has a minute flat area forming the tip. The sensitivity of stab igniters depends not only on the nature of the filling, but also on the pressing load: the greater the compaction the less striker energy is needed. The material of the input closure is also important, and a varnished or lacquered paper disc is usual for this. The overall functioning time is approximately inversely proportional to the striker velocity. Typically, the time between strike impact and output closure rupture is about 0.5 milliseconds. An example of a stab igniter–flash receptive detonator system is shown in Figure 6-10.

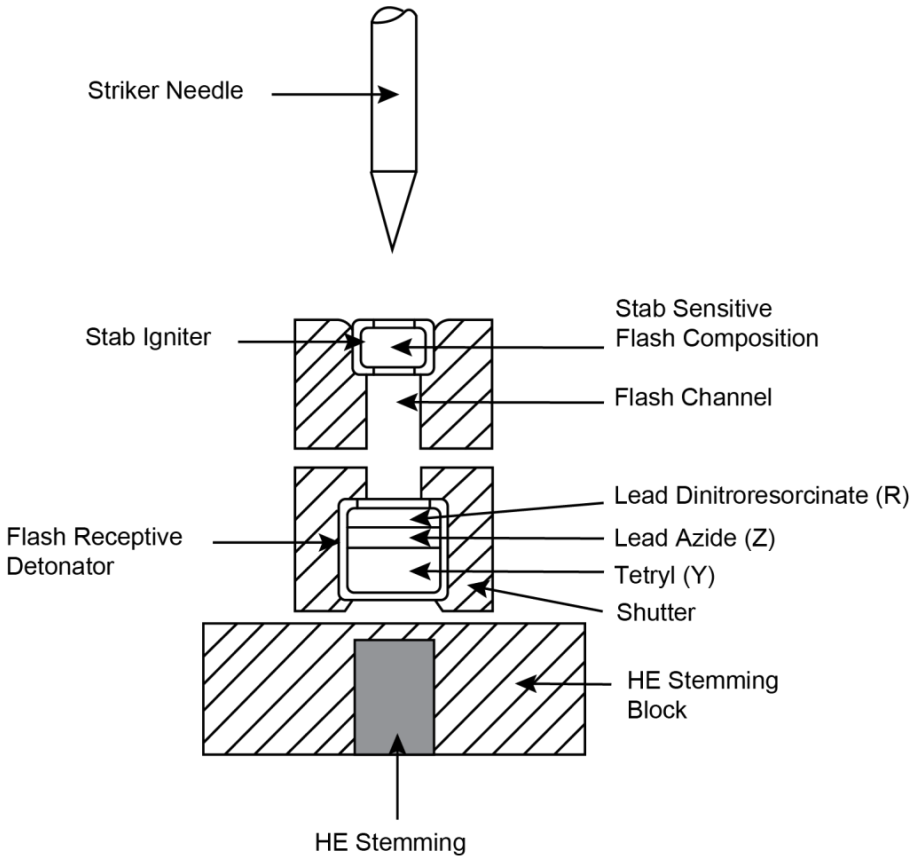


Figure 6-10 Example of a stab igniter – flash receptive detonator system

6.2.2.4 Percussion caps

Percussion caps constitute a class of igniter which are used in the Services for a variety of stores, including small arms cartridges, mortar bomb primary cartridges, some cannon and artillery primers, grenade fuzes, pyrotechnic stores and thermal batteries, also seat ejection and canopy jettison systems for aircraft. There are three types of percussion cap, namely; “Berdan”, “Boxer” and “Rimfire”. The main differences between Berdan and Boxer caps lie in the location of the anvil. In the Berdan cap the anvil is an integral part of the cap chamber (cartridge) whilst in the Boxer cap the anvil is a separate stirrup piece that sits inverted in the primer cup whereas the Rimfire dispenses with the need for an anvil. Each type is discussed below:

6.2.2.4.1 Berdan

The Berdan initiation system features an anvil that is an integral part of the cartridge case, formed by a projection of the cartridge case into the centre of the cap chamber, as shown in Figure 6-11. A cap chamber is formed in the base of the cartridge case and connected to the interior of the cartridge case by two fire holes. Some modified forms of the Berdan initiation system exist: The French modified Berdan has a narrow strip of metal forced up from the floor of the cap chamber to form a mound with a gap in the cap chamber floor underneath. The mound acts as the anvil and the gap becomes the fire hole.

The Chinese modified Berdan has a central, triangular fire hole in the floor of the cap chamber, into which is forced a small metal ball. This ball is too large to pass through the fire hole, and instead is retained in the fire hole, projecting into the cap chamber to act as the anvil, with the gaps around the metal ball allowing the flame to pass into the cartridge case cavity.

Berdan Caps are now manufactured from drawn cartridge brass. However, in the past, copper alloy and cupro-nickel were used extensively in their manufacture. The ideal metal should expand easily to provide efficient obturation while being strong enough to withstand the striker blow without being pierced and withstand the pressures generated by the initiation of the priming composition. Modern, brass, Berdan caps are manufactured as a parallel-sided cup shape, see Figure 6-12, and then varnished internally. A cap composition (or primer composition) is pressed into the cup and covered by a paper disc; this may be pressed in with the cap composition or separately. After filling, the cap is sealed with varnish. This type of percussion cap is usually only encountered in Land Service use with the NATO 7.62 mm family of munitions

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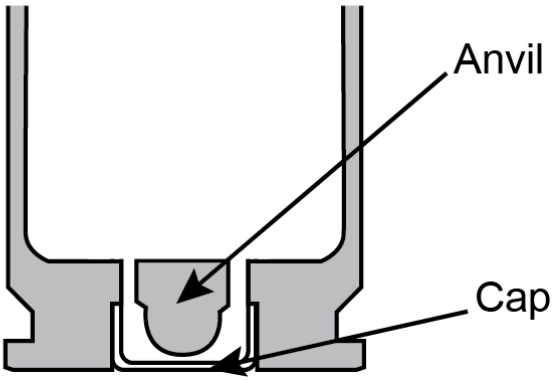


Figure 6-11 Berdan type percussion cap fitted in small arms cartridge

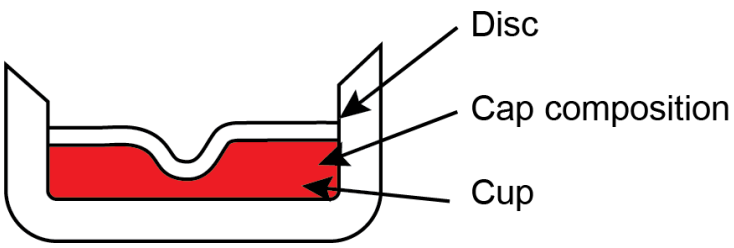


Figure 6-12 Berdan percussion cap

6.2.2.4.2 Boxer

The Boxer initiation system is in common use within most natures of Land Service SAA natures, with the exception of the 0.22 inch munitions. The Anvil is an integral component of the percussion cap. It is usually made from brass and has three holes or gaps machined into it to allow passage of the flame on firing, see Figure 6-13. The cap chamber has one central fire hole connecting to the interior cavity of the cartridge case. Boxer caps are manufactured in a similar fashion to Berdan caps, though the inclusion of the anvil necessitates an additional step of assembly to fit the anvil into the cap after pressing the paper disc into the Cap. The assembly, including anvil, are then varnished.

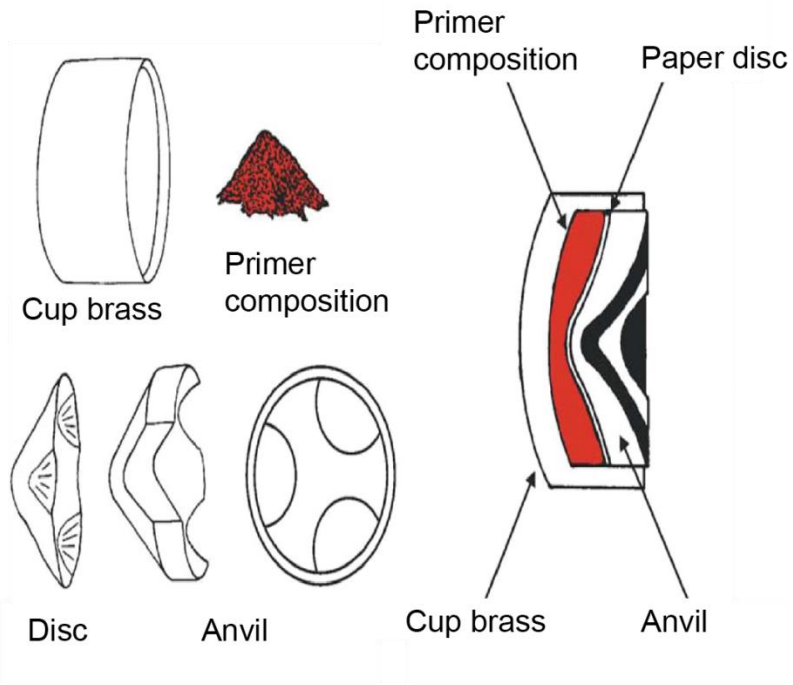


Figure 6-13 Boxer percussion cap

6.2.2.4.3 Rimfire

The Rimfire Case initiation system, shown in Figure 6-14, is used mainly in the 0.22 inch family of munitions. It dispenses with the percussion cap and anvil, in favour of locating the priming composition in a hollow rim formed internally in the base of the cartridge case. The priming composition is initiated by the off-centre firing pin crushing a part of the rim of the cartridge case, rather than crushing a cup against a central anvil.

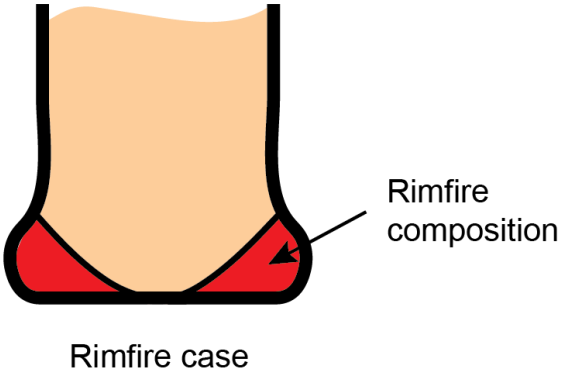


Figure 6-14 Rimfire percussion system

Both Berdan and Boxer percussion caps are classified as centre fire caps and in both cases the type of explosive filling is generally similar (i.e. VH2 or VH4 lead styphnate based compositions) whereas the Rimfire type system use Eleyprime composition.

When comparing stab igniters and percussion caps, the igniferous output required of the explosive filling is similar. However, the mechanism of initiation of a centre fire percussion cap is somewhat different from that of a stab igniter in that a cap filling rests against a metal anvil and the impact of the hemispherical-tipped firing pin on the cap causes the filling to be nipped between the deformed cap and the anvil. Initiation is therefore by impact and not by a combination of impact and friction as in a stab igniter. Also, in a cap there is ample space next to the filling for the gas to escape via the firehole(s).

An important difference between stab igniters and percussion caps is that the latter form part of an obturation (gas-sealing) system. On firing, the system has to contain a quantity of gas at high pressure for an appreciable fraction of a second, or even seconds. It is therefore vitally important that the cap does not become perforated or dislodged from its seating by the violence of its own discharge; otherwise a serious failure of the system will occur. This constraint limits both the weight of the filling and its brisance. In practice, percussion cap fillings are very small, typically between 0.025g and 0.16g. Another fairly stringent requirement is the sensitiveness (see 20.2.1) to impact which, in terms of F of I, is between 7 and 13. The requirement of non-corrosive primary explosive compositions for SAA caps has already been mentioned.

Lead styphnate is the favoured base ingredients for Service cap compositions. Lead styphnate itself is a primary high explosive which under confinement can detonate with considerable brisance. There is therefore, an upper limit of about 45% to the lead styphnate content of a cap filling; above this, mass explosion of the filling can occur, causing cap blowback and obturation failure.

Of the British service cap compositions, VH2 is the most violent and is used in SAA to give the rapid ignition on which a small propellant charge relies for its ballistic regularity. It is also used in aircraft seat ejection cartridges and canopy

jettison systems. VH4 is less violent and is used in 51 mm and 81 mm mortar bomb primary cartridges, aircraft practice bombs and flares, and in hand grenades.

6.2.2.5 Conducting composition igniters

The simplest way to employ an electric current to initiate a primary explosive is the conducting composition (CC) method. The explosive is rendered conducting by the addition of graphite, but its resistivity is kept high. If an electric current, even of low voltage, is then passed through a small charge of the composition, the heating effect will rapidly ignite it. High voltage pulses are even more effective. The conducting composition principle is more reliable than the bridgewire system, in that it employs no fragile resistance wire which can break or corrode. It also permits cheaper manufacture of ammunition. A number of non-obturating CC igniters are used in the Service for fuzes in aircraft bombs and in guided weapons. The basic features of a conducting composition igniter are shown in Figure 6-15.

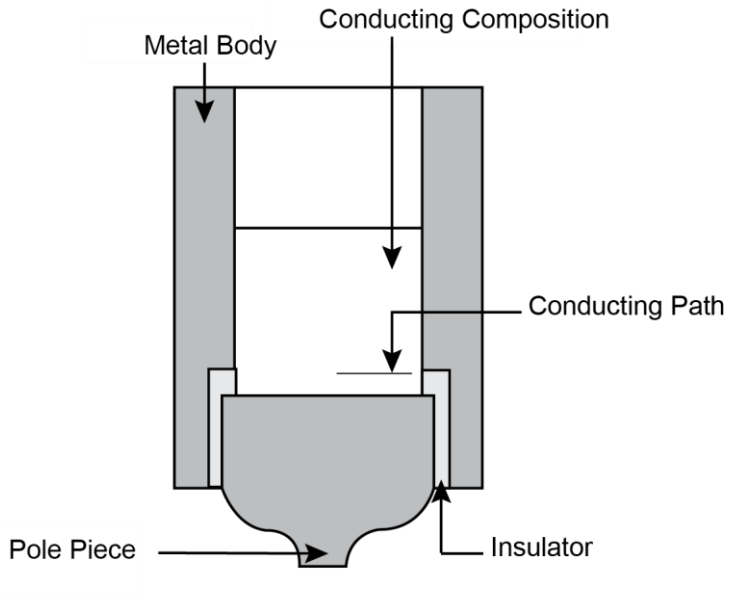


Figure 6-15 Basic features of a conducting composition igniter

The CC system is much used in the Service and can be adapted to caps in gun ammunition (i.e. CC Cap Electric, 30 mm Aden) and other, non-obturating igniters and detonators. The cap conducting cap composition was originally developed as a component of a Naval primer which must fire in a circuit with an applied voltage of 220 V with a 4 Ω series resistance. In theory they can be used for any size of gun system to which electrical power can be supplied, but in practice are used in higher calibres. Service conducting caps are made of brass. They are larger than SAA percussion caps, being typically about 11 mm in diameter and about 4 mm in length. The base of the cap is formed by the pole piece, which is insulated from the brass forming the rest of the cap. The conducting filling, roughly equal in weight to that in a percussion cap, rests on

the pole piece and is surrounded by an annular distance piece. An electric current applied to the pole piece via the firing pin of the gun must pass through the composition in order to reach the distance piece and return via the body of the cartridge and the gun. The conducting filling is RD1654, composed of lead styphnate, RD1303, with a proportion of graphite in the range 4%-6%. The firing voltage can be wide ranging, varying from 5V dc to the 115V ac supplied to the 30 mm Aden gun. An Aden conducting cap composition cap is shown in Figure 6-16.

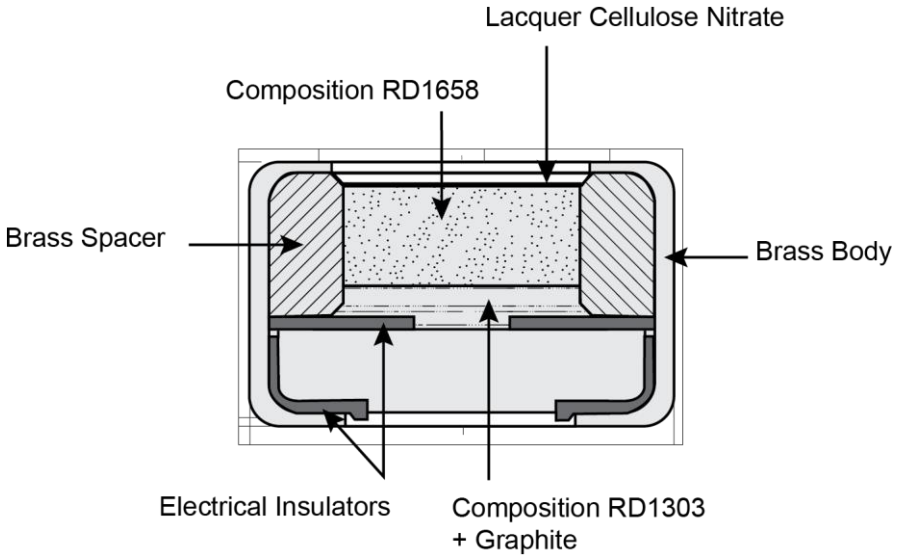


Figure 6-16 Aden conducting composition cap

6.2.2.6 Bridgewire igniters

Bridgewire igniters, often referred to as “Hot-Wire” igniters or Igniters Electric Bridgewire (IEBW), are an alternative to CC igniters, where a low voltage supply is available. These low voltage EEDs consist of a resistive wire bridge in close thermal contact with an explosive material. They are initiated by passing a current through the wire to produce a temperature rise in the explosive sufficient to cause a self-sustaining thermal reaction, leading to explosion. Thin metal bridgewires are commonly used to ignite explosive materials such as pyrotechnics, propellants and primary or secondary explosive powders. A low current, typically 3-5A, passing through the bridge wire heats it to approximately 900 K. This starts a reaction in the explosive material, usually an ignition or deflagration, which then increases to a useful output. The time between application of the current pulse and the peak output is the functioning time of the device. A wide range of ordnance applications make use of such electro-explosive devices (EEDs) including igniters, actuators and detonators. Hot-wire devices usually have a resistance of 1 Ω for electrostatic safety. A 1 Ω hot-wire device is a compromise between the energy required to ignite the energetic material and the energy dissipated by the bridge when subjected to electrostatic discharge (ESD).

They are divided into two types; bridgewire types and fusehead types. Both types contain a bridgewire, but the difference lies in the design of the insulating support for the bridgewire and in the way the primary explosive is placed against the bridgewire. In the so-called bridgewire type igniter, Figure 6-17, the wire is secured to one face of a plug of insulating material through which the lead wires are inserted to connect with the bridgewire. This assembly occupies the major part of the interior of a brass, aluminium or stainless steel sleeve. A charge of powdered primary explosive is then pressed into the remaining space, covering the bridgewire. Finally, the surface of the filling is sealed, approximately flush with the output end of the sleeve. This design is employed in a wide variety of Service uses. It can also be used as the igniting portion of an electric detonator. Bridgewire igniters are very small, some only 10 mm - 20 mm in length. Those which form part of an obturating system for a gun cartridge are known as bridgewire caps, analogously to CC caps.

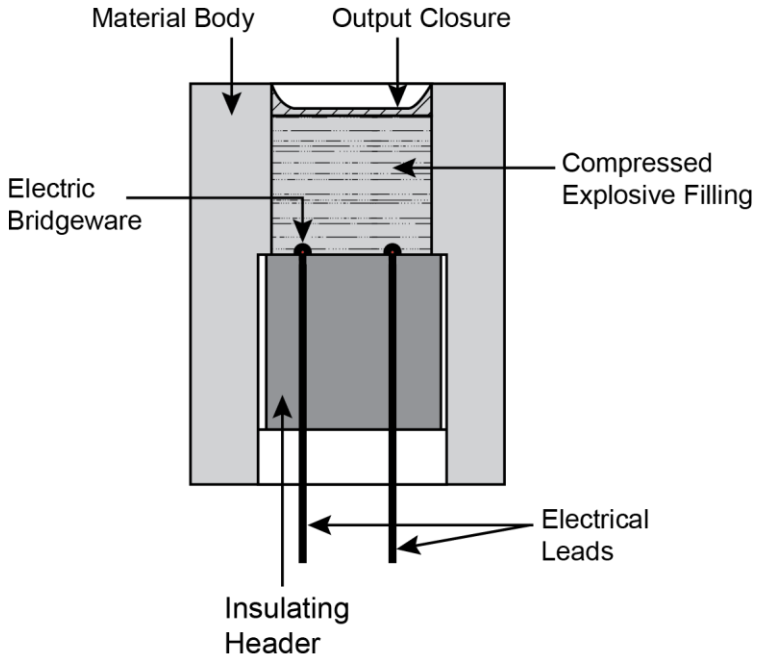


Figure 6-17 Basic features of a bridgewire igniter

The various explosive fillings of Igniters Electric Bridgewire (IEBWs) include the following:

- RD1320A Barium styphnate
- RD1349 β-monobasic lead styphnate

Bridgewire igniters have found use in such stores used in Frangible Pillar Assemblies, flash-receptive detonators, Cartridge Ejector Release Units (CERU), Thermal Batteries, GW SAUs, etc.

6.2.2.7 Fusehead igniters

A fusehead, Figure 6-18, consists of a bridgewire, two lead wires and an insulating support, all of which are contained in a miniaturised, self-contained

unit compared with the relatively bulky support in a bridgewire igniter. Fuseheads are made from a laminate consisting of an insulating material sandwiched between two pieces of copper foil. A small strip of this laminate forms the support. The bridgewire is soldered across the tip, joining the two pieces of copper foil, and lead wires are soldered to the other ends of the two pieces of foil. The bridgewire is then dipped in a quick-drying liquid initiating composition. When this coating has dried a coating of a flash composition is similarly applied. These and possibly additional coatings form an explosive match-head on the wire. The assembly acts as a versatile igniting device which can be used for igniting gun cartridge primers or providing the igniferous part of electric demolition detonators. The civil version of the demolition detonator, manufactured in very large numbers for commercial blasting, also relies on a fusehead, which is secured in the open end of a detonator tube by a thermoplastic plug.

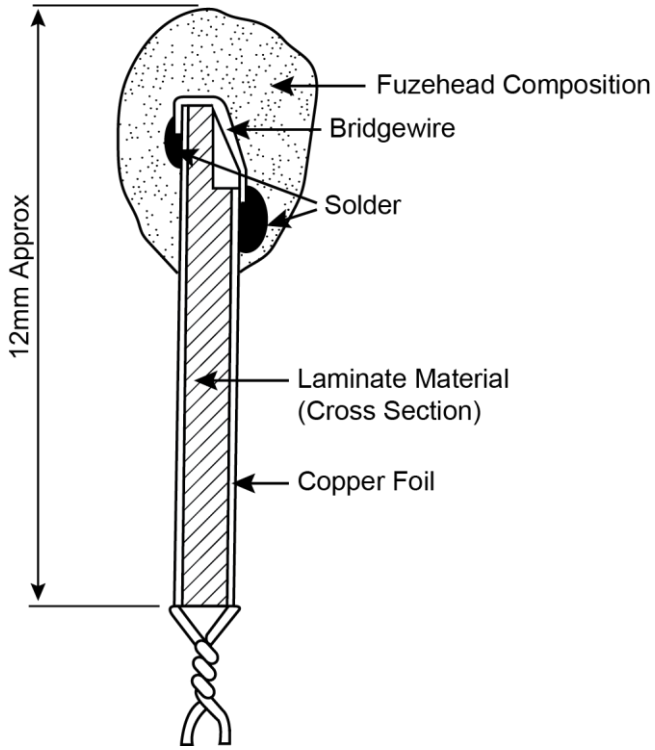


Figure 6-18 Basic features of an electric fusehead

The initiating compositions for Service fusehead igniters include mixtures of potassium chlorate with either lead mononitroresorcinate or charcoal. Other fuseheads employ normal lead styphnate or monobasic lead styphnate, RD1349. The flash composition forming the outer coating may be potassium chlorate/charcoal, cerium/red lead, 2,4-dinitroresorcinate (LDNR), normal lead styphnate or 88% tribasic lead styphnate/12% Boron (RD1361B). The liquid matrix for the initiating and flash compositions is either nitrocellulose or ethyl cellulose. Fusehead igniters are used in several military stores including for example, electric detonator demolition (L2A2) and thermal batteries.

6.2.2.8 Pyrofuse igniters

The pyrofuse igniter is an electrically initiated thermite reaction device used in the Naval service for igniting small rocket motors. It consists of a coil of pyrofuse wire wound on a bobbin and supplied with electrical power. The wire has a core of aluminium and an outer layer of palladium. When a current is passed through it, the wire undergoes resistive heating. An exothermic alloying process occurs between the two metals. This rapidly heats the wire to above its boiling point and it disintegrates in a burst of hot particles and vapour. The device has also been used in a 3 inch rocket motor.

6.2.2.9 High voltage igniters

An electric igniter which can be initiated only by a high voltage source is safer than the bridgewire and CC types, which can be initiated accidentally by stray low voltage currents. The bridgeless high-voltage squib (BHVS) utilises the conducting pyrotechnic composition SR72C consisting of copper (II) oxide (67%), aluminium (33%). This thermite-type mixture is ignited by the passage of a current from a 0.5 pF capacitor charged to 2000V. The BHVS is used in certain rocket motor igniters where the necessary high voltage is available. Further to the BHVS, high voltage exploding bridgewire (EBW) initiators have been employed for the ignition of certain large rocket motors.

6.3 DETONATORS

The Service definition of a detonator is “a device containing a sensitive explosive intended to produce a detonation wave”. Most but not all detonators are devices designed to convert burning to detonation. The range of timescales in which different kinds of detonator combine the two processes is very wide, from a few microseconds in the more advanced types to a designed delay of several seconds in some commercial blasting detonators. Irrespective of the means by which the detonator is designed to be initiated, the preliminary burning process generally involves fillings of the types discussed in the proceeding paragraphs and occupies the major portion of the total functioning time. The ultimate detonation process, with only a very small filling of high explosive to be consumed, occupies only about 1 µs.

Service detonators can be divided into fuze detonators and demolition detonators. A fuze is a device to control the initiation of a main charge. The role of a fuze detonator is to initiate the main charge of a high explosive munition or sub-munition. Generally, it does so through a disruptive explosive train, and in most cases the fuze detonator itself is a miniature explosive train.

A demolition detonator is the first disruptive initiator in a hand-placed explosive train for the purpose of a demolition. A Service demolition detonator is considerably larger than a fuze detonator, partly because the explosive filling is larger but mainly because it contains its own igniter in the form of an electric fusehead. In another respect, a demolition detonator is comparable to a fuze detonator in that they both contain a miniature disruptive train within a metal

container. There is little to distinguish the Service detonators, L1A2 and L2A2 Detonator Demolition from their nearest civil counterparts, the high-strength, so-called 'instantaneous' electric blasting detonator, but the latter has many variants in terms of different manufacturers, strengths, delay times and means of initiation.

6.3.1 Primary Explosives Used in Detonators

Detonator fillings comprise both primary and secondary high explosives and most of them are much more brisant than the most violent of the primary igniferous types, such as lead styphnate. The igniferous types are included in detonator fillings only to provide sensitivity to input and to assist the process of burning to detonation. Detonative primary explosives used and typical devices are detailed in the following sections. The methods of manufacture of primary explosives are detailed in Chapter 10.

6.3.1.1 Lead azide

Lead azide was discovered by Curtius who first prepared and characterised its explosive properties in 1891. Lead (II) azide is a primary high explosive which has been the mainstay of Service detonator fillings since the early to mid-20th century. Like all other primary explosives, it does not completely meet the ideal requirements, but its safety, reliability and performance are all acceptable when it is manufactured and used in the light of accumulated knowledge and experience. Lead azide (PbN_6) is the lead salt of hydrazoic acid (HN_3) and has the structural formula shown in **Figure 6-19**.

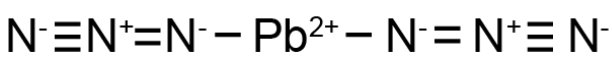


Figure 6-19 Lead azide

It is manufactured in the form of microscopic white crystals which have an absolute density of 4.8 gcm^{-3}. The crystals do not melt on heating but detonate violently at 320 °C – 360 °C depending on the rate of heating. Lead azide has good thermal stability at moderately elevated temperatures.

Lead azide, unlike most other practical explosives, contains no carbon, hydrogen or oxygen. Its explosion products comprise only nitrogen and lead vapour; therefore its calculated heat of explosion is low, being simply its heat of formation with the sign changed. For the same reason its gas volume, usually calculated as the nitrogen volume only, is one-third of that of a CHNO explosive. The calculated power index (see Table 4.6) is only 13 but in the lead block test the practical result is 37. These properties are unexceptional for a primary explosive, but the advantages of lead azide lie elsewhere. Its simple mode of decomposition enables it to burn instantly to detonation even in milligram quantities. It has high density, and moreover can be compressed nearly to its absolute density without loss of sensitivity, a phenomenon known

as 'dead-pressing' where sensitiveness (see 20.2.1) is reduced at high densities. It therefore has a high detonation velocity for a primary explosive and high brisance. The consequent ability of lead azide to induce detonation in secondary explosives is almost unrivalled in its class. This has enabled the size of detonator fillings to be reduced to conveniently small dimensions, an immense benefit in the design of military explosive trains. Lead azide is not, however, sufficiently sensitive for either flash or stabbing to be used in Service detonators without an appropriate topping of a more sensitive explosive such as RD1651 (L mixture).

Lead azide has four polymorphic forms, α, ß, γ, δ which differ in their sensitiveness (see 20.2.1) to impact and friction. The manufacture of lead azide suitable for loading into detonators was subject of interest and concern to both military and commercial operators since the replacement of mercury fulminate began in the 1920s and 1930s. Preparation of lead azide was associated with difficulties brought about by the extreme sensitiveness of the material, in part due to polymorphic modification. Under certain conditions lead azide will spontaneously explode.

Lead azide is hydrolytically unstable and can degrade in the presence of moisture, carbon dioxide and certain vapours given off by some synthetic polymers, to produce hydrazoic acid a highly sensitive explosive and extremely toxic compound. This acid in turn will attack copper and any copper rich alloys present in ammunition or fuzes to produce the extremely sensitive copper azide. Lead azides are compatible with lead styphnate and with tetrazene. There are several manufactured forms of lead azide as discussed below.

6.3.1.2 Service lead azide (SLA)

Service lead azide (α-form) consists of small rhombic crystals and must not contain dust, needle shaped crystals or large crystals, as these may be super sensitive. The material is not sufficiently sensitive to pricking by a needle to allow it to be used in stab-sensitive detonators without a sensitiser or a top increment of a stab-sensitive composition such as RD1651 (L mixture) containing RD1337 (lead 2.4-dinitroresorcinate, barium nitrate and tetrazene).

Service lead azide suffers from several disadvantages. It is especially sensitive to ignition by friction in the presence of grit. Over the years there have been many instances of ignitions during filling operations generally attributed to this. Also, because of its hard crystalline nature Service lead azide does not have good binding properties when consolidated into narrow channels for fuzes where high resistance to break-up forces is an essential safety requirement. This has resulted in the development and production of new types of lead azide processes and products which have advantages in processing, loading and functioning.

The main application of Service lead azide was the main filling for a wide range of service detonators including 2.3 grn LZY, 6.5 grn LZY, 2.6 grn LZ, 3.5 grn LZ, 6 grn ZY, 2 grn RZY, 1.5 grn RZY, Table 6-5.

6.3.1.3 Pure lead azide, RD1339

The purest of the lead azides, RD1339, is the α-form, and is of controlled crystal size. It has an F of I of 30 and a detonation velocity of 4550 m s^{-1} at a pressed density of 3.8 gcm^{-3}. The crystallisation of lead azide in the presence of non-ionic surface active agents was studied with the objective of developing a safe and reproducible method of preparation of pure lead azide suitable for technical applications where highest output was required. As a result, pure lead azide designated RD1339 was developed for mixing with powdered graphite without segregation for application to conducting composition detonators(2). No existing lead azide composition could meet this requirement.

The main application of pure lead azide, RD1339 is a conducting composition (RD1339/graphite) for use in electric detonators (i.e. detonator electric CC No1 and No2, Mk1, detonator electric NBC 170mg, 2.6 grn).

6.3.1.4 Colloidal co-precipitated lead azide, RD1343

The other lead azide composition in Service use is RD1343. This is originated from the early discovery that the occasional spontaneous detonations of lead azide which occurred during manufacture can be avoided altogether by adding hydrophilic colloids to the precipitating solutions. Further to this a demand for lead azide of greater purity and initiating efficiency, weight for weight than the dextrinated type (see RD1352) and to obtain a form of lead azide suitable for pressing into open ended sleeves without the danger of flaking on the surface, resulted in the development of RD1343, a “phelgmatised lead azide” so called as it contained a small proportion of a cellulose substance, (sodium carboxymethylcellulose) that desensitises the azide and helps to bind the pressed crystals. RD1343 was designed to give the best combination of a simple process, high azide value and optimum physical properties. Its natural moisture content is very low and it is non-hygroscopic. The material consists of white, discrete free flowing crystals which give a material of increased bulk density and reduced hygroscopicity. The product is free from small particles but has excellent pressing properties.

Note: RD1343 is an improved version of lead azide RD1333, having improved flow properties for automatic loading systems.

The main application of, colloidal co-precipitated lead azide, RD1343 is the filling for detonators excluding CC types and includes 1.5 grn RZY, 2.3 grn LZY, 2.6 grn LZ, 2 g RZY, 5.5 grn LZ, Table 6-5.

6.3.1.5 Dextrinated lead azide, RD1352

Dextrin (a form of starch) is a favoured additive in the preparation of lead azide. It suppresses the formation of the undesired β-polymorph, acts as a desensitiser, albeit at the expense of performance and tends to give white “dumb-bell” shaped or well-rounded crystals which are free from large single crystals and large aggregates. The product designated RD1352, has consistent

chemical and physical characteristics, including higher azide content and higher bulk density. These benefits result from the use during the precipitation stage of an ionic surfactant (dispersing agent) in addition to the dextrin.

The uniformity and good flowing properties of dextrinated lead azide, RD1352 and colloidal co-precipitated lead azide, RD1343 make them both very suitable for use in automatic loading machines.

The main application of dextrinated lead azide, RD1352 is use in NATO or USA detonator types (i.e. Relay detonators M7, M17; Stab detonators M22, M24; M215 detonator non-electric etc.). In UK Service stores RD1352 is used in Detonator demolition L1A2 and L2A2.

6.3.1.6 Lead azide GAM

Lead azide GAM developed and introduced in 1967 consists of a mixture of **G**elatin, Lead **A**zide and **M**olybdenum disulphide. Molybdenum disulphide was added to overcome the poor cohesive properties of Gelatin/Lead azide mixture. The electrical properties of the GAM product are excellent; however, the bulk density and power of GAM lead azide are lower than those of Dextrinated lead azide. The main application of lead azide GAM, is use in the DR series of detonators, as shown in Table 6-5.

6.3.1.7 Basic lead azide

It has been reported[3] that the High Energy Materials Research Laboratory (HEMRL), Pune, India, has undertaken research studies on primary explosives with a view to synthesising a series of new lead azides, which are safer, powerful and free from the drawbacks of current lead azide. It has been reported that HEMRL has successfully synthesised and developed a new and safer lead azide called basic lead azide (BLA) which has been assigned the empirical formula $[3Pb(N_3)_2.2PbO]$. The material is reported to be a crystalline free flowing and non-hygroscopic material having a bulk density of 2.0 ± 0.2 g cm^{-3}, which detonates high explosives efficiently and has a better thermal and hydrolytic stability compared to other lead azides. Further to this the material has better compatibility with copper than service lead azide (SLA) and is less sensitive to impact and friction than SLA having a F of I = 65-72 (see 20.10.2.1) compared to a F of I = 20 – 30 for SLA. BLA has been made sensitive to flash pick up by the addition of trinitrophloroglucinol (TNPG) during manufacture and therefore, requires a smaller quantity of lead styphnate in detonating compositions such as ASA (Lead **A**zide/Lead **S**typhnate/**A**luminium). Based on the characteristics of ASA composition and the properties of BLA, a composition using BLA, designated as BLASA, was formulated (BLA/LS/Aluminium powder: 80/19/1 % w/w) and compared to ASA (65.0/32.5/2.5 % w/w). The sensitiveness to impact and friction of ASA and BLASA (F of I = 15 and 64 for ASA and BLASA respectively) showing that the BLASA composition to be much less sensitive than the ASA composition. BLASA compositions are now used instead of ASA composition in a range of

tubular and closed detonators manufactured in India but to date have not found service in the UK.

6.3.1.8 Properties of lead azides

The properties of Service lead azide (SLA), RD1339, RD1343, RD1352 and Lead azide GAM, as defined in UK Military Explosive Safety Certificate No's SC120B, SC1514, SC1585, SC1501 (SLA, RD1339, RD1343, RD1352 respectively and relevant UK Defence Standards) are detailed in Appendix A Table A-5.

6.3.1.9 Silver Azide

Silver(I) azide was first prepared by Curtius in 1890 and is the silver salt of hydrazoic acid and has the structural formula AgN_3 shown in

$$Ag^{+}– N^{-} \equiv N^{+} = N^{-}$$

Figure 6-20.

$$Ag^{+}– N^{-} \equiv N^{+} = N^{-}$$

Figure 6-20 Silver azide

Its white microscopic crystals, which darken on exposure to light, have a density of 4.81 g cm^{-3}. There is only one crystal form at ordinary temperatures. Silver azide does not melt on heating but detonates at 273 °C, which is a considerably lower temperature than that of the lead salt. Its thermal stability at intermediate temperatures is even better than that of lead azide. Silver azide has an F of I of 25, a lower detonation velocity than lead azide and about the same capacity to initiate secondary explosives to detonation. Like lead azide, when used in detonators it needs to be initiated by a more sensitive explosive.

The chief advantage of silver azide over lead azide is that it is not subject to hydrolysis by moisture; therefore, it is used as a replacement for the lead salt in certain detonators exposed to humid environments. Silver azide has its own disadvantages; like lead azide, it is incompatible with copper, but unlike lead azide it is also incompatible with tetrazene which precludes its use in RD1651 (L mixture) which contains tetrazene. Furthermore, it is incompatible with sulphur compounds including antimony sulphide. There are two Service silver azides having the designations RD1336 and RD1374.

6.3.1.10 Silver azide, RD1336

RD1336 consists of a free flowing material consisting of aggregates of orthorhombic shaped crystals. Difficulties in applying this material to automated detonator filling, "fortress filling" resulted in the development of a modified silver azide, designated RD1374.

The main application of silver azide, RD1336 was in composite detonators (of the flash receptive type) to replace lead azide when the environmental conditions may cause deterioration of the lead azide. (i.e. 2.25 g RWY, 2.1 g RWY, 1.45 g RWY).

6.3.1.11 Silver azide, RD1374

RD1374 has a smaller particle size to RD1336 giving a material of higher bulk density (1.4 g cm^{-3}) compared to RD1336 (0.75 g cm^{-3}) which is better for automated detonator filling processes such as “fortress filling”. The main application of silver azide, RD1374 is as a direct replacement for RD1336 used in the 2.25 grn RWY detonator for Fuze L106.

6.3.1.12 Properties of silver azides

The properties of silver azide, RD1336 and RD1374 as defined in UK Military Explosive Safety Certificate No SC1584A and relevant UK Defence Standards are detailed in Appendix A Table A-6.

6.3.2 UK manufactured detonative primary explosives

Examples of detonative primary explosive compounds and compositions presently manufactured in the UK along with their use in military stores are detailed briefly Table 6-5.

Table 6-5 Detonative Primary Explosive Compounds/Compositions and Their Use

Primary Explosive	Designation	Use
Lead Azide GAM	Lead Azide GAM	Detonators DR7004, DR7009, DR7046, DR7047, DR7050, DR7052, DR7054 (long tube fusehead initiated detonators)
Dextrinated Lead Azide	RD1352	Detonator demolition L1A1, L2A2 (ASA composition)
Service Lead Azide	SLA	Detonator 6.5 grn LZY, Depth Charge MII MoD 3-Detonator 2.3 grn LZY Base Percussion L56A1 (120 mm HESH & WP) Detonator 2.3 grn LZY,
Colloidal Lead Azide	CLA	Detonator DR7025 (SAUs)
Silver Azide	RD1374	Detonator 2.25 grn RWY (Rapier)

6.3.3 Types of Detonator

6.3.3.1 Disruptive mixtures

In the same way that igniferous mixtures are used in igniters, some mixtures used in detonators combine the useful properties of two or three ingredients. Lead azide can be sensitised to impact by the addition of tetrazene, and alternatively can be made into a conducting composition by the inclusion of

graphite. Service detonators Detonator Demolition L1A2 and L2A2 contain the flash-sensitive A.S.A. Mixture, comprising, Lead **A**zide (68 % w/w), Lead **S**typhnate (29 % w/w), **A**luminium (3 % w/w). This mixture readily burns to detonation. The inclusion of aluminium is twofold, firstly it improves its free-flowing capability and secondly it prevents the mixture building up on the punches during pressing. However, the inclusion of aluminium has a sensitising effect on the composition. The F of I of A.S.A. mixture is 15, an indication of the danger attending any maltreatment of demolition detonators.

6.3.3.2 Composite detonators

In general, the output required of Service detonators is obtained more by composite arrangements of single explosive compounds than by mixtures. The most common igniferous layers are L Mixture (RD1651), employed for its sensitivity to stabbing, and R Composition (2,4-LDNR) which is flash-sensitive. The igniferous layer is followed in most cases by lead azide in the form of RD1339 or RD1343, replaced in a few instances by silver azide, RD1374.

Fuze detonators, though necessarily small in size, are required to have sufficient detonation pressure to transmit a shock wave across an air gap and through a metal septum to the boosting explosive. To achieve this reliably, many fuze detonators contain a layer of secondary boosting explosive adjacent the azide layer. This base charge has for many decades been of tetryl, but is currently being replaced by the other types of secondary high explosives such as RDX or PETN.

As with igniters, the fillings of composite detonators are often designated by initial letters, as follows:

L	=	L Mixture, RD1651
R	=	2,4-lead dinitroresorcinate (LDNR), RD1337
RDX	=	RDX, RD1347
W	=	Silver azide, RD1374
Y	=	Tetryl (CE)
Z	=	Lead azide, RD1343.

The ways of combining these letters are the same as for composite igniters.

A composite flash receptive detonator, 2.1 grn RZY (2,4 LDNR, Service lead azide, tetryl) is shown in Figure 6-21.

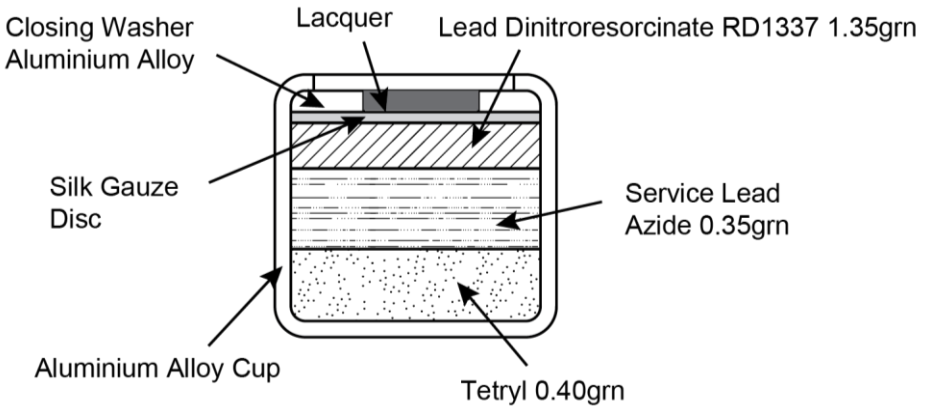


Figure 6-21 2.1 grain RZY composite detonator

6.3.3.3 Stab detonators

Stab detonators are similar to stab igniters in respect of their means of initiation, cup material (aluminium, aluminium alloy or tinned copper), the initiating layer (L Mixture) and typical weight of filling (2 grains - 3 grains, 0.1 g - 0.2 g). They are mostly of the LZ, LZY, or LZ/RDX categories. The majority of them are filled and pressed from the input (open) end, leaving the base of the cup intact; this is known as direct loading (DL). Some are filled by indirect loading, that is, the output end of the cup is perforated and the layers are filled and pressed from that end, after which the hole is closed by an aluminium disc. Indirect-loaded (IL) stab detonators have a lower performance than direct-loaded (DL) ones as measured by the thickness of metal septum through which they can initiate a booster charge. Also they are less tolerant than DL detonators to variation of the thickness of the cup base; the IL type needs a very small (0.13 mm) and critical thickness of the closing disc for its effectiveness.

The functioning time for a stab detonator, from striker contact to base rupture, is of the order of 0.3 milliseconds, which is not very different from the total time of an igniter/flash-receptive detonator combination. It would appear, therefore, that most of the functioning time is taken up by the process of the L Mixture igniting from the effect of the stab, and that the process of the azide layer burning to detonation takes comparatively little time. To put the functioning time into perspective, it should be remembered that some time must be added for the acceleration of a spring-loaded striker to a speed of 1 ms^{-1} - 2 ms^{-1}. Stab detonators have been widely applied in fuzes following the format example shown in Figure 6-22.

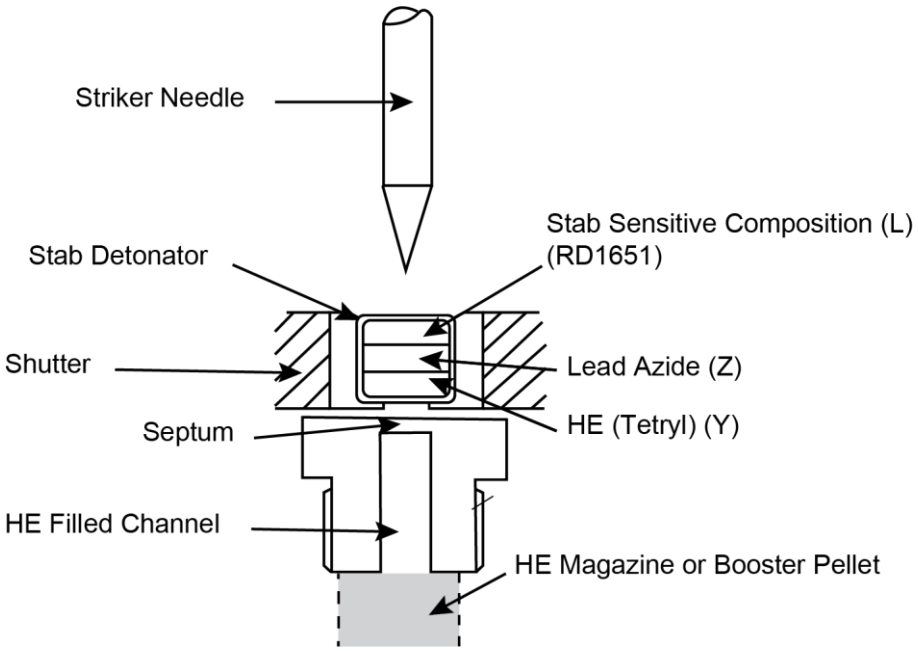


Figure 6-22 Example of (LZY) stab detonator initiation system

The stemmed channel provides a small localised region where the detonative impulse from the detonator can be accepted, built up and passed to the HE magazine. The output from the stemmed channel is not very powerful so it is necessary to use a magazine or booster pellet to transmit the detonation effectively to the next part of the system. Stab detonators include the 2.3 grn and 6.5 grn LZY (RD1651, Lead azide, Tetryl) detonators which have found use in a wide range of Fuzes and Depth Charge Mk 11 MOD3.

6.3.3.4 Flash-receptive detonators

Flash-receptive detonators are a common form of fuze detonator used in a wide range of weapons systems ranging from grenades to Guided Weapon safety and arming units (SAUs). This type of detonator can be initiated by a stab or an electrical igniter, either directly, Figure 6-23, or via a delay column. As in the case of a stab detonator, the disruptive output of a flash-receptive detonator is directed at a booster explosive via a metal septum. Most Service flash-receptive detonators have aluminium alloy cups. The fillings have total weights in the range 1.45 grains - 2.5 grains (0.094 g - 0.16 g) and they are mostly of the RZY, RWY, or R/W/RDX categories. As with stab detonators they can be either direct or indirect-loaded. Flash-receptive detonators have found use in a range of SAUs and Fuzes such as Fuze, Torpedo.

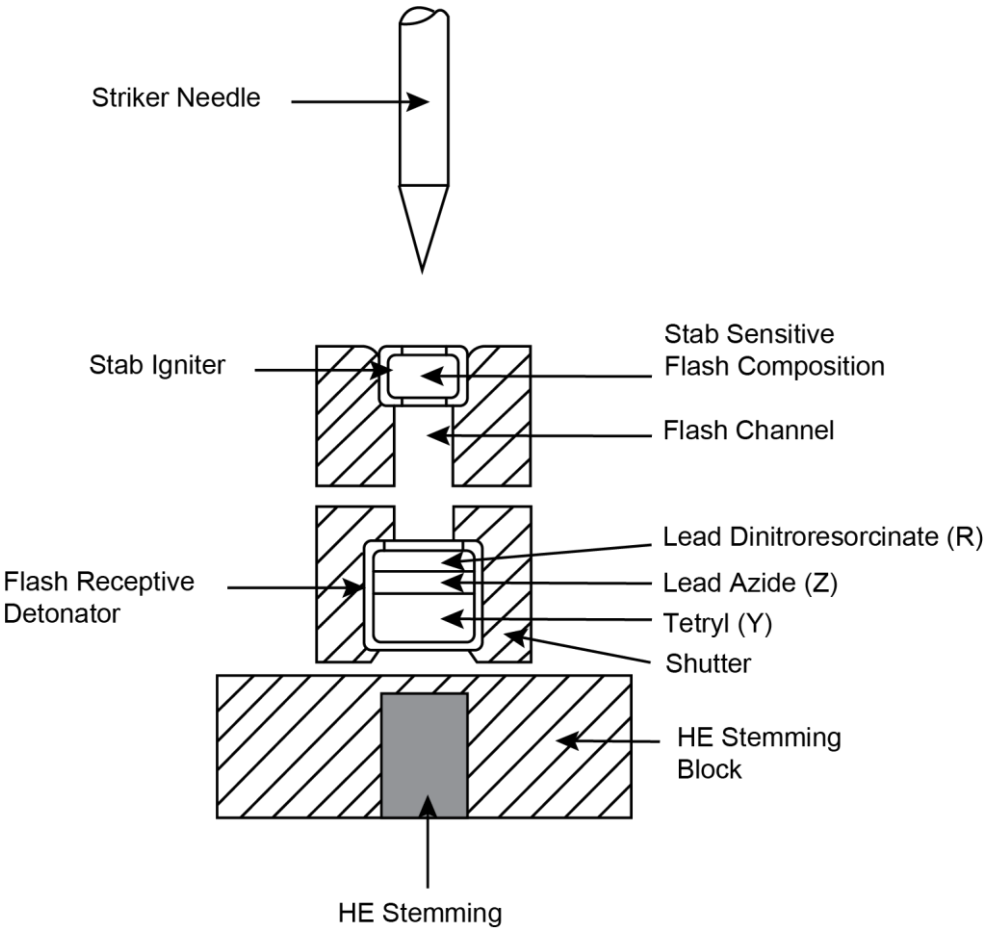


Figure 6-23 Example of stab igniter-flash receptive detonator system

6.3.3.5 Conducting Composition (CC) detonators

Conducting composition detonators are low energy input, fast response explosive devices with a detonative output. They are small enough to be housed in a shutter, moving from shorting terminals in the unarmed position to firing terminals in the armed position. CC detonators are based on the same principle as CC igniters and are of about the same size as other types of fuze detonator. However, they do not employ the lead styphnate/graphite mixture as do CC igniters, but instead lead azide RD1339 with about 3 % w/w graphite added, or, in some cases lead azotetrazole (LAT)/graphite with azide as the next layer. Current types have RDX as the secondary explosive. The detonator cup is usually of brass, plated with gold or silver. CC detonators have previously been used in a number of fuze applications, including BL755 bomblets and LAW 80. An example of a CC detonator is shown in Figure 6-24 and an example of its use within an initiation system is shown in Figure 6-25.

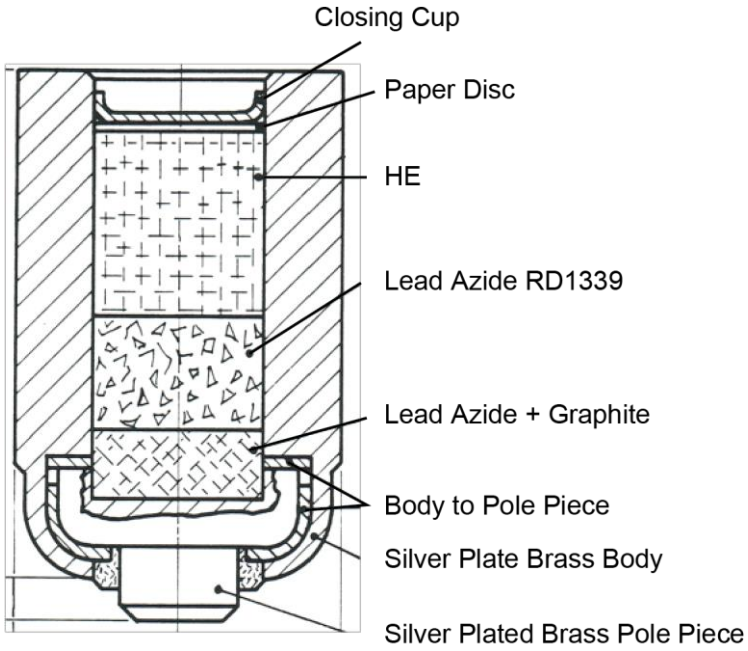


Figure 6-24 Example of an electric conducting composition detonator

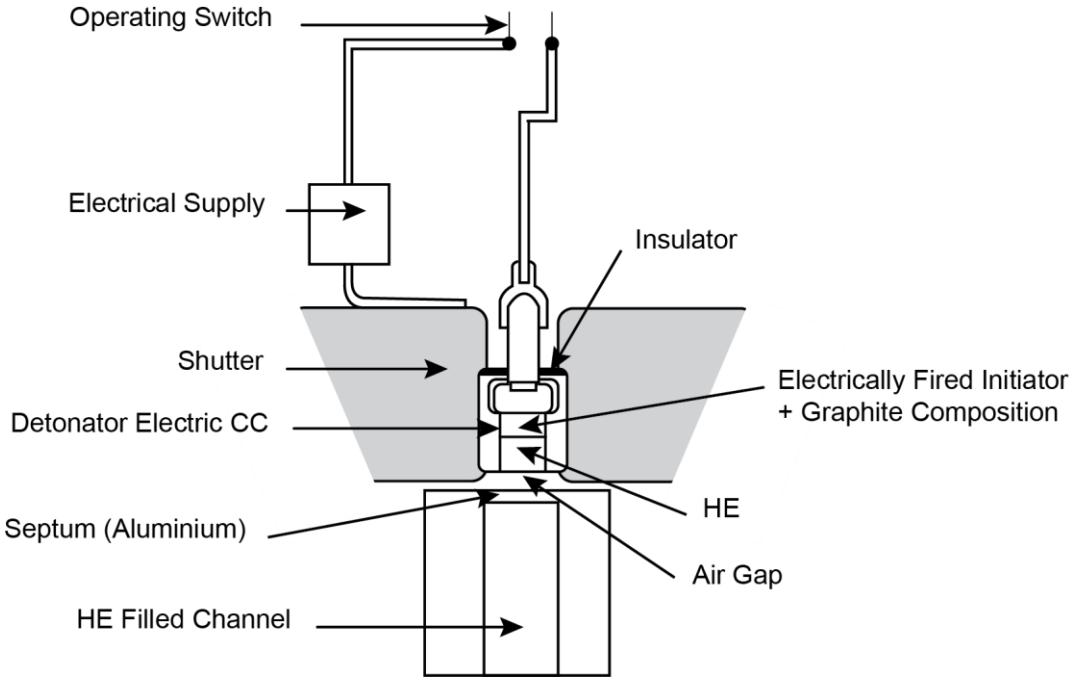


Figure 6-25 Example of an electric conducting composition detonator initiation system

6.3.3.6 Bridgewire detonators

Bridgewire detonators contain a disruptive filling which is initiated by a fusehead or other bridgewire device included in the same container, usually an aluminium tube. Detonator N16, a special purpose long tube device based on a 200/400 series igniter, was designed for use in explosive bolts and was used in Fuze Electric Boost Separation in the Sea Dart missile. Fusehead detonators include

the Service Detonator Demolition L2A2. These detonators are considerably larger than other detonators, consisting of a 60 mm long x 6.4 mm diameter aluminium tube. The initiating composition for the L2A2 detonator is ASA mixture (see 6.3.4.1) and this is followed by a base output charge of PETN. Initiation of the ASA mixture is achieved using an electrically initiated Type E fusehead which is crimped into the open end of the detonator, Figure 6-26. A non-electric detonator (L1A2), Figure 6-27, is identical to the L2A2 but is initiated by Safety Fuse rather than by an electrically initiated fusehead.

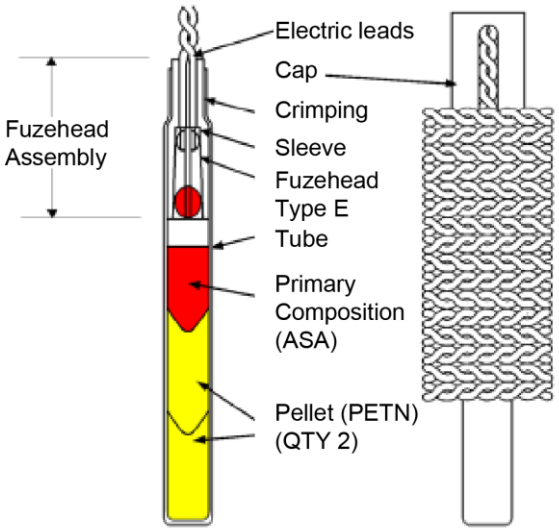


Figure 6-26 Detonator Demolition Electric L2A2

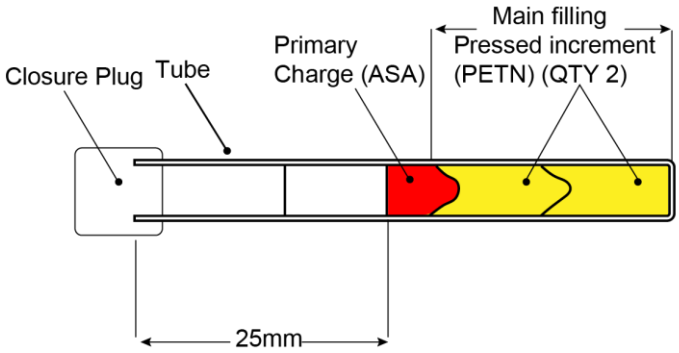


Figure 6-27 Detonator Demolition Non-Electric L1A2

6.3.3.7 Exploding bridgewire detonators

All the igniters and detonators described thus far in this chapter contain primary explosives, which can be easily initiated by physical mishaps or by stray electric currents even of low magnitude. Although protection against accidental functioning is provided as far as possible, no explosive train containing primary explosives is as safe as one which contains only secondary explosives. Moreover, an electric circuit which is designed to initiate a train only when

powered by a high voltage is clearly safer than one intended to operate from a low-power source. An initiator which provides both of these safety features is the exploding bridgewire (EBW) detonator. EBWs are high voltage devices which consist of a low resistance bridgewire in intimate contact with a low density secondary explosive. To activate, a large amount of energy is dissipated into the bridgewire in a small time interval (typically less than 1 μs). The resultant high power causes the bridge wire to explode and detonate the explosive.

In contrast to the hot-wire initiator, the exploding bridgewire (EBW) device uses shock to initiate a reaction. The shock wave produced by the explosion of the bridgewire initiates detonation directly in a secondary explosive. Because of this, primary explosives are not required. When the initiation characteristics of secondary explosives are considered, only pentaerythritoltetranitrate (PETN) pressed at low densities can be initiated by the relatively low shock output of an EBW. Therefore, PETN is the current explosive used in EBWs. EBW initiation of other secondary explosives can be achieved but the energy input requirements necessitate relatively large firing systems.

The EBW detonator which has been commonly used in UK Service is the N1 Mk2, Figure 6-28. This is a small device, 17.4 mm long, with a moulded thermoplastic body. The bridgewire is of gold, approximately 0.9 mm long and 0.4 mm in diameter. The bridgewire is secured to the insulating body of the detonator and spot welded at each end to a nickel wire contact pin in a similar way to that in a low-tension bridgewire detonator. A filling of low-density PETN is in contact with the wire, and another layer of PETN, pressed to a higher density, is contiguous with the first layer. To initiate the detonator a pulsed current is passed from a 6.5 pF capacitor charged to 2000 V. The current which can rise to more than 700 A heats the bridgewire through the melting, boiling and vaporisation phases. A rapid explosive reaction is initiated which builds up to full detonation throughout the length of the low density filling. Detonation is transferred to the high density pellet, which results in a very powerful output providing reliable detonation of the secondary explosive stemming.

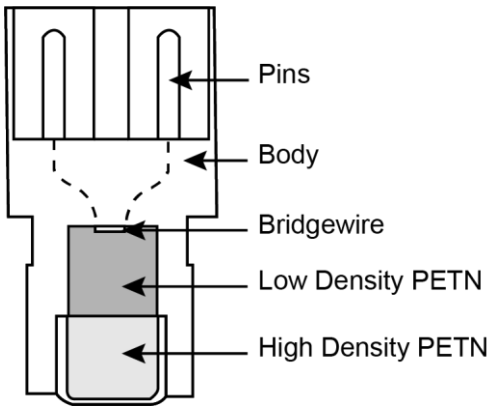


Figure 6-28 Exploding bridgewire detonator N1 Mk2

The EBW detonator is safe from initiation by low currents applied accidentally but is prone to “dudding” if a discharge raises the temperature of the explosive

in contact with the wire to a level which modifies its physical condition or melts the bridgewire. EBW detonators can be used in any weapon system in which a high voltage source is available, and have found use in Guided Weapon systems. Since an EBW detonator contains no primary explosive it can be incorporated in an ‘in-line’ fuze where there is no requirement to physically move a component of the explosive train to arm the device. The functioning time of an EBW detonator, being a few microseconds, is far faster than that of any other electrical type except the exploding foil initiator (EFI) detonator and faster than that of any mechanical type. The drawbacks of EBWs are generally due to the thermal stability properties of the PETN, which has a melting point 141.3 °C. However, it is not sufficiently stable above 71 °C limiting the temperature at which EBWs can be used for military requirements, to the range -50 °C to +71 °C. HNS cannot be initiated in EBWs at practical firing energies and therefore the safety advantages conferred by this material are unavailable for EBW applications. However, EBWs can be initiated with longer firing pulses than EFIs and control of fireset inductance is less stringent.

6.3.3.8 Exploding foil initiator detonators

Exploding foil initiator (EFI) detonators often referred to as “Slapper” detonators are safe and reliable high voltage detonators, which can replace Exploding bridgewire (EBW) detonators in explosive trains. They were first devised by J Stroud at Lawrence Livermore National laboratory in the USA in the early 1970’s. Since that time their development has continued in the USA and Europe and they are now used as in-line detonators for use in electronic safety and arming units (ESAUs) in several UK Service munitions including Sea Wolf missiles and the Spearfish and Sting Ray torpedoes. The EFI detonator like the EBW, depends upon direct shock initiation of secondary explosives.

The EFI, Figure 6-29, contains a thin film metal bridge, usually copper deposited on a thin film of polyimide plastic, creating a foil/flyer assembly which is in turn attached to a thin stripline firing cable with copper conductors and to a barrel which consists of an annulus of plastic about 0.25 mm thick. The firing cable, foil/flyer and barrel are laminated together to form a single assembly just a few millimetres thick. This assembly is offered up to a high explosive pellet of either HNS or PETN to form a complete detonator. Because of the space saving method of stripline construction and the simple, reproducible functioning mechanism, EFI detonators are smaller than EBW detonators and give better timing simultaneously between detonators. Firing times are much less affected by variations in fireset parameters. An EFI detonator-stripline assembly is shown in Figure 6-30.

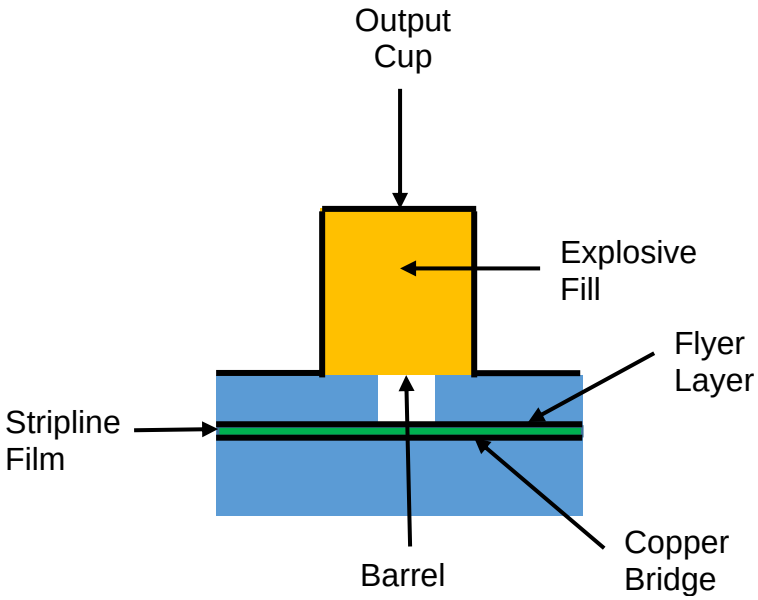


Figure 6-29 EFI detonator

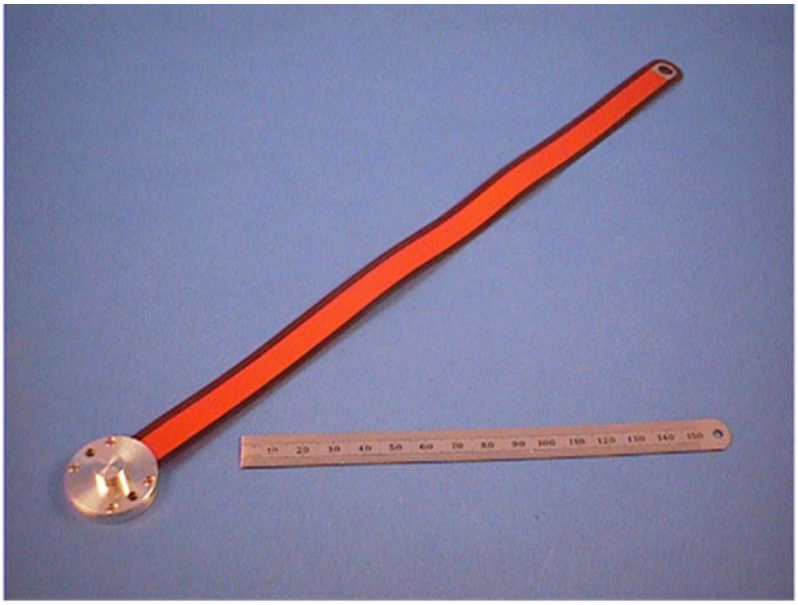


Figure 6-30 EFI detonator-stripline assembly

The device is activated by rapidly delivering a fast rising high current pulse of 2000 V to 3000 V from a capacitor discharge fireset circuit into the bridge. The bridge explodes and accelerates the plastic flyer down a barrel onto a high density pellet of the secondary explosive. The velocity of the flyer is sufficient (>3000 m s^{-1}) to cause shock initiation of the explosive pellet. Both HNS and PETN are very sensitive to short pulse shock initiation. HNS is the most favoured material as it has a high melting point (318 °C) a high temperature of ignition (324 °C) and is considered to be sufficiently insensitive for in-line

initiation system use. PETN however, has a relatively low melting point (141 °C), low temperature of ignition (181-182 °C) and demonstrates high explosiveness (see 20.2.1).

There are two types of EFI, namely narrow barrel and wide barrel with the latter often referred to as an infinite barrel type. If the diameter of the barrel is the same as the length of the bridge foil, the design is called a narrow barrel. If the diameter of the barrel is more than twice the bridge foil length, the design is called a wide barrel. A narrow barrel needs to be accurately aligned and the flyer may break off unevenly around the edge of the barrel with loss of bridge energy giving variable shaped fliers which may give variable initiation performance. There are no barrel/bridge alignment problems with the wide barrel type of EFI. Barrels can be several millimetres in diameter and are typically around 0.3 mm in length. The barrel length needs to be short since if the flyer bubble bursts it decelerates and it could fail to initiate the explosive pellet.

The constructional techniques used for EFI detonators can be exploited to design multiple EFI systems which are light and economical in their use of space. An array of copper foil bridges can be etched in the desired geometry. Similarly, a network of firing current conductors can be etched on a single length of plastic which extends to the fireset, and a matrix of barrel holes can be cut into a thin sheet of plastic. These components can be laminated together to form a single thin strip which aligns with a matrix of HNS pellets in a suitable metal or plastic sheet. This arrangement lends itself to easy incorporation into large array initiation systems and has the potential for achieving high levels of reproducibility. The main advantage of using EFIs over EBWs is that these devices will detonate the relatively insensitive secondary explosive HNS. Further advantages include:

- The metal bridge is completely separated from the explosive by an insulating film and an air gap, providing the electrical isolation of the explosive filling.
- Very high current rise time (dI/dt) is required to make an EFI function.
- They have a high no-fire threshold.
- The explosive can be pressed to a high (near crystal) density, which provides maximum shock energy output.
- HNS is thermally stable.
- EFI design is relatively simple and easily fabricated. There is only one high density explosive pellet and three to four inert components.
- EFIs can function with superior firing reproducibility than EBWs.
- The EFI filled with HNS is suitable for the initiation of in line explosive trains.
- The major disadvantage with EFIs is that because of impedance limits for the explosion of the driving foil, cable lengths are limited to less than 1 metre and only then using special flat low-impedance cables. However, it may be possible to use greater lengths of cable by changing fireset operating parameters and increasing the overall firing energy.

6.3.3.8.1 Low-Energy EFI (LEEFI) detonators

In recent years the desire to reduce the size, cost and mass of the fireset has driven the investigation of lower-energy EFI initiators which can reliably, safely and precisely operate at reduced firing voltages. The 2000V - 3000V operating voltage range of conventional EFI fireset technology has been constrained by operational requirements and also by the availability of suitably-rated components (which must survive the extreme requirements associated with munition and borehole operating environments). Recent development of low-energy EFI technology has been carried out at Teledyne - e2v Technologies (UK) [(4)] and has resulted in the reduction of the all-fire threshold of the exploding foil bridge structure, to enable initiators and compact firesets that will reliably operate at firing levels of around 1200V or less with STANAG 4187 requirements currently mandating that the no-fire level to be at 500V (or more). Typical no-fire threshold (NFT) and all-fire threshold (AFT) characteristics for LEEFI and a standard EFI for comparison are shown in Table 6-6.

Table 6-6 No Fire and All Fire Thresholds for LEEFI and Standard EFI[(4)]

EFI	Hot (+85 °C)		Cold (-54 °C)	
	AFT (V)	NFT (V)	AFT (V)	NFT (V)
LEEFI	1189	702	1227	1010
Standard EFI	1794	1398	1824	1568

LEEFI based firesets can now operate at in the region 1200V to 1400V with the result that it is possible to reduce both the physical size and mass of the fireset components. An advantage of this being that integrated Safety and Arming Units (SAUs) can be significantly reduced in size and mass, (nominal 40 mm diameter/250 g compared with 100 mm diameter/1kg of a conventional EFI fireset).

Advantages of LEEFIs include, reduced operating voltages, component miniaturisation and improved system integration with the potential for integration into a SAUs for a range of Complex Weapons.

6.3.3.8.2 EFI takeover onto pyrotechnic material

Further to the above, it has been shown that an EFI can be modified to produce the reliable direct ignition of a pyrotechnic composition (B/KNO_3). This has enabled the development of a small direct ignition Electronic Ignition Safety Device. By simplifying the energetic chain, the explosive material required in a Through Bulkhead Initiator (TBI) has been eliminated thereby removing mechanical shock generated during ignition. Based on EFI technology an EFI in-line Ignition Safety Device (ISD) for the Fuzing of Solid Fuel Motors by the direct initiation of a B/KNO_3 pyrotechnic pellet has been developed[(4)].

6.3.3.9 Semiconductor bridges (SCBs)

Electrical initiated explosive devices (EIEDs) use electrical conducting composition, hot bridge wires, exploding bridgewire, semiconductor bridge (SCB) or thin metal film bridge as electrical conducting element. Explosive igniters which used electrical conducting composition required few micro joules of energy for initiation. But they are prone to accidental initiation due to electrostatic discharge or radio frequency interference. Hot bridgewire explosive devices require a few mJ of energy for initiation but are unsafe. Exploding bridgewire based explosive devices are safe but are unsuitable for use in electronic fuses due to high voltage required for their operation. As a result of the short comings there was a need to develop a low energy, reliable, safe initiator for use in fuses. It was reported in 1985[5] that a Semiconductor Bridge (SCB) could be used in place of the bridgewire for initiation of explosive. Bridgewire device function delay is in milliseconds with the no fire and all fire current levels often being dependent upon the energetic material and the physical construction of the explosive device.

SCBs are finding increased use as initiators for both explosive and pyrotechnic devices. They offer advantages in reduced voltage and energy requirements, coupled with enhanced safety features. The advantages afforded by SCBs include; high safety, rapid response, low input energy, high reliability and consistency. The no fire level of devices can be changed by altering the area of the bridge without greatly affecting the all fire energy. SCBs are explosively safe and highly resistive to ESD. The current pulse required to function SCBs is a unique signal preventing their accidental functioning. SCBs are compatible with micro electronic circuitry and can be applied into micro-electromechanical systems (MEMS). A SCB comprises a substrate of non-electrically conductive material, a doped semiconductor layer on the substrate, as well as first and second metal lands forming ohmic contacts on the doped semiconductor layer. An explosive charge bridges the gap between the metal lands across the doped layer, Figure 6-31 with an example of a SCB detonator shown in Figure 6-32.

When fast rising current pulse is applied on the SCB the SCB generates hot plasma for ignition of the explosive powder pressed against the bridge. Ignition is via micro-convection heat transfer process and not just by thermal conductive heat transfer as with hot-wires.

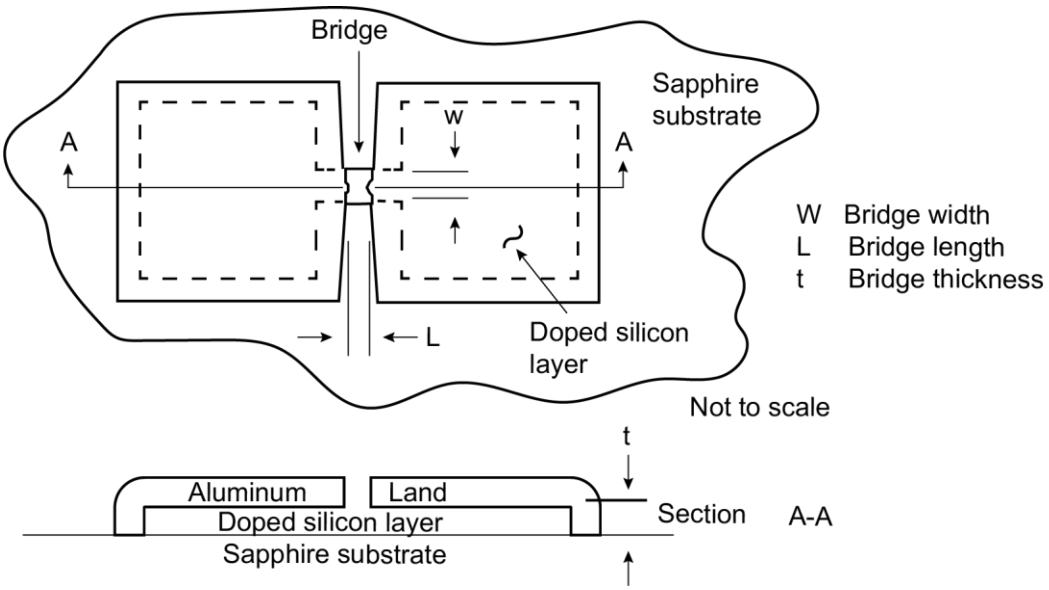


Figure 6-31 SCB schematic

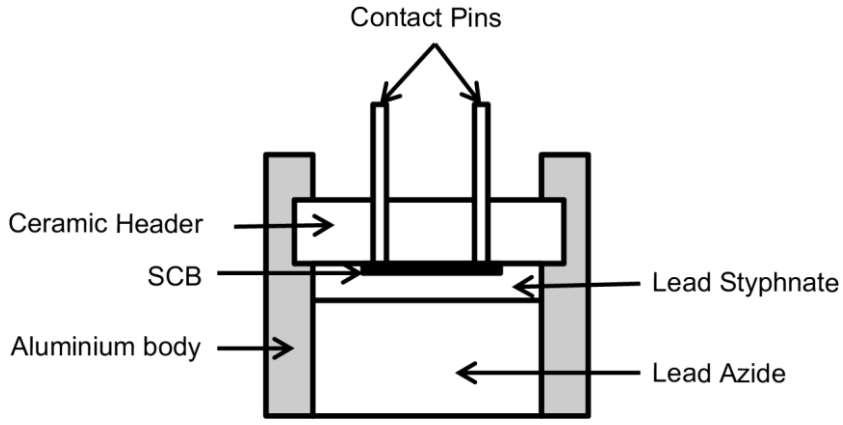


Figure 6-32 SCB detonator schematic

SCB devices have been used to ignite materials including thermites (aluminium/copper oxide), gas generators (actuators), rocket motor igniters based on a mixture of titanium sub hydride and potassium perchlorate pressed against the SCB and copper oxide/aluminium thermite. A further application lies in the use of SCB igniters for the activation of thermal batteries using a mixture of titanium sub hydride and potassium perchlorate. SCBs will not initiate secondary explosives but will initiate a Deflagration to Detonation (DDT) transition with PETN and tetraamine-cis-bis(5-nitro-2H-tetrazolato-N^2) cobalt(III) perchlorate (BNCP). Research into the development of prototype BNCP detonators incorporating a semiconductor bridge has and continues to be carried out in the USA[6]. Typical operating characteristics of SCBs, EBWs, EFIs and hot-wires are given in

Table 6-7.

Table 6-7 Typical Operating Characteristics of Hot-Wire, SCB, EBW and EFI

Operating Characteristic	**Device**			
	Hot-Wire	SCB	EBW	EFI
Firing Current (A):				
Threshold	1	>1.5	200	2000
Operating	5	20	>500	3000
Threshold Firing Voltage (V)*	20	30	500	1500
Threshold Firing Energy (J)	0.02	0.005	0.2	0.2
Threshold Power (W)	<0.1	100	100,000	3,000,000
Typical Function Time (μs)	1000	10-50	2	0.1

Note*: The threshold firing voltage is the voltage required to fire 50 % of the samples. The values listed are nominal and detonators have been fired with lower energy and power requirements. For the EBW values assume a 1 μF capacitor while 0.15 μF is assumed for the EFI.

6.3.3.10 Micro-electromechanical systems (MEMS)

Micro **E**lectro **M**echanical **S**ystems often referred to as MEMS are based on fabrication technology for creating mechanical devices on a micron (μm) scale. Individual features of MEMS are on the micron (μm) scale but systems can be several millimetres in size. It is an emerging technology which is used in many commercial applications and has an increasing use, mainly as sensors, for military weapons. Components based on MEMS technology having been widely used since the early 2000s.

With the increasing move towards smarter, smaller munitions this creates a problem of decreasing space within weapons to accommodate all the necessary components including the guidance and navigation system, fuze and explosives. In order to reduce the size of initiation systems employed in weapons there is a growing interest in the miniaturisation of fuze components. Research in the USA and Europe is presently being undertaken into the miniaturisation of initiation systems using MEMS which includes actuators, igniters, detonators and safety arming units (SAUs). MEMS initiators would provide reduced quantities of sensitive primary explosive in each weapon. Space savings could be utilised for a range of systems (i.e. on-board guidance and control systems). A further advantage of MEMS devices would be the possible integration with electronic safety and arming units.

The practical implementation of MEMS technology is extremely challenging but will enable the reduction in the quantities of sensitive primary explosives used in initiatory devices used in weapons. From a manufactures and environmental perspective, the development of MEMS initiators will considerably reduce the use of toxic heavy metals and waste products and will increase the safety of weapon production by reducing the need for handling bulk quantities of primary explosives.

Recent USA research into MEMS initiators to name but a few includes; igniters for rocket motors, detonators, EFIs, actuators and an ignition safety device utilising a SCB. In the UK, research addressing the problems associated with the incorporation of very small amounts of primary explosives in detonators and actuators has been carried out. The patented MEMS design uses a capillary micro-chamber filled with an explosive material, which precipitates into a second chamber, through micro-cavities with an igniter substance that's detonated when an electric current passes through a simple thermal wire(7).

6.4 LEAD FREE PRIMARY EXPLOSIVES

Virtually all low voltage and mechanical initiation systems in UK service use primary explosive compounds and compositions based on lead and other heavy metals. Concerns over the hazards to health of using lead containing primary explosives, both in their manufacture and use has led to numerous investigations, worldwide, to identify suitable compounds, either known or novel and free from lead and other heavy metals, which could be used as replacements.

In Europe, current EC legislation(8); Registration, Evaluation, Authorisation and Restriction of CHemicals (REACH) (see 1.3.2.4.6), will severely limit, and may prohibit the future use of lead and heavy metal containing primary explosives or at least make their availability uncertain. Several USA and UK research programmes have been and continue to be carried out to identify suitable lead free materials. Any proposed lead replacements must retain energetic properties upon exposure to the atmosphere and must be; insensitive to light; sensitive to detonation but not too sensitive to handle and transport; thermally stable to at least 200 °C, chemically stable for extended periods; devoid of toxic metals such as lead, mercury, silver, barium, or antimony. In the USA replacement materials must be free of perchlorate, which may be a possible teratogen and has adverse effects on thyroid function however, to-date the use of perchlorate in both the UK and Europe is not an issue.

A major advantage of lead containing primer compositions (i.e. VH2, VH4 primer compositions) is that they deposit metallic lead onto the gun barrel surface during functioning. The thin film coating acts as a lubricant for the barrel and protects it from corrosion. Lead free primers may generate more abrasive oxides causing greater barrel wear especially with high powered rounds. A number of lead free materials do not meet service requirements as they are

unstable, have excessive sensitiveness (see 20.2.1) or they are not environmentally benign.

Several lead free compounds have been used as replacements for lead styphnate and lead azide. These include, 2-diazo-4,6-dinitrophenol (DDNP), Figure 6-33, which has been used as an initiating explosive in stab detonators and percussion primers, and potassium 4,6-dintrobenzofuroxan (KDNBF), Figure 6-34, which has been used in percussion initiated primer compositions. DDNP was first prepared in the mid-1800s by Griess. Its temperature of ignition (see 20.10.2.3) is reported to be between 161-188 °C depending on material purity and mode of preparation. DDNP has found applications in several initiating devices including stab detonators and percussion primers. DENEL RSA in 1994 carried out investigations and developed percussion cap primer compositions based on DDNP[9] whilst DYNAMIT NOBEL AG developed a range of lead free primer compositions, commonly known as SINTOX Primer Composition, based on DDNP. DDNP is virtually the only readily available replacement for lead styphnate in present percussion cap priming compositions. However, despite this, DDNP does exhibit a number of disadvantages, it is light sensitive which can reduce its ignition temperature, it is incompatible with lead azide, it causes allergic reaction in workers, it can be dead pressed and has low density (reported to be 1.63 - 1.72 g cm^{-3}) thereby requiring a relatively large volume which could reduce its usefulness for some applications. Further to this, production processes produce large volumes of waste water; it has a high electrostatic sensitiveness (see 20.10.2.6) and has reported questionable shelf life and reliability issues[10]. However, in the USA, DDNP is considered to be satisfactory and safe to use in both commercial and military applications.

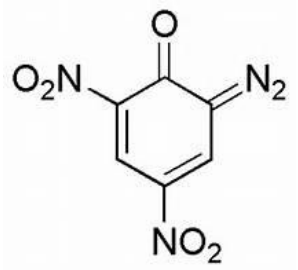


Figure 6-33 Diazodinitrophenol (DDNP)

KDNBF (Figure 6-34) was first prepared by Drost in 1899. Further to this in 1953, Costain[11] investigated several meta salts of dinitrobenzofuroxan (DNBF) with KDBNF having low solubility, good stability up to 70 °C chosen for further studies in the development of graphite bridge igniters. There was little interest in KDNBF in the UK until the early 1970s when Thomas (PERME Waltham Abbey, UK) investigated the preparation of the material in a form suitable for fusehead applications[12]. Further to this in 1978 a material was developed to meet a Service requirement for a gas producing composition for use in a miniature explosive cutting system[13]. This KDNBF was known as RD1372.

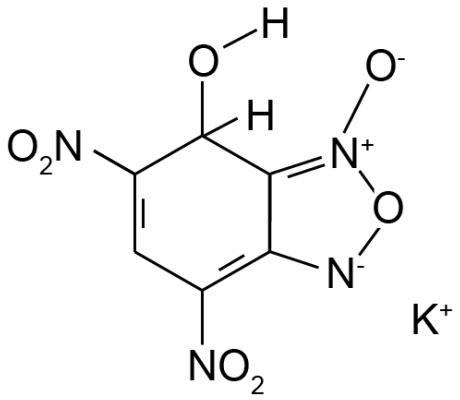


Figure 6-34 Potassium 4,6-dinitrobenzofuroxan (KDNBF)

In the UK in the mid-1990s, Royal Ordnance PLC, Chorley developed a range of low toxicity lead free primer compositions suitable for the replacement of the lead styphnate containing VH2 and VH4 percussion primer compositions used in a range of small arms ammunition. These lead free compositions were based on KDNBF and typically contained potassium or strontium nitrate (oxidiser), tetrazene (sensitiser) and calcium silicide (frictioner). However, these compositions are no longer produced in the UK. A major problem with the manufacture of KDBNF lies with the low product yield and relatively low product volumes which impacted on the commercial viability of the production of KDBNF on a commercial scale.

Other lead free compounds include the thermally stable coordination complexes, (2-(5-cyanotetrazolato)pentaamminecobalt(III) perchlorate) (CP), Figure 6-35, and tetramine-cis-bis(5-nitro-2H-tetrazolato-N^2) cobalt(III) perchlorate (BNCP), Figure 6-36, which has been used in prototype SCB detonators. However, the perchlorate content of both CP and BNCP makes them unacceptable for future use.

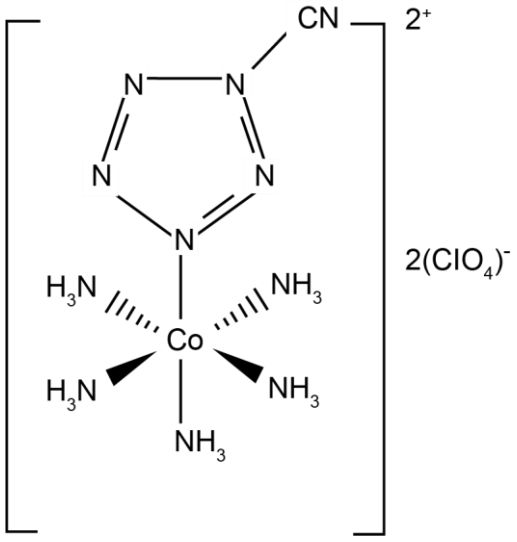


Figure 6-35 Pentamine (5-cyano-H-tetrazolato-N^2) cobalt III perchlorate (CP)

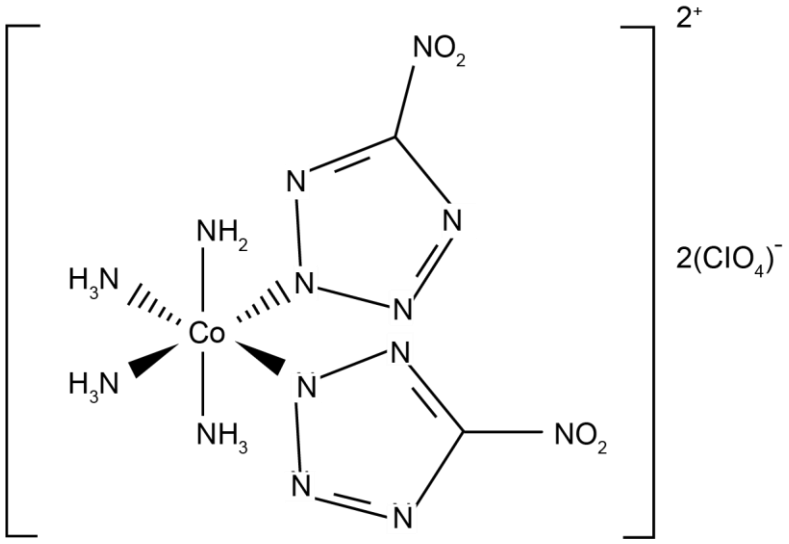


Figure 6-36 Tetraamine-cis-bis (5-nitro-2H-tetrazolato-N2) cobalt III perchlorate (BNCP)

Further to the previously mentioned materials, mixtures of aluminium nanoparticles and heavy metal oxides known as Metastable Intramolecular Composites (MICs) are known to have appropriate sensitivity. However, instability toward atmospheric oxygen and moisture, safety concerns during large scale production, and residual heavy metal contaminations has prevented their adoption as lead salt replacements.

Silver (I) azide has long been considered a possible replacement for lead azide in detonators. Unlike lead azide it is not subject to hydrolysis and is presently used as a lead azide replacement in certain detonators such as the UK Service detonator 2.25 grn RWY. However, silver azide does have some disadvantages namely; like lead azide it is incompatible with copper, but unlike lead azide it is incompatible with tetrazene and sulphur containing compounds such as rubbers and antimony sulphide. This incompatibility precludes its use as a lead azide replacement in several initiator devices containing tetrazene like RD1651-L mixture.

At the present time the most promising replacements for lead azide and lead styphnate are the copper(I) salt of 5-nitrotetrazolate known as DBX-1, Figure 6-37, and the potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (KDNP), Figure 6-38. Both materials have been extensively investigated at Pacific Scientific Energetic Materials Co, USA[14,15,16].

DBX-1 has been patented[17,18] as a potentially green direct drop-in lead azide replacement. The material has demonstrated superior explosive output and high thermal stability. Unlike lead azide it is stable under humid conditions and does not react with copper and other metals and is compatible with a range of secondary explosives including RDX, HMX and CL20. In addition, it has sensitivity and output characteristics which are equivalent to or exceed lead azide and it does not show any tendency to dead press even at high loading pressures (275.8 MPa). DBX-1 is known to slowly decompose when stored in

water however, due to its positive qualities; it is being sought as a replacement for lead based primary explosives. The material has been submitted for qualification as a primary explosive in weapons development to the Department of Naval Sea Systems Command (USA) and seems to be a suitable drop in replacement for the lead azide and lead styphnate based stab detonator mixture NOL-130 (basic lead styphnate 40 % w/w, dextrinated lead azide 20 % w/w, barium nitrate 20 % w/w, antimony sulphide 15 % w/w, tetrazene 5 % w/w) for use in the M55 stab detonators. KDNP, Figure 6-38, has a very similar chemical structure to KDNBF, Figure 6-34, but the physical properties differ markedly. KDNBF exists as a Jackson-Meisenhelmer adduct having a relatively low thermal stability. However, KDNP is a true ionic salt and has high thermal stability. The impact, friction and electrostatic sensitiveness of KDNP are better than that of lead styphnate making it safer to handle. KDNP is a suitable replacement for lead styphnate used either alone or as an ingredient in compositions. It has found use in several applications including impulse cartridge-bridgewire mix, TOW missile initiator units-pressed onto bridgewires and percussion initiated primers (sensitised with tetrazene) and has been qualified as a primary explosive for US Service use by the Department Naval Sea Systems Command.

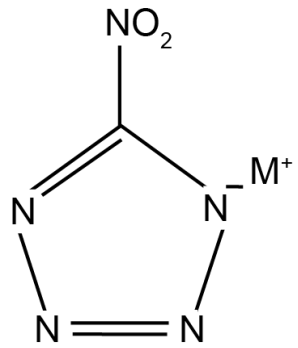


Figure 6-37 Copper(I) 5-nitrotetrazolate (DBX-1)

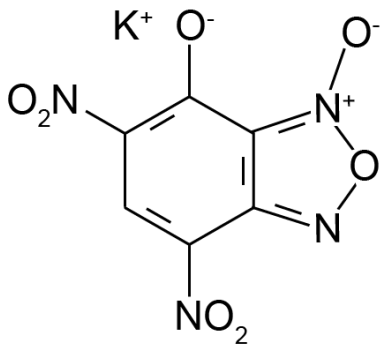


Figure 6-38 Potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (KDNP)

The methods of manufacture of DDNP, KDNBF, DBX-1 and KDNP are detailed in Chapter 10.

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APPENDIX A PROPERTIES OF PRIMARY EXPLOSIVES

Table A-1 Properties of Lead Styphnates

Parameter	α-Normal Salt		β-Monobasic Salt	
	RD1303	**RD1367**	**RD1346**	**RD1349**
Density	3.07 g cm^{-3}	Not Specified	4.06 g cm^{-3}	4.06 g cm^{-3}
Bulk Density	0.80-1.36 g cm^{-3}	1.5 ± 0.15 g cm^{-3}	1.15 ± 0.25 g cm^{-3}	1.30 g cm^{-3}
F of I	20	20	30	20
Temperature of Ignition	257 °C (Explodes)	255 °C (Explodes)	240 °C (Explodes)	234 °C (Explodes)
Ignition by Electric Spark (M/M min energy)	25 µJ @ 520 pF	15 µJ @ 520 pF	4.5 µJ @ 520 pF	36 µJ @ 520 pF
Ignition by Electric Spark (R/M min energy)	15 µJ @ 60 pF	<0.3 µJ	5.5 µJ @ 35 pF	8 µJ @ 40 pF

Table A-2 Properties of Barium Styphnates

Parameter	RD1320	RD1320A	RD1320B	RD1340
Density	2.56 g cm^{-3}	2.56 g cm^{-3}	2.56 g cm^{-3}	2.56 g cm^{-3}
Bulk Density	1.49 g cm^{-3}	1.00 g cm^{-3}	1.04 g cm^{-3}	1.10 g cm^{-3}
F of I	50	50	40	40
Temperature of Ignition	310 °C (Explodes)	310 °C (Explodes)	310 °C (Explodes)	318 °C (Explodes)
Ignition by Electric Spark (R/M min energy	1250 µJ @ 2000 pF	1300 µJ @ 2000 pF	2900 µJ @ 2000 pF	1430 µJ @ 520 pF

Table A-3 Properties of Lead Dintroresorcinate

Parameter	RD1308	RD1337
Density	3.95 g cm^{-3}	3.17 g cm^{-3}
Bulk Density	0.70 ± 0.10 g cm^{-3}	0.60 g cm^{-3} (min)
F of I	17	10
Temperature of Ignition	242 °C (Explodes)	242 °C (Explodes)
Ignition by Electric Spark (M/M min energy	15 µJ @ 76 pF	21 µJ @ 520 pF
Ignition by Electric Spark (R/M min energy	16 µJ @ 100 pF	160 µJ @ 100 pF

Table A-4 Properties of Tetrazene

Parameter	RD1357A
Density	1.70 g cm^{-3}
Bulk Density	0.50 – 0.75 g cm^{-3}
F of I	10
Temperature of Ignition	135 °C (Explodes)
Ignition by Electric Spark (M/M min energy	2 µJ @ 520 pF
Ignition by Electric Spark (R/M min energy	225 µJ @ 1200 pF

Table A-5 Properties of Lead Azides

Parameter	SLA	RD1339	RD1343	RD1352	Lead Azide GAM
Density	4.78 g cm^{-3}	4.68 g cm^{-3}	4.68 g cm^{-3}	4.38 g cm^{-3}	Not Specified
Bulk Density	2.0 g cm^{-3}	0.6 g cm^{-3}	1.4 g cm^{-3}	2.2 g cm^{-3}	1.35 g cm^{-3}
F of I	30	23	30	20	Not Specified
Temp. of Ignition	>300 °C (Detonates)	>300 °C (Detonates)	319 °C (Detonates)	300 °C (Detonates)	Not Specified
Ignition by Electric Spark (M/M min energy)	2 µJ @ 520 pF	8 µJ @ 255-520 pF	2 µJ @ 520 pF	Not Specified	Not Specified
Ignition by Electric Spark (R/M min energy)	225 µJ @ 1200 pF	800 µj @ 759 pF	Not Specified	Not Specified	Not Specified

Table A-6 Properties of Silver Azides

Parameter	RD1336	RD1374
Density	5.0 g cm^{-3}	5.0 g cm^{-3}
Bulk Density	0.75 g cm^{-3}	1.4 g cm^{-3}
F of I	30	23
Temperature of Ignition	362 °C (Detonates)	385 °C (Detonates)
Ignition by Electric Spark (M/M min energy)	2.5 µJ @ 520 pF	0.45 µJ @ 20 pF
Ignition by Electric Spark (R/M min energy)	400 µJ @ 1200 pF	4.9µJ @ 20 pF

CHAPTER 7
EXPLOSION PROCESSES

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7 THE EXPLOSION PROCESS

Authors – S G Murray and G Appleby-Thomas (Cranfield University)

7.1 AWARENESS SUMMARY

As introduced in Chapter 1 and expanded on in Chapter 2, explosives produce their effects through the liberation of heat and gas products through chemical reactions. There are two processes by which this occurs, the Burning Process and the Detonation Process. This chapter considers the key concepts and underlying physics associated with the reaction of explosives through the processes of burning or detonation. Explosives that detonate in their designed use are called High Explosives and those that burn in their designed use are often called Low Explosives. However, virtually all High Explosives can burn and many Low Explosives are capable of detonation. This latter point is important when considering the safety of munitions, for example those that contain large propellant charges such as are found in missile rocket motors. In its correct use the rocket propellant will burn, however, in certain accident scenarios it may be induced to detonation. Usually the desired outcome in the designed use of explosives will depend on the method of initiation as described in Chapter 5 Initiation of Explosives.

When an explosive material burns explosively it is said to undergo deflagration. There is no specific definition of the term deflagration but it is often considered to be when explosives burn at such a speed as to allow the expanding gas products to perform work such as to accelerate projectiles in guns or create blast. When explosives deflagrate they are undergoing the burning process.

The chemical decomposition of an explosive, releasing gaseous reaction products and subsequent production of heat occurs in both the burning and detonation processes. However, the mechanisms by which these processes occur in the explosive are very different. These two reaction categories are summarised below and described in detail in the subsequent sections.

7.1.1 Burning Explosives

When an explosive burns the explosive chemistry producing heat and gas occurs at any exposed surface. Most of the heat flows away from the burning surface in the gas products; however, some heat is conducted and radiated in to the unburnt explosive below the burning surface. This will reach its ignition temperature and then become the burning surface. Therefore, the burning process will travel in to the bulk of the explosive. This is shown in Figure 7-1 where a stick of explosive is burning along its length.

When the temperature at any explosive's surface reaches the ignition temperature that surface will ignite. For a propellant charge inside a cartridge case, which will have numerous individual grains of propellant, all surfaces of each grain will be ignited in the very early stages of ignition following functioning

of the igniter. This includes internal holes as found in multi-tubular propellant grains.

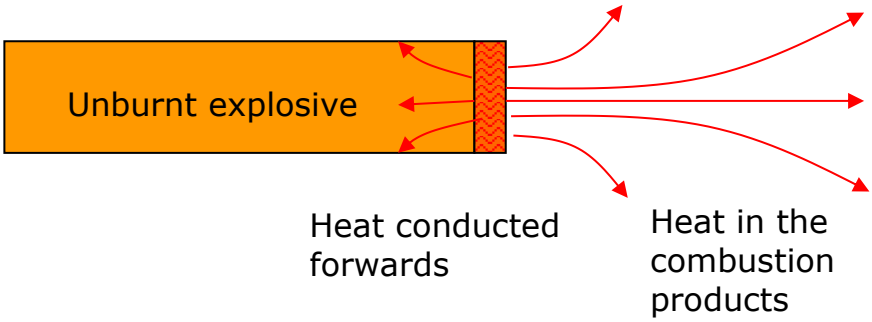


Figure 7-1 Heat transfer during the burning process

A major influence on the speed by which the burning surface progresses in to the bulk of the explosive, called the linear burning rate, is the pressure above the surface and is commonly known as Vieille's Law. As the pressure increase so does the linear burning rate. For example a typical gun propellant will have a linear burning rate of 5 mm s^{-1} at atmospheric pressure but at breech pressures this will approach 400 mm s^{-1}.

As burning is a surface phenomenon how fast a mass of explosive can burn will depend on the available surface area. If a propellant charge consists of spherical propellant grains then for the same mass of propellant if the grain size for charge A has a radius of x mm and charge B of x/2 mm, the charge B will have twice the surface area of charge A.

How quickly bulk explosive, such as a propellant charge, burns is a variable called the mass burning rate, will depend on what initial surface area is available and how it may change during the burning process. When the propellant charge burns in the breech of a gun pressure also will affect the mass burning rate, and these factors together are the basis of internal ballistics. For the duration of the propellant burn the pressure will be changing as will the available propellant surface area. This complex interaction consequently requires challenging calculations to model the process.

Further details of the burning process can be found in section 7.2.

7.1.2 Detonating Explosives

When an explosive detonates the explosive chemistry is initiated by the passage of a shockwave through the explosive charge. A shockwave is an intense pressure wave travelling faster than the speed of sound in that material. As the speed of sound in explosive is around 1,800 m s^{-1} and for most service explosives detonation velocities are in the range of 6,500 – 8,500 m s^{-1} it can be seen that detonations occur at 10,000 to 100,000 times faster than the propellant burning in a gun. An explosive charge 1 m in length can completely detonate in a few hundred millionths of a second (micro-seconds) if initiated from one end.

A detonation will often have a curved shockwave travelling away from the point of initiation in to the bulk of the explosive charge. This will occur in 3 dimensions as shown in Figure 7-2 although in small diameter charges this can be almost planar (flat).

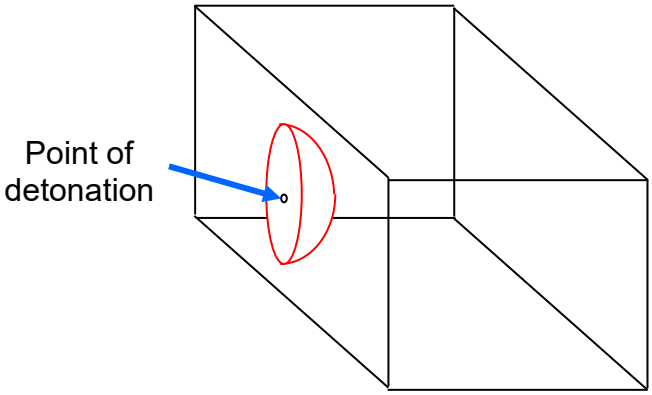


Figure 7-2 Shockwave expanding hemispherically in a block of explosive

Energy to drive the shockwave comes from the explosives chemistry occurring immediately behind it. There is a point behind the shockwave called the Chapman-Jouget (C-J) plane; material to the right of this plane as seen in Figure 7-3 will have particle velocity towards the shockwave and that behind to the left will move in the opposite direction and become the expanding gas products. The energy transferred to the shockwave and its forward velocity will reach a steady state so the shockwave reaches a constant velocity known as the Velocity of Detonation (VoD or D). Only energy released to the shockwave side of the C-J plane can influence the detonation shockwave.

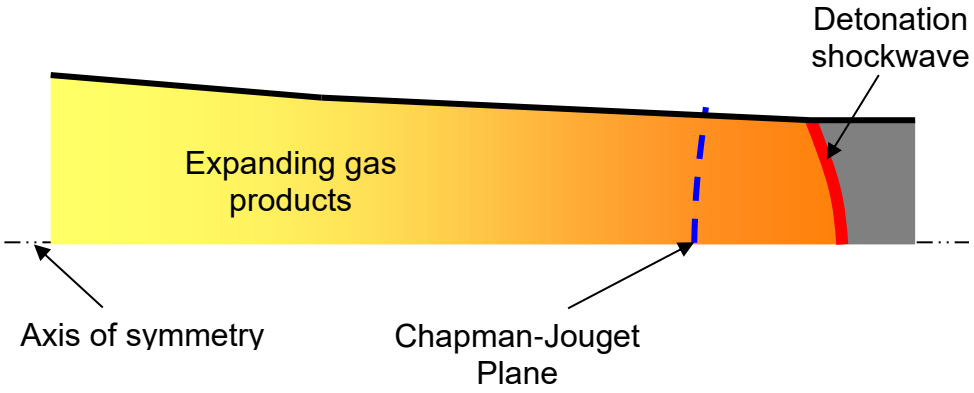


Figure 7-3 A detonating explosive charge showing the Chapman-Jouget plane

The Chapman-Jouget plane is often considered also to define the reaction zone and for explosives formulated from explosive molecules such as TNT, RDX and HMX, etc. this is normally true. However, if the explosive formulation is one containing slow reacting chemical systems such as those containing aluminium powder or those that are fuel oxidiser mixtures such as ANFO, they are considered to be classed as non-ideal explosives and reactions producing explosion products continue outside the zone denoted by the shockwave and the C-J plane.

Figure 7-4 shows how the reaction zone may come behind the C-J plane and explosive chemistry occurring between the C-J plane and the end of the reaction zone cannot influence the shockwave. This will reduce energy available to the shockwave and so the VoD values will be lower for non-ideal explosives than those where the chemistry all occurs before the C-J plane is reached. However, hot dense gas products are still being produced and will add to the power of the expanding gases.

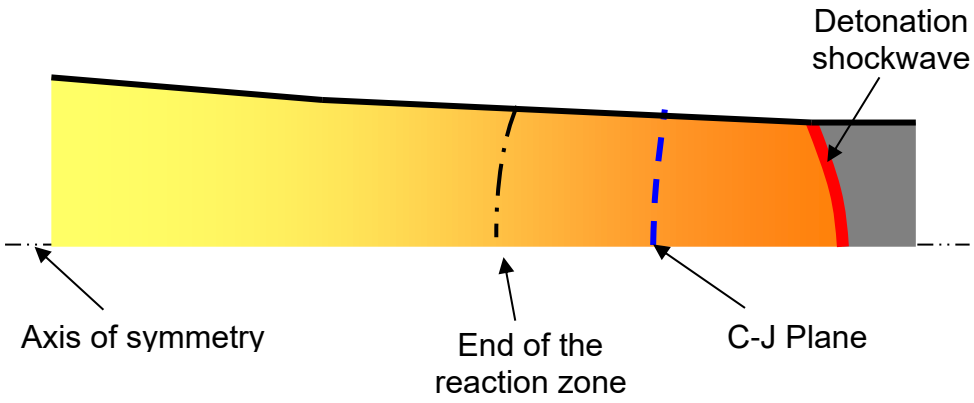


Figure 7-4 The reaction zone for non-ideal explosives

As the diameter of a detonating charge increase so does the distance between the shockwave and the C-J plane giving more time for chemical reaction. However, the converse is true and as the diameter becomes very small the energy released before the C-J plane becomes insufficient to support the shockwave. A point is reached where the charge will not detonate known as the critical diameter (see 7.3.3.3), which is usually quoted for what is essentially a bare uncased charge. Light confinement such as 0.2 mm paper may be used for example if the explosive is a powder. Under these conditions PETN powder has a critical diameter of 0.3 mm whereas the value for cast TNT at a density of 1.61 g cm^{-3} is 7 mm.

Each explosive capable of detonation will have an upper limiting value for its VoD, which is that normally quoted unless other conditions are invoked. Below a certain diameter this will progressively reduce until the critical diameter is reached and for this circumstance confining the charge can increase the VoD from the unconfined charge of the same diameter. Confinement will also reduce the critical diameter. Both the VoD and critical diameter are affected by the density of the explosive.

7.2 THE BURNING PROCESS

7.2.1 Propagation of the Burning Reaction

Once an explosive material has been raised to its ignition temperature it begins to undergo a chemical reaction producing heat and gas. The product gases will flow away from the surface removing most of the heat, however, through

radiation and conduction, heat will transfer in to the explosive below the burning surface as shown in Figure 7-5. This will raise the underlying material to its ignition temperature where it now becomes the burning surface. All available burning surfaces of the explosive will continue this process until it is completely consumed. In this manner, a solid piece of explosive that is burning on all available surfaces will decrease in all dimensions as shown in Figure 7-6 for a cylinder. This is known as Piobert's Law.

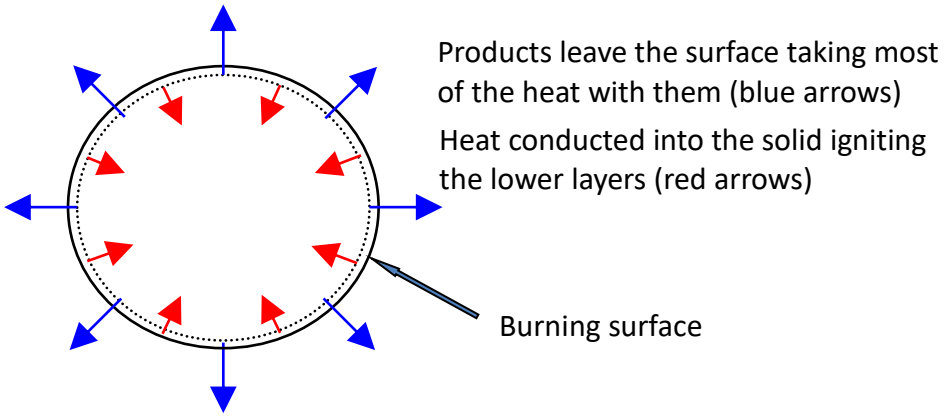


Figure 7-5 Heat transfer for burning explosive

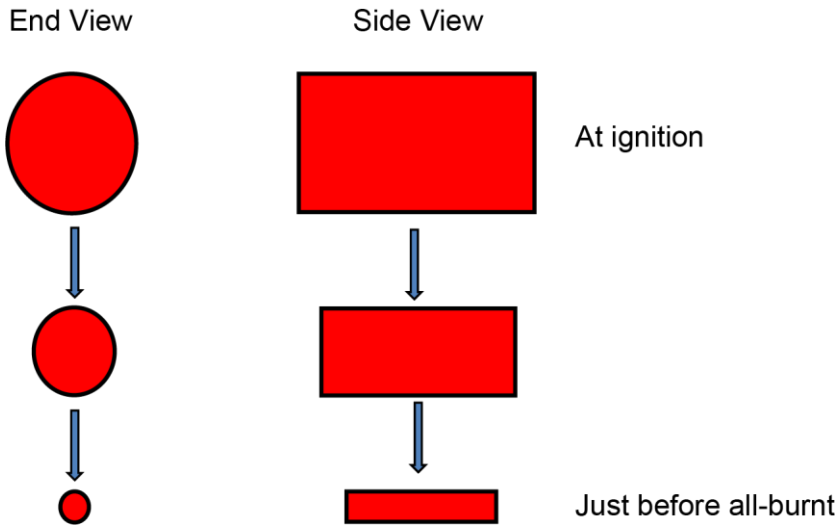


Figure 7-6 Changing dimensions of a burning cylinder

7.2.2 Mass Burning Rate

The most common application of burning explosive is the use of propellants in guns or rockets and to optimise performance it is important to understand how quickly the propellant is converted to heat and gas, that is, the mass burning rate (g s^{-1}). To understand the factors that can affect the mass burning rate consider a cube of explosive burning on only one face as shown in Figure 7-7.

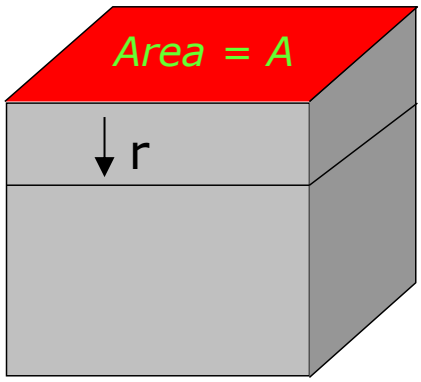


Figure 7-7 Cube of explosive burning on one face (red)

The area of explosive burning is denoted as A (cm^2) and the speed at which the burning surface is moving in to the explosive, called the linear burning rate (also called 'rate of burning'), denoted as r ($cm\ s^{-1}$). Therefore, the speed at which a volume of explosive is being consumed is A x r ($cm^3\ s^{-1}$). Since mass = volume x density (ρ) then mass burning rate ($g\ s^{-1}$) can be measured using Equation (7-1).

$$\text{Mass burning rate} = A \times r \times \rho \qquad \textbf{(7-1)}$$

7.2.3 Factors Affecting Mass Burning Rate

7.2.3.1 Surface area

Using gun propellant as an example, when a propellant charge made up of a large number of small pieces of propellant known as 'grains' is burning each grain will burn on all exposed surfaces. Therefore, if the grains were spheres, as they burned their diameter would reduce and therefore so would their surface area (A). Based only on surface area this would suggest that the mass burning rate for solid propellant grains would decrease from the moment all of the grain surfaces were burning. However, if the propellant grain has internal perforations, for example a cylinder with multiple tubular holes as shown in Figure 7-8, then each hole will increase in surface area as the grain burns. This will create a somewhat complex change in surface area as each hole is increasing in surface area but the outside of the cylinder will be decreasing. In this case the total surface area of the grain would constantly increase throughout the burn.

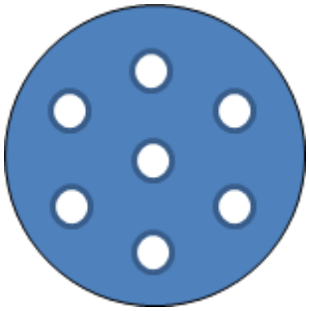


Figure 7-8 Cross section of a multi-perforated propellant grain

The internal ballistics for both guns and rockets depends heavily on the changes to overall surface area of the burning propellant. If the overall surface area reduces it is called regressive burning, whereas if it increases as described above for multi tubular granular propellant grains it is progressive burning. For a grain that is a hollow tube the surface area remains approximately the same and is known as neutral burning. Figure 7-9 shows a number of different shapes found in gun propellant charges. Solid shapes such as cord and flake will have regressive burning, multitubular will have progressive burning with tube and slotted tube having approximately neutral burning. Slotted tube is usually found for stick propellant, where the grains are very long like uncooked spaghetti. Without the slot the internal pressure within the stick would cause it to shatter and produce uncontrolled changes in surface area.

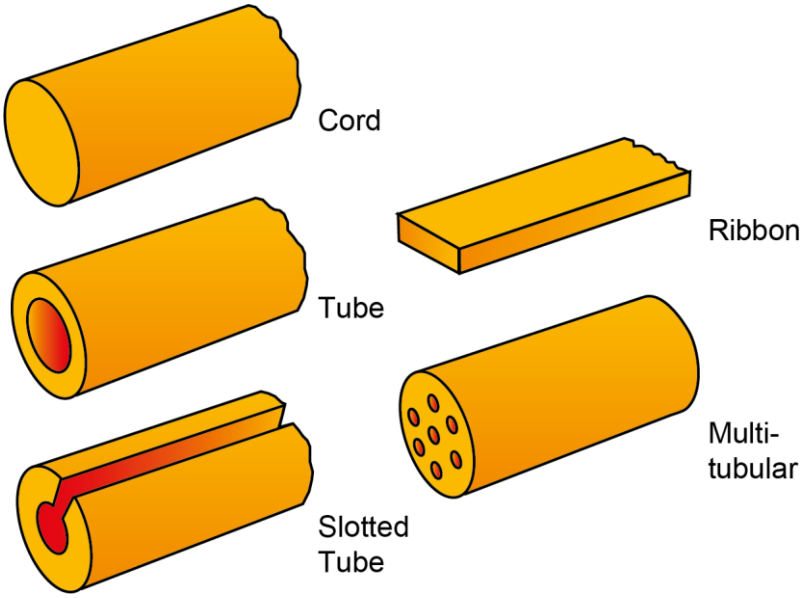


Figure 7-9 Examples of gun propellant grain shapes

Similarly, for rocket propellants the surface area during the burn can be controlled. Figure 7-10 gives some examples of single grain rocket propellants where the outer surface is bonded to the rocket motor casing and so will only burn on the rear face or inside an internal conduit. In these cases the cigarette burn will be neutral with a small surface area whereas the star centre will also

be neutral but with a bigger surface area as the conduit is usually the full length of the grain. A tubular rocket grain will be progressive as the tube increase in diameter during the burn.

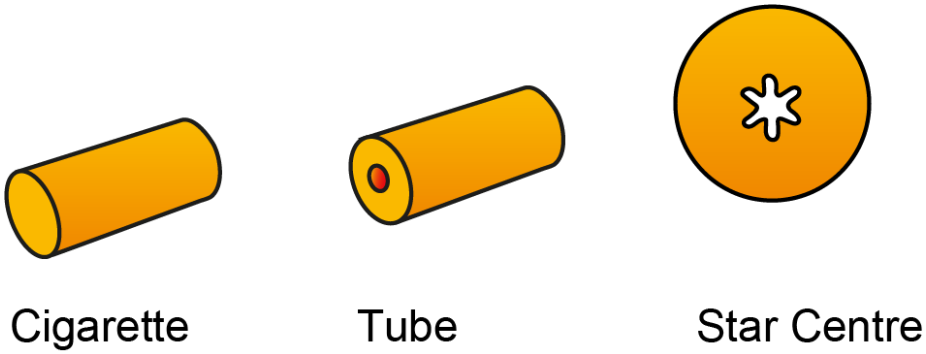


Figure 7-10 Examples of rocket propellant grain shapes

7.2.3.2 Pressure

When propellant charges burn in a gun they are under confinement within the breech and so as soon as the burning begins the pressure (P) will begin to rise, which has a major effect on the linear burning rate (r). The effect of pressure on the linear burning rate was discovered in the 19th Century and is known as Vieille's Law or de Saint Robert's Law. As pressure increases over the burning surface of an explosive the linear burning rate increases. For some applications of burning explosives such as aircraft pyrotechnic decoy flares it is equally important that as pressure decreases the linear burning rate also decreases. This relationship for non-porous homogeneous explosives is given in Equation (7-2) where a is the pressure index, n is the burning rate coefficient also called the pressure exponent. These values are particular to specific explosives.

$$r = a\,P_c^{\,n} \qquad \textbf{(7-2)}$$

7.2.4 Processes Occurring at the Burning Surface

7.2.4.1 Homogeneous explosives

The processes that occur adjacent to the burning surface are somewhat complex. For Double Base propellant, an intimate mixture of nitrocellulose and nitroglycerine, the initial release of heat is in a layer above the surface known as the fizz zone. Heat is transferred back from this zone in to the solid explosive raising its temperature and initiating chemical reaction. There is a zone following the fizz zone called the dark zone where little additional heat is released before the final chemistry occurs in the flame zone. This is shown diagrammatically in Figure 7-11 Temperature increase from unreacted explosive to final products. The linear burning rate is controlled by any factor that affects the heat flux from the fizz zone back to the burning surface. These include pressure that decreases the length of the dark zone and increases fizz zone temperature and also energy density of the explosive.

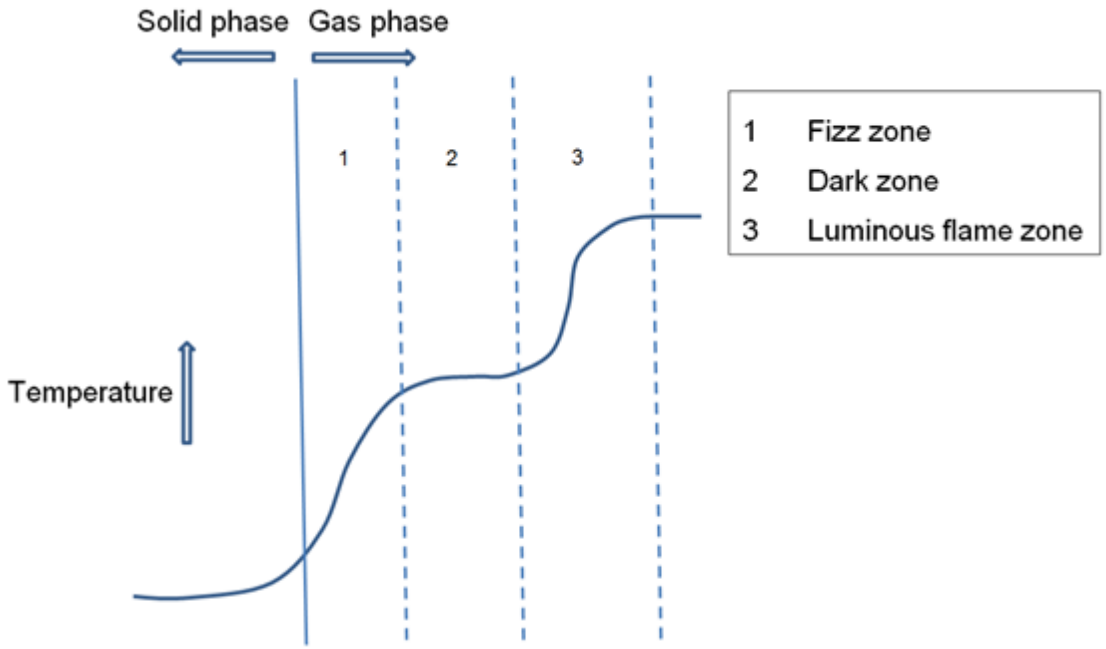


Figure 7-11 Temperature increase from unreacted explosive to final products

7.2.4.2 Heterogeneous explosives

When solid oxidisers such as ammonium perchlorate are present in a burning explosive such as composite rocket propellant the processes that are occurring differ from those that occur for homogeneous explosives. This propellant consists, in its simplest form, of a matrix of ammonium perchlorate (AP) crystals, which may vary in size from 50 – 400 µm, set in to a polymeric fuel binder such as hydroxyterminated polybutadiene (HTPB).

In this combustion process the AP crystals undergo exothermic decomposition although the products of this still contain oxidising chemical species. This decomposition is driven by the heat evolved in the overall combustion process, which also cause the HTPB to break down in to volatile pyrolysis products. A final diffusion flame is produced where the oxidising chemicals from the AP mix and react with the HTPB pyrolysis products producing the final reaction products of the propellant combustion.

As for homogeneous explosives Vieille's Law can often be applied to heterogeneous explosives but here a major influence on burning rates is the particle size of the AP in the mixture.

7.3 THE DETONATION PROCESS

7.3.1 Introduction

Detonation is defined as a chemically sustained shock wave that is a steady state phenomenon, with an associated characteristic velocity. Unlike

burning/deflagration where heat transfer by radiation and convection dominates the reaction rate, detonation is governing by the energy released from chemical reaction supporting the shockwave. Initially, the products move in the same direction as the shockwave. The rate at which a detonation front propagates through a detonating explosive is known as the detonation velocity, D. As detonation is a shockwave it must be travelling faster than the speed of sound in the material, which for explosives is approximately 1800 m s^{-1}.

7.3.2 Wave Propagation

7.3.2.1 Stress waves

If materials are loaded at a relatively low pressure / deformed at a relatively low rate-of-strain (typically < 1 GPa and 10^5 /s respectively), a stress wave will be established. Such waves are dispersive, with the amplitude varying smoothly across the wave profile and reducing with both propagation distance and time as shown in Figure 7-12; e.g. lower pressure portions of the wave propagate at a higher velocity than higher pressure portions.

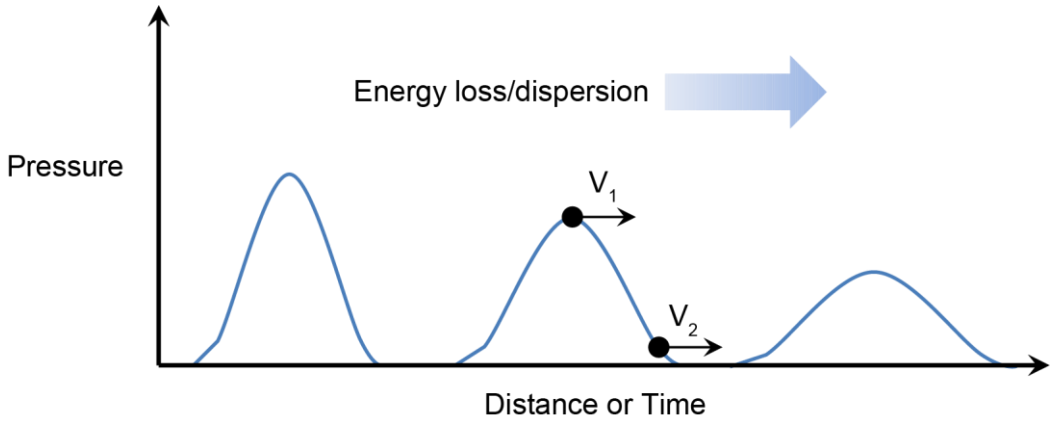


Figure 7-12 Schematic illustration of a stress wave (velocities at higher pressure portions of the wave are less than those at lower pressure portions, e.g. $v_1 < v_2$)

7.3.2.2 Shockwaves

Unlike stress waves, shockwaves are not dispersive. When materials are either loaded at a very high pressure of rapidly loaded (e.g. a high strain-rate) there is insufficient time for momentum to be transmitted away from the point of loading. Consequently, material momentum is entirely confined along the direction of loading with the material said to be 'inertially confined'. Under such circumstances, for example where an explosive is detonated on the surface of a piece of metal, a shockwave will be established, with higher pressure portions of the wave initially moving more rapidly until a discrete front is established as shown in Figure 7-13.

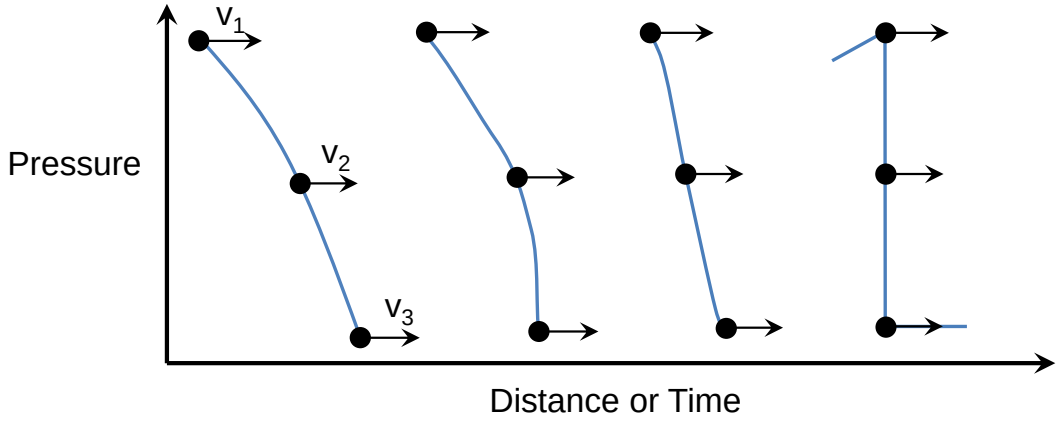


Figure 7-13 Schematic illustration of the formation of a shock wave (velocities at higher pressure portions of the wave are faster than those at lower pressure portions, e.g. $v_1 > v_2 > v_3$)

As a vertical front, a shockwave represents a sudden change from one set of state variables (temperature, pressure, etc.) to another. Such behaviour, while initially slightly counter intuitive, is, in reality, relatively common-place. The reader will be familiar with the concept of a shockwave in air, e.g. as an aircraft breaks the speed of sound at a given altitude. This example provides insight into some key areas associated with shock physics namely:

1. A shock is only formed when the aircraft is moving faster than the speed of sound in the medium (air) through which it is propagating. In this circumstance the system is said to be 'overdriven', and
2. The speed of sound in air changes with altitude. This is primarily due to the change in air density with altitude, a concept which applies more generally for both shock and detonation waves, where velocities are faster in denser systems.

Addressing the points highlighted above, in solid material, longitudinal elastic sound speed (c_L) is a function of density (ρ) and Young's modulus (E) and may be calculated from Equation (7-3).

$$c_L = \sqrt{\frac{E}{\rho}} \qquad \textbf{(7-3)}$$

In turn, the bulk sound speed (c_0) in a material is related to c_L and the shear wave speed (c_s), which is always < c_L, by Equation (7-4).

$$c_0^2 = c_L^2 - c_s^2 \qquad \textbf{(7-4)}$$

Consequently, it is immediately apparent from Equation (7-3) that supported sound speeds will be lower in lower density materials. As well as density, often referred to as specific volume (v) where $v = 1/\rho$, there are four additional

variables which define a shock. These are the velocity of the front itself, U_s, the velocity of the continuum elements (particles) which propagate the shock, u_p (with $u_p < U_s$), the amplitude of the pressure / stress established by the shock (P / s) and the change in material internal energy which results from the passage of the shock, E. Relationships between any of these two variables, when combined with application of the laws of conservation of mass, energy and momentum across the shock front, are sufficient to define the entire set of unknowns. Such relationships are known as Hugoniot equations-of-state.

7.3.2.2.1 Equations-of-state

Typical examples of such equation-of-states are presented in the Pressure-volume plane in Figure 7-14, where data from the literature for a variety of low density materials including the polymeric material Sylgard®(1).

Figure 7-14 shows both experimental data-points and a best-fit to the data following Equation (7-5) which is based on the conservation of momentum across a shock front, where the subscripts '0' and '1' refer to initial and final material states respectively.

$$P_1 - P_0 = \rho_0 U_s u_p \quad \textbf{(7-5)}$$

From the curves presented in Figure 7-14 it can be seen that as the material is compressed, as expected, pressure increases. However, it should be emphasised that the hydrodynamic (fluid-like/P) curves fitted to this data do not represent a continuum. In line with the fact that a shock, by definition, represents a sudden and discreet change in state variables, a Hugoniot curve of the type shown in Figure 7-14 simply represents a loci of physically accessible end states from a given initial state (typically for the Hugoniot curve 'ambient' conditions). Consequently, if a change in initial state variables should occur (e.g. a change in initial environmental conditions, a phase change such as the reaction of an explosive during the detonation process or initial mechanical pre-loading, etc.), then use of a new equation-of-state may be required centred on this new initial state. Such a situation is illustrated in Figure 7-15 for the situation where an impacted material is loaded for a second time.

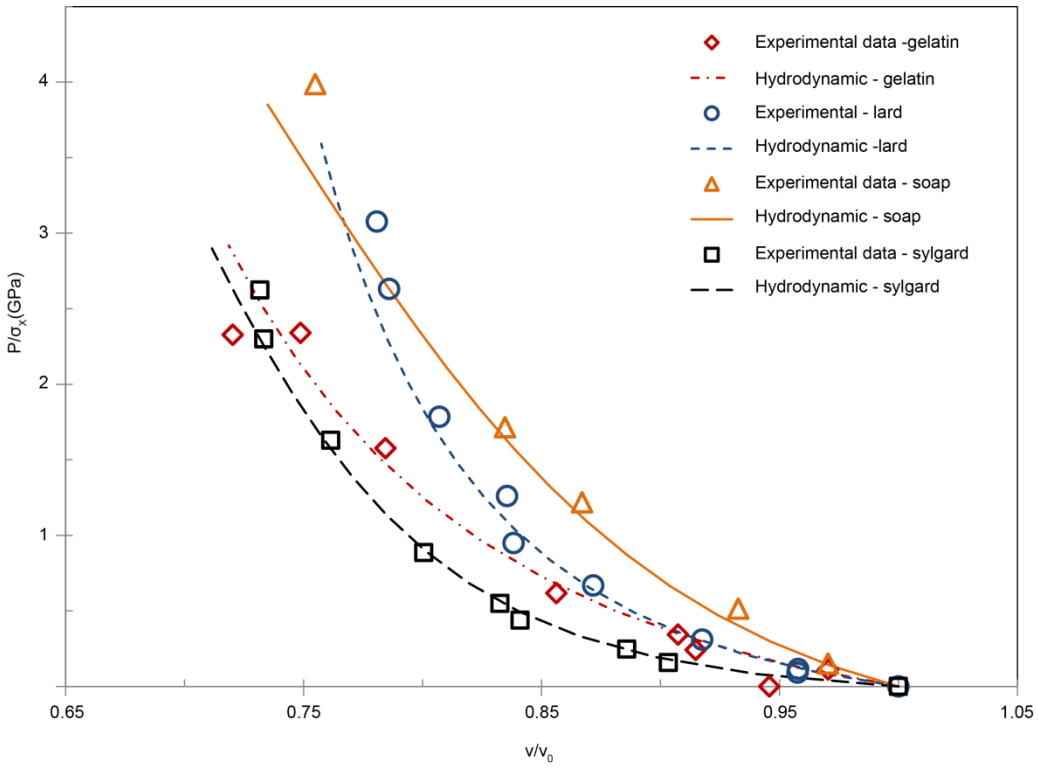


Figure 7-14 Hugoniot equations-of-state in the P-v plane for a selection of low density materials[1]

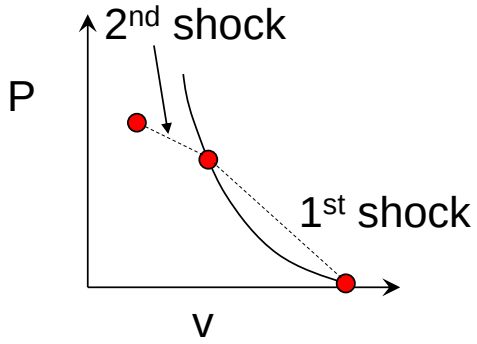


Figure 7-15 Schematic illustration of the effects of a second loading event on a pre-shocked material (Hugoniot centred on the initial ground state shown as a solid black curve)

7.3.2.2.2 Generic equations-of-state

Use of multiple equations-of-state to describe complex loading events would be impractical, primarily due to the cost (both temporally and fiscally) in terms of the resultant requirement to derive new equations-of-state centred on every potential loading scenario which could lead to the final loaded state. To this end, generic forms of the equation-of-state are often employed which allow

prediction of multiple loading paths without explicit knowledge of equation-of-state curves centred on every possible loading eventuality. A useful semi-empirical form for material equations-of-state is the Mie-Grüneisen form as shown in Equation (7-6).

$$\mathrm{P}(v,e) = \mathrm{P}_0(v) + \frac{\Gamma(v,e)}{v}[e - e_0(v)] \qquad \textbf{(7-6)}$$

$\mathrm{P}(v,e)$ represents the pressure at a given volume v / internal energy e; Γ is a value known as Grüneisen gamma which is linked to key thermodynamic properties, and; the system starts at the initial state described by the subscript '0'.

Equation (7-6) essentially describes an equation-of-state surface in the Pressure-Volume-Energy plane, with Γ controlling the curvature of the resultant surface. As an example, an equation-of-state surface calculated using Equation (7-6) for the epoxy resin RTM6 is shown in Figure 7-16. As illustrated in this figure, the Hugoniot equation-of-state describes one allowed curve across this permissible (shock phase-space) surface. Such a generic equation-of-state would therefore allow the calculation of material end-state following multiple loading events, subject to the caveat that no change in state (phase change or similar) occurs.

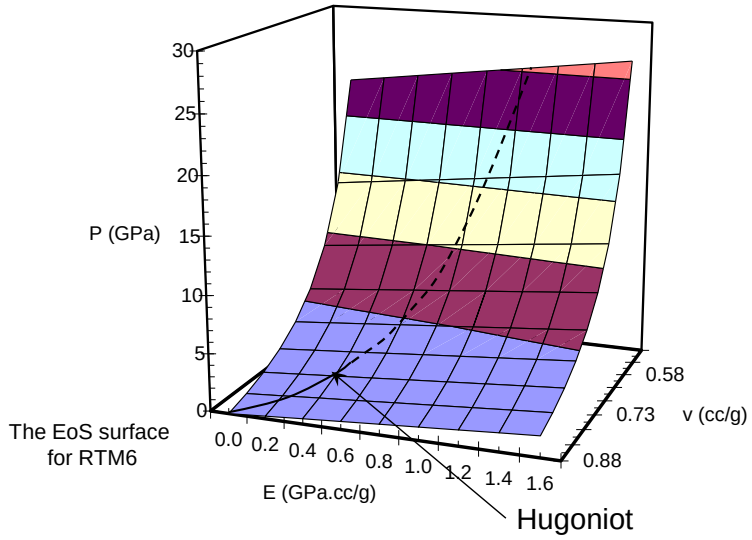


Figure 7-16 Generic equation-of-state surface for RTM6[2] (Γ assumed equal to unity)

7.3.2.3 Impedance and shock wave reflection (scabbing / spall)

When a stress of shock wave encounters an interface, the nature of the subsequent transmitted and reflected waves is a function of the properties of the materials either side of the interface. Wave interaction is governed by a property known as impedance (Z), defined in Equation (7-7). Where ρ_0 is the initial material density and U_s the shock speed under given loading conditions.

$$\mathrm{Z} = \rho_0 U_s \quad \textbf{(7-7)}$$

However, in the event that the material is in the elastic regime, Z is termed acoustic impedance and $U_s \rightarrow c_L$ as defined in Section 7.3.2.2. In general, the use of acoustic impedance is sufficient to predict the nature of wave interaction across an interface. This allows for the following modification to be made to Equation (7-7).

$$\mathrm{Z} = \rho_0 c_L = \rho_0 \sqrt{\frac{E}{\rho_0}} = \sqrt{\rho_0 E} \quad \textbf{(7-8)}$$

Knowledge of the impedance of different materials can subsequently be used to predict wave propagation across an interface from material A to material B via conservation of force (equilibrium) and particle velocity (continuity) across the interface (Equations (7-9) and (7-10) respectively).

$$\sigma_A + \sigma_B = \sigma_C \quad \textbf{(7-9)}$$

$$\mathrm{u}_A - \mathrm{u}_B = u_C \quad \textbf{(7-10)}$$

For a two-layer system as shown in Figure 7-17, such an approach leads to Equation (7-11) which, combined with the equilibrium and continuity equations, allows calculation of the transmitted stress across the interface.

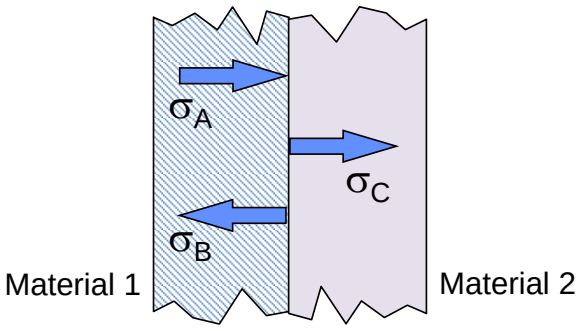


Figure 7-17 Schematic illustration of wave transmission/reflection at the boundary of two materials of differing impedance

$$\sigma_C = 2\left[\frac{Z_2}{Z_2 + Z_1}\right] = 2\left[\frac{\sqrt{\rho_2 E_2}}{\sqrt{\rho_2 E_2} + \sqrt{\rho_1 E_1}}\right]\sigma_A \quad \textbf{(7-11)}$$

From Equations (7-9) and (7-11), the effect of removing the rear-most material in Figure 7-17 (leading to an air or 'free' rear surface) is apparent. Essentially, E_2 and ρ_2 will $\rightarrow$ 0, leading to a reflected stress wave, σ_B, with the opposite sign

and same magnitude as the originally incident wave. Assuming an initially compressive loading, such a reflection will therefore be tensile in nature. This phenomenon is exploited in the High Explosive Squashed Head (HESH) round. As illustrated schematically in Figure 7-18. This munition deposits and subsequently detonates an explosive charge on the surface of a target (e.g. armour plating on a vehicle); the resultant compressive wave reflects at the rear surface of the target as a tensile wave, moving back into the target. Eventually, the material will enter a state of net tension. At this point, as materials are, in general, very-much stronger in compression that tension, the target will fail under dynamic tensile loading and a plate of material (a 'scab') will spall / separate, moving away in the direction of the initial compressive loading.

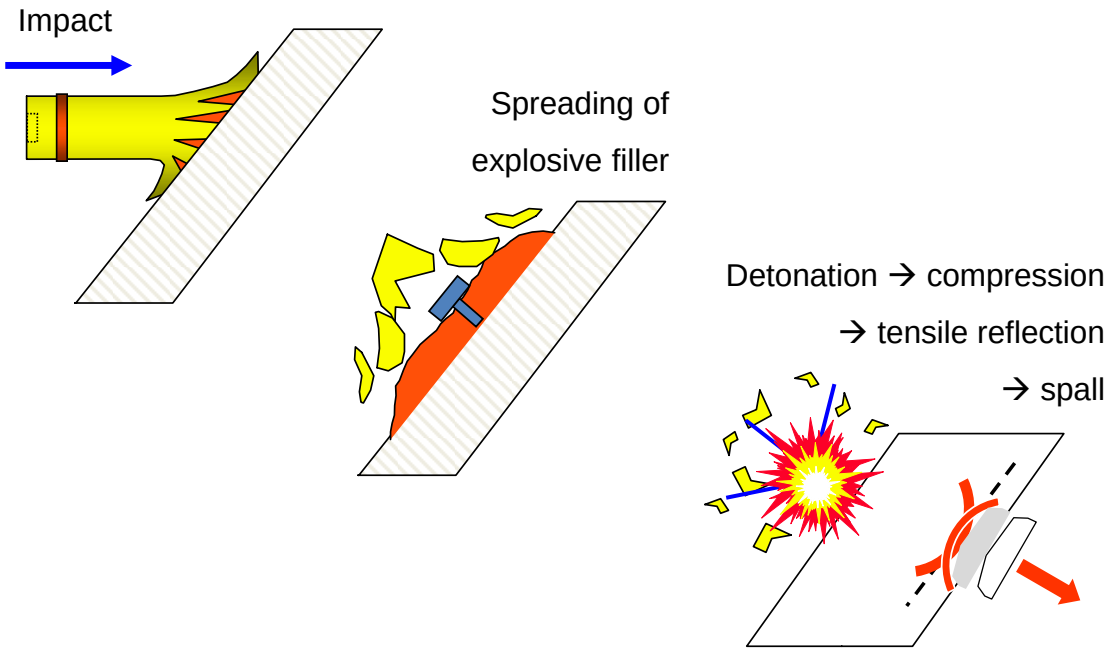


Figure 7-18 Schematic illustration of the operational stages of attack by a HESH round on armour

7.3.3 Detonation Physics

7.3.3.1 Detonation waves

Detonation consists of the passage of a shock wave through an explosive supported by the energy released by chemical reactions. As the detonation wave passes through an explosive there exist three core zones, with these highlighted for a one-dimensional case in Figure 7-19, namely: (1) un-reacted material ahead of the detonation wave; (2) a reaction zone where chemical reaction occurs, releasing the energy which supports the detonation, and; (3) a zone behind the reaction zone containing the resultant gaseous products at elevated pressure and temperature which provides useful work. This expanded region of gas is known as the Taylor release wave. The detonation / shock front

itself exists at the border of the reaction zone and the un-reacted material; however this is infinitesimally small and consequently neglected here.

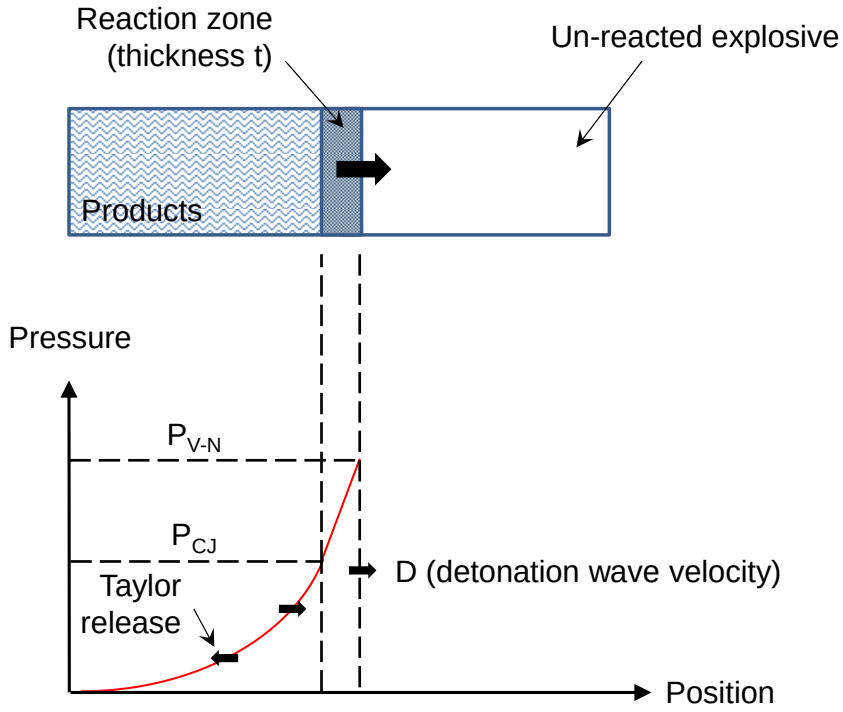


Figure 7-19 Detonation wave propagating into un-reacted explosive (scale of reaction zone exaggerated for clarity)

Figure 7-19 also highlights the waveform which results from the detonation process, generally known as a Taylor wave (although strictly, this term refers to the release portion of the wave behind the detonation front only). It comprises several key features, namely:

- A spike to a peak, known as the von-Neumann pressure P_{V-N}, at the interface between the reaction zone and the un-reacted explosive (e.g. at the shock / detonation front). This peak rapidly decays behind the front (the scale of the reaction zone is exaggerated in Figure 7-19 for clarity).
- A lower pressure, known as the Chapham-Jouguet (CJ) pressure – P_{CJ}, representing the pressure at the interface between the reacted and un-reacted explosive.
- An exponential-like drop-off in pressure behind the reaction zone caused by the change in chemistry of the detonation products. Essentially, as the detonation wave is now un-supported it is released back down the isentrope along a Taylor wave from the CJ pressure back to the ambient conditions for the detonation products.

As detailed in Figure 7-19, the detonation reaction is finished at a point corresponding to the CJ pressure. This interface between the reaction zone and the detonation products, known as the Chapham-Jouguet interface, must be moving at the same rate as the main detonation front if the process is to be

considered stead-state, thereby maintaining a constant reaction zone thickness. In practice, as shown in Equation (7-12), the velocity of the reaction zone relative to the un-reacted explosive (e.g. the detonation velocity, D), is simply the sum of the sound (shock) speed (C) within the compressed gas found at the CJ interface and the particle velocity across the CJ interface ($u_{p\text{-}CJ}$).

$$D = C + u_{p-CJ} \quad \textbf{(7-12)}$$

Usefully, the structures highlighted in the wave-form presented in Figure 7-19 can be related back to the Hugoniot equations-of-state for the explosive. Unlike inert materials, because a change in phase occurs as detonation breaks out two separate equations-of-state are required to fully describe an explosive. These separate equations-of-state are those for the un-reacted explosive and the detonation products respectively. Usefully, the various features present on the detonation wave in Figure 7-19, such as the von-Neumann pressure, can be resolved from these two characteristic equation-of-state curves. This is illustrated in Figure 7-20.

Particular features apparent in Figure 7-20 are as follows:

- The Hugoniot curve for the detonation products lies above that of the unreacted material, e.g. the detonation products have a lower density than the unreacted material (it is this expansion which allows for useful work).
- The gradient of a Hugoniot curve is a function of wave velocity; in order for the detonation wave detailed in Figure 7-19 to move at a constant velocity, the rate of propagation of the reaction zone behind the front must be equal to that of the detonation front itself. Consequently, the Rayleigh line followed by the reacting explosive must lie on a tangent to the detonation production Hugoniot curve through the initial volume (v_0); a steeper curve would cause the detonation wave to be caught via the reaction zone, whereas a less-steep tangent would lead to dispersion of the detonation front, both non-physical options for steady-state detonation.
- Such a tangent to the detonation products Hugoniot curve through the initial volume (v_0) intercepts the detonation products Hugoniot at the Chapham-Jouguet pressure and the unreacted explosive Hugoniot at the von-Neumann pressure.
- The gradient of the aforementioned tangent is $(\rho_0 D)^2$; consequently, knowledge of the initial volume and Hugoniot curves for both reacted and unreacted explosive allows calculation of the detonation velocity e.g. in Figure 7-20, taking ρ_0 = 1.6 g cm^{-3}, D = 7.6 x 10^3 m s^{-1}.

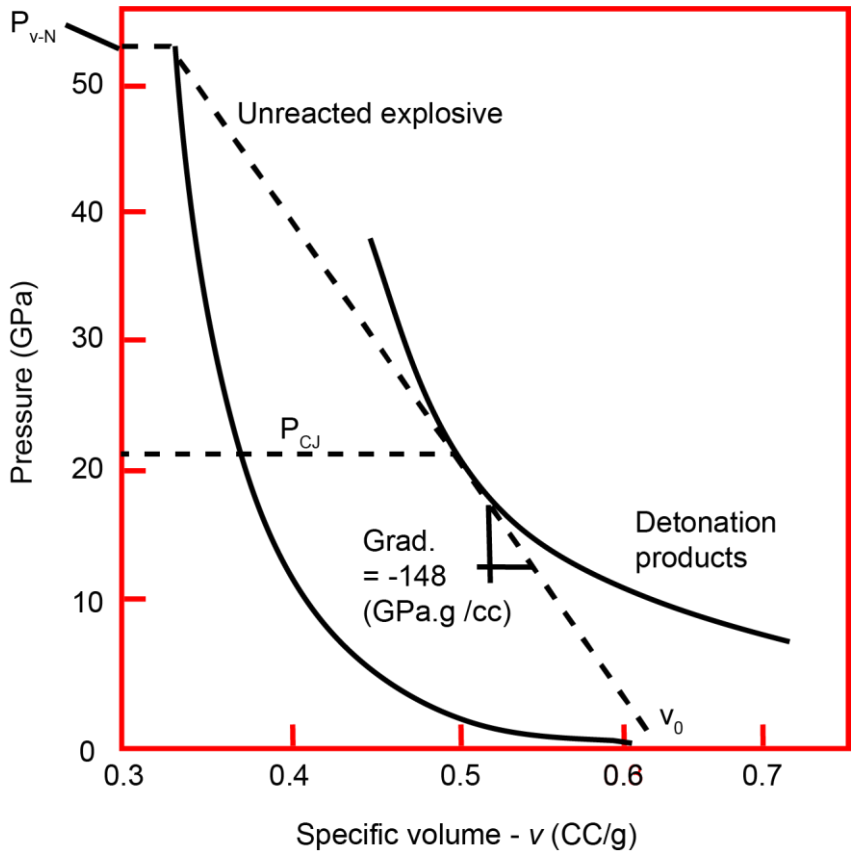


Figure 7-20 Illustration of the relationship in the P-v plane for equations-of-state of un-reacted explosive and resultant detonation products[3]

7.3.3.2 Equations-of-state – energetic materials

As discussed in Section 7.3.2.2, conservation of mass, energy and momentum across the shock front allow description of a shocked system. The same continuity equations apply for an explosive, however, additional account needs to be made of key thermodynamic factors. Further, as the system is reacting, in line with the description set out in Figure 7-20, to form an equation-of-state which allows prediction of key state variables, Hugoniot relationships are required for both the un-reacted explosive and the resultant detonation products. Several different approaches exist with regards to prediction of the detonation behaviour of an explosive. If the chemistry of the products is treated explicitly, the final-state equation-of-state may be calculated from a weighted combination of the individual product / component equations-of-state (e.g. application of a 'rule-of-mixtures' approach). Such chemical equilibrium based approaches are implemented in a number of thermochemical / hydrodynamic computational codes, in particular the Fortran BKW implementation utilised, for example, in the CHEETAH code[4].

Alternatively, an explicit equation-of-state will be required. Semi- and fully-empirical forms of the equation-of-state for explosive systems / products are relatively commonly employed. The disadvantage of such approaches is that

they require the use of experimentally measured constants for specific explosive compositions, for example, constants derived for a given composition with a given initial pressed density, rather than necessarily being based upon underlying physical principles, something which would allow scaling to different compositions. Forms of the equation-of-state employed for energetic materials range from versions based on the Ideal gas law through to purely empirical forms for detonation products where constants have typically been experimentally measured for given common explosives. Typical equations-of-state adopted by the shock / explosives community include the thermal relation-based Kuznetsov-Shedov equation focused on RDX and the more general semi-empirical Brinkley-Kistiakowsky-Wilson (BKW) relation, which accounts for the molecular weight of detonation products. A further example of such an approach is widely employed the Jones-Wilkins-Lee (JWL) formulation.[5, 6] This equation, which takes the general form shown in Equation (7-13), with typical values for experimentally measured constants for a variety of different explosives presented in Table 7-1, allows prediction of behaviour (in particular the expansion isentrope) from CJ state parameters.

$$\mathrm{P} = Ae^{-R_1\frac{v}{v_0}} + Be^{-R_2\frac{v}{v_0}} + \mathrm{C}\left[\frac{v}{v_0}\right]^{-[1+\omega]} \qquad \textbf{(7-13)}$$

Table 7-1 Typical JWL equation-of-state constants for selected explosive compositions (Table / data from Ref.[6])

Explosive composition	CJ parameters			JWL parameters					
	ρ_0 (g/cc)	P_{CJ} (GPa)	D (mm/μ s)	A (GPa)	B (GPa)	C (GPa)	R_1	R_2	ω
Composition B	1.717	29.5	7.98	524.2	7.678	1.082	4.20	1.10	0.34
HMX	1.891	42.0	9.11	778.3	7.071	0.643	4.20	1.00	0.30
PETN	0.880	6.2	5.17	348.6	11.29	0.941	7.00	2.00	0.24
TNT	1.630	21.0	6.93	371.2	3.231	1.045	4.15	0.95	0.30

Essentially, Equation (7-13) acts as the reference pressure, $P_0(v)$, in a Mie-Grüneisen description of both un-reacted and detonation products, in line with Equation (7-6). With such a formulation, Γ is typically assumed to be constant in value for simplicity[5].

7.3.3.3 Effects of charge diameter

Detonation in a given explosive has been shown to only be supported once the diameter of a charge exceeds a given critical size. Further, detonation velocity is found to vary with charge diameters for lower diameter values, with a constant velocity only obtained once the charge becomes sufficiently wide that it

may be considered semi-infinite in scale (e.g. the outer edges of the charge have no influence on the central detonation region). This phenomenon has been linked to the thickness of the reaction zone (Figure 7-19), with the behaviour of explosives with thinner reaction zones showing less dependence on charge diameter. The general form for the relationship between charge diameter and detonation velocity is shown in Figure 7-21.

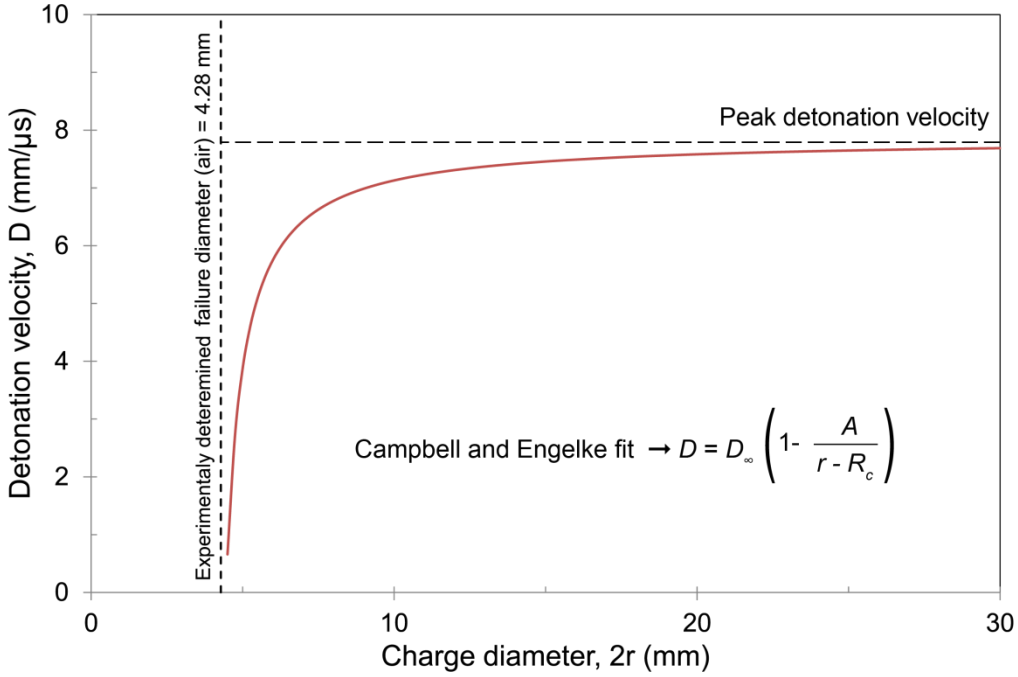


Figure 7-21 Variation of explosive detonation velocity with charge diameter (2r) for Composition B, based on Campbell and Engelke fit data[6]

Several features are apparent in Figure 7-21 including:

- At higher charge diameters the detonation velocity can be observed to asymptote towards a constant / peak value.
- At lower charge diameters an exponential drop-off in detonation velocity is observed, with a critical diameter below which detonation cannot be sustained.

7.3.3.4 Hot spots

In solid polycrystalline explosives, detonation has been strongly linked to the presence of regions within the material where shock loading can lead to significantly elevated local heating. These hot-spot (see 5.3) regions are thus considered the likely source for initiation of the detonation process, with hot-spot density therefore of key import in terms of explosive sensitivity (see Section 7.3.4). Six key mechanisms which can lead to such localised heating under shock loading / compression have been identified and are detailed below[3, 7]:

1. Jetting of explosive material between the explosive's grains

2. Collapse of pores (with high temperatures reached when the collapsing inner walls of the voids collide)
3. Viscous heating, e.g. due to plastic material flow around pores
4. Localised shock ring-up due to the presence of higher-impedance particles / inclusions
5. Frictional heating due to differential particle flow
6. Formation of adiabatic shear bands (a plastic failure mechanism which leads to significant localised heating).

7.3.4 Effects of Pressure – POP (Popolato) Plots

For a heterogeneous explosive where hot-spot formation is crucial to detonation, pressure has been observed to play a key role in sensitivity to initiation. This is illustrated in Figure 7-22 which shows the variation with pressure of the distance required before detonation breaks out for three different varieties of PETN. Several key points may be drawn from this POP plot:

- In general, run-to-detonation distance, assuming that the charge diameter is greater than the critical diameter, decreases as pressure increases. Factors influencing this behaviour include the associated higher temperatures achieved at higher pressures, which would inevitably lead to faster (shorter distance) reaction times.
- Higher density explosives are observed to require a greater pressure to obtain a given run-to-detonation distance. This is due to two effects: (1) higher density materials (e.g. those that have been pressed / compacted) will likely exhibit a lower number of pores or similar regions where hot-spot formation could potentially lead to initiation, and (2) lower pore sizes / volume fractions (due to pre-compression) will lead to lower peak temperatures on material collapse, thereby further reducing the probability of initiation / increasing the distance of sustained shock loading required for detonation to break-out.

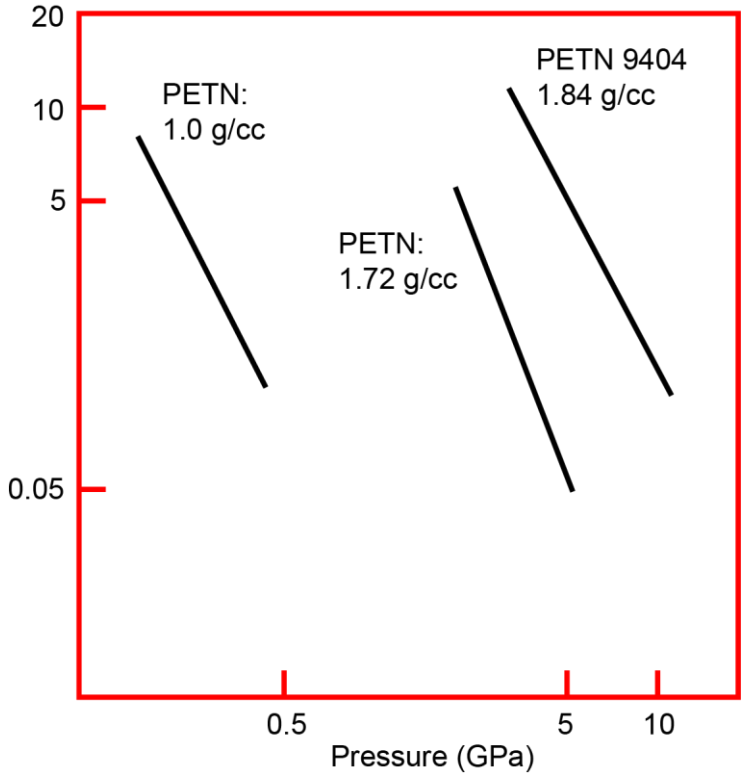


Figure 7-22 Pressure vs Distance to Initiation (POP) plot for three forms of PETN[3]

An addition observation from is that, in general, a loading pulse should have a long enough duration to subsequently span a spatial extent equal to or greater than the run-to-detonation distance if initiation is to be ensured.

7.3.5 Effect of Detonator Strength

Choice of detonator is of key importance in terms of an explosive train. In line with the observation at the end of Section 7.3.4, the loading pulse generated by a detonator needs to have sufficient temporal / spatial duration, as well as pressure, to allow detonation to break out. This is illustrated more clearly in Figure 7-23, which illustrates the result of the impact of a 10-mm thick Sintox™ flyer plate on to an explosive target containing a series of wire-element gauges measuring particle velocity (u_p) (see 7.3.2.2) in a plate-impact configuration[3]. The input pulse (in blue) is observed to have a square shape whose duration corresponds to a combination of the flyer plate thickness and impact velocity. The measured particle velocities are seen to rapidly ramp-up as the shock propagates through the explosive, indicative of a change in chemistry as detonation begins to break-out.

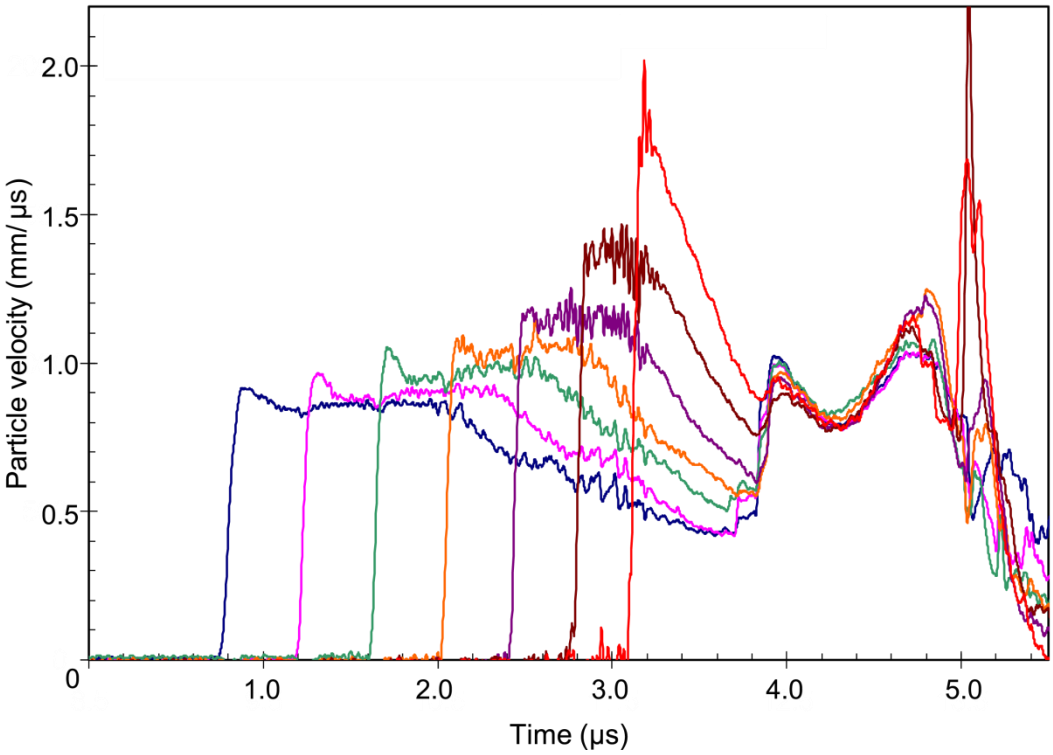


Figure 7-23 Particle-velocity traces at various depths showing the results of the impact of a 10-mm thick Sintox™ flyer plate generating an initial 5.1 ± 0.25 GPa stress in an explosive target[8]

In addition to pulse duration, the amplitude of the loading pulse also needs to be appropriate to the explosive in question. As an example of the importance of this issue, while precise details of the underlying physical causes are beyond the scope of this book, it is interesting to note that the detonation velocity of nitroglycerine is highly dependent on the method of initiation, ranging from ~1,500 to 7,700 m s^{-1}[9].

7.4 WAVE SHAPING

Detonation fronts typically propagate hemispherically away from the point of initiation. However, in order to use an explosive to achieve useful work it is often desirable to modify the nature of the detonating front. Techniques to achieve this aim can either involve modification of the detonation front within the explosive charge (internal wave shaping), or once the front has left the charge (external wave shaping).

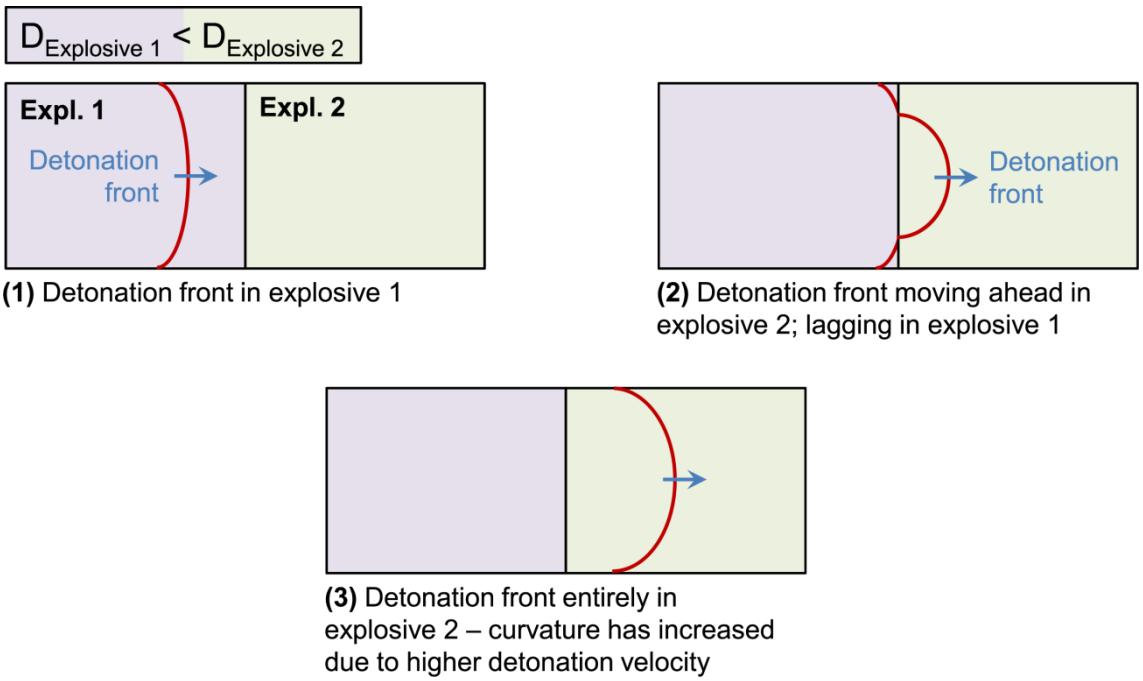
7.4.1 Internal Wave Shaping

A number of techniques exist to allow modification of the detonation front within the explosive charge itself. These range from exploitation of the different wave velocities inherent to different types of explosive to mechanical means.

7.4.2 Explosive Lenses

At the most basic level as a detonation wave crosses the interface between two explosives with different detonation velocities the wave-front will distort. This is illustrated in Figure 7-24 which illustrates a centrally-initiated hemispherically-fronted detonation wave propagating from an explosive (no. 1) with a slower inherent wave velocity to one (no. 2) with a faster inherent wave velocity. The wave-front is observed to accelerate as it crosses the boundary, leading to a greater degree of curvature once the wave has fully entered explosive no. 2.

For comparison, in Figure 7-25 an initially hemispherical wave-front propagates from an explosive with a high detonation velocity to one with a slower velocity. The net effect is a constriction of the wave with the resultant formation of a nominally planar front. The system acts as a plane-wave generator.



(1) Detonation front in explosive 1

(2) Detonation front moving ahead in explosive 2; lagging in explosive 1

(3) Detonation front entirely in explosive 2 – curvature has increased due to higher detonation velocity

Figure 7-24 Schematic illustration of the propagation of a detonation wave across a planar interface from an explosive with a lower detonation velocity ($D_{Explosive1}$) into an explosive with a higher detonation velocity ($D_{Explosive2}$)

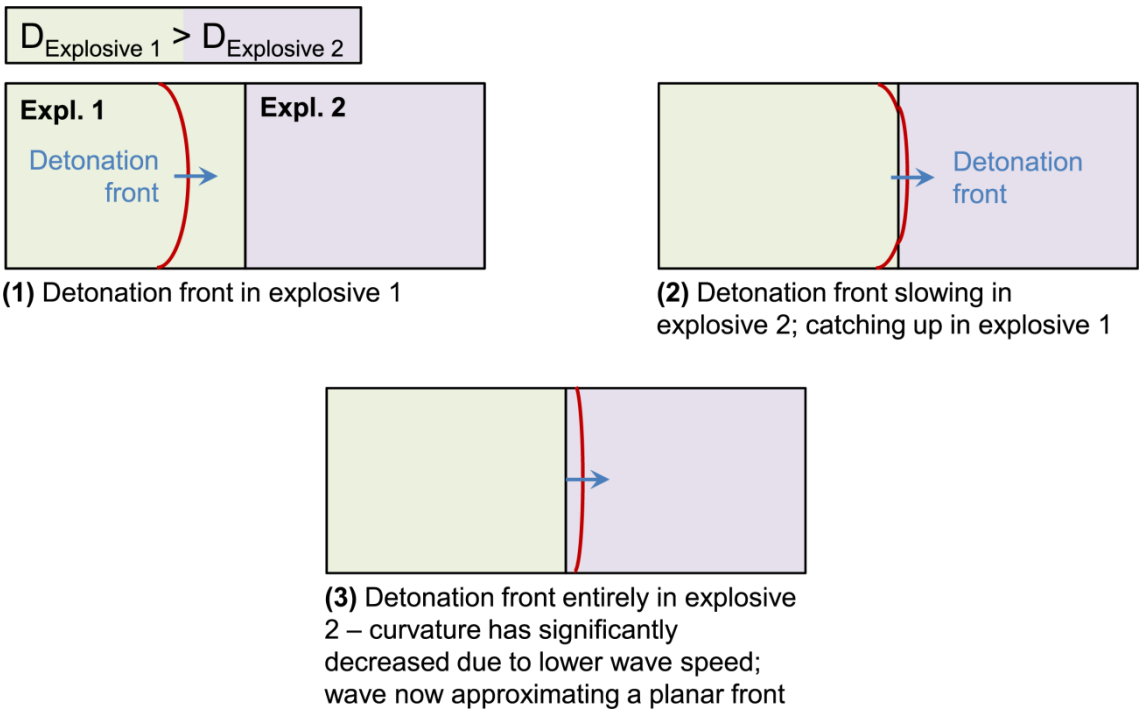
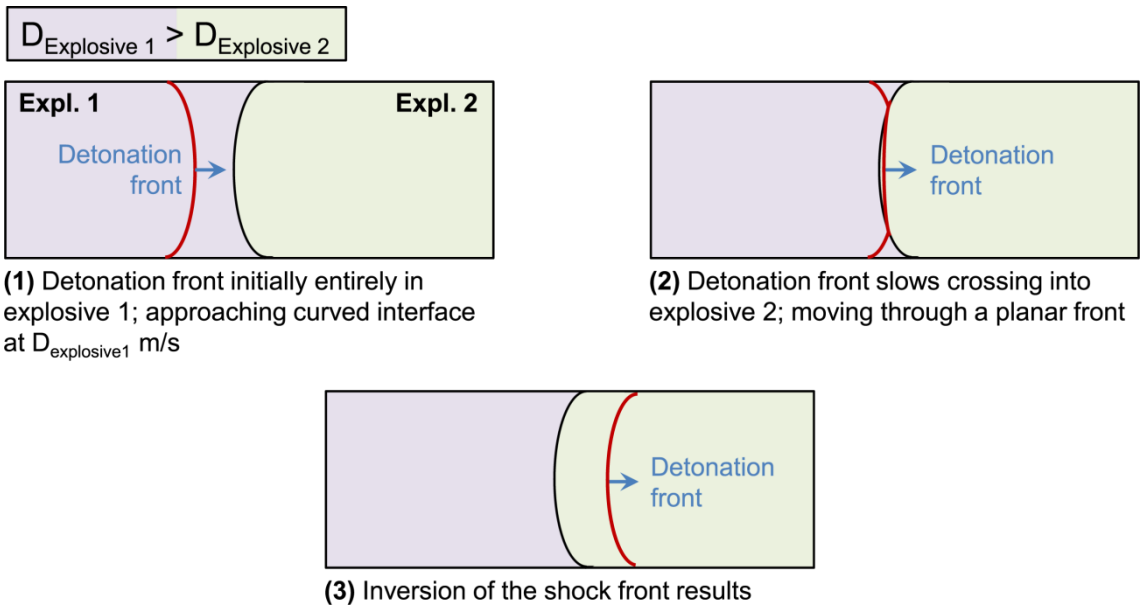


Figure 7-25 Schematic illustration of a 'plane wave generator' involving the propagation of a detonation wave across a planar interface from an explosive with a higher detonation velocity ($D_{Explosive1}$) into an explosive with a lower detonation velocity ($D_{Explosive2}$)

In addition to the influence of explosive detonation velocity, if the explosive interface has a non-planar form than additional effects can be obtained, potentially allowing for further refinement of the resultant wave shape. This is illustrated in Figure 7-26 for the case in which a hemispherical wave-front moves from an explosive supporting a high detonation velocity to one supporting a lower velocity consistent with Figure 7-25, although in this case with a curved rather than planar interface. In this case, the initially curved wave-front is modified both by a reduction in velocity and by the geometry of the interface, leading to the inversion of the curvature of the wave.



(1) Detonation front initially entirely in explosive 1; approaching curved interface at $D_{explosive1}$ m/s

(2) Detonation front slows crossing into explosive 2; moving through a planar front

(3) Inversion of the shock front results

Figure 7-26 Schematic illustration of the propagation of a detonation wave across a curved interface from an explosive with a higher detonation velocity ($D_{Explosive1}$) into an explosive with a lower detonation velocity ($D_{Explosive2}$)

From the cases presented in Figure 7-24 to Figure 7-26, it can be seen that differing combinations of explosive (e.g. wave velocities) and interface geometries would therefore allow for the formation of complex, refined, wave front structures.

A classic example of such a construct is the implosion device as used in early nuclear weapons, in which a series of hemispherical detonation waves are created via an array of explosive structures, an arrangement known as an explosive lens, to allow simultaneous arrival at, and subsequent symmetric collapse of, a central spherical structure comprising fissile material. Such an arrangement is illustrated schematically in Figure 7-27.

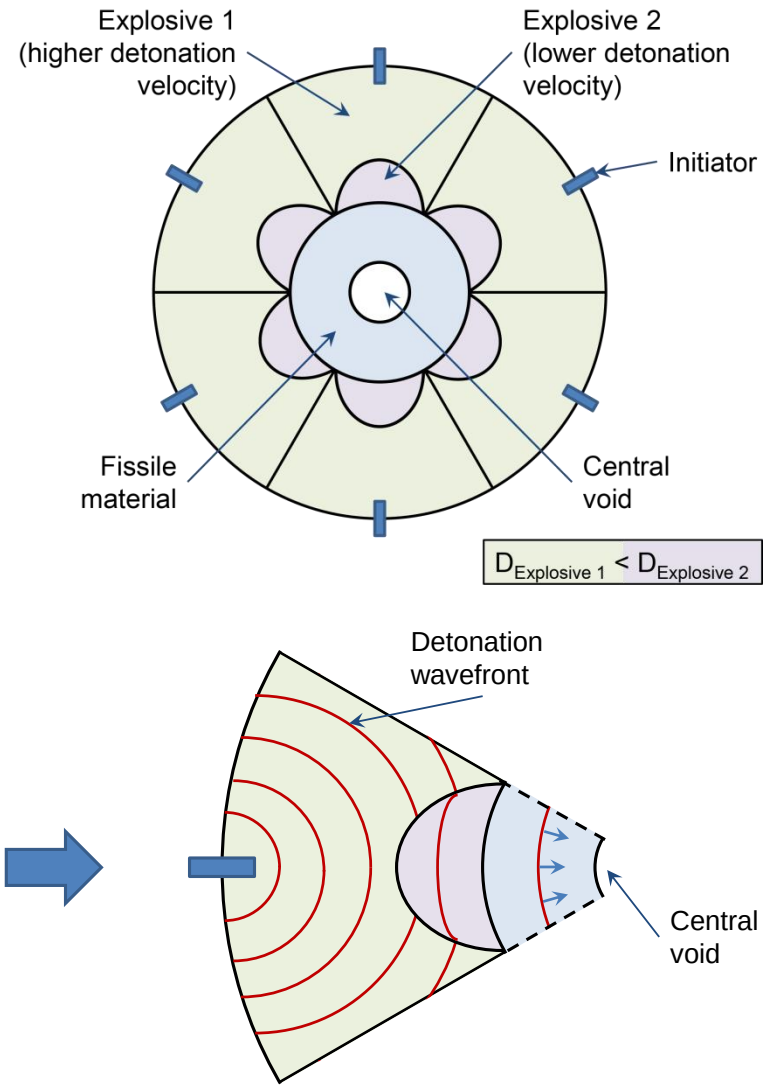


Figure 7-27 Schematic illustration of an implosion device

7.4.3 Wave Shapers

In addition to the use of differing explosives to control wave propagation, the form of a detonation front can also be modified via mechanical modification of the system. In particular, inclusion of a barrier of some description within an explosive construct will modify wave propagation. One application of such an approach lies with shaped charge warhead design (see 8.4.1). A typical shaped charge arrangement is shown in Figure 7-28. Essentially, at its most basic level, the device comprises a case containing an explosive head situated above a conical liner. On initiation from the rear of the explosive head the device is constructed such that the resultant detonation wave symmetrically loads the

liner leading to a symmetric collapse and formation of a shaped charge jet and accompanying slug of material.

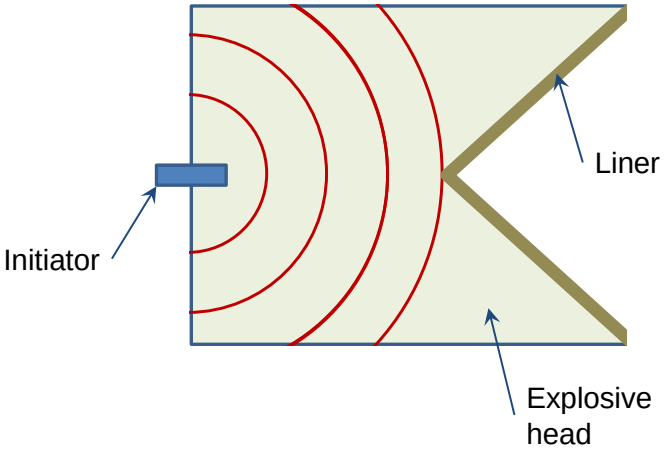


Figure 7-28 Diagram illustrating a cross-section through a typical shaped charge warhead arrangement (detonation waves emanating from the initiator indicated in red)

This arrangement can be further optimised by the inclusion of a device known as a 'wave shaper' within the explosive. The effect of such a device is illustrated in Figure 7-29, which allows for a more compact warhead. Hemispherical detonation waves are diffracted by the wave shaping insert while still ensuring simultaneous convergence of the front at radially opposite elements of the shaped charge liner.

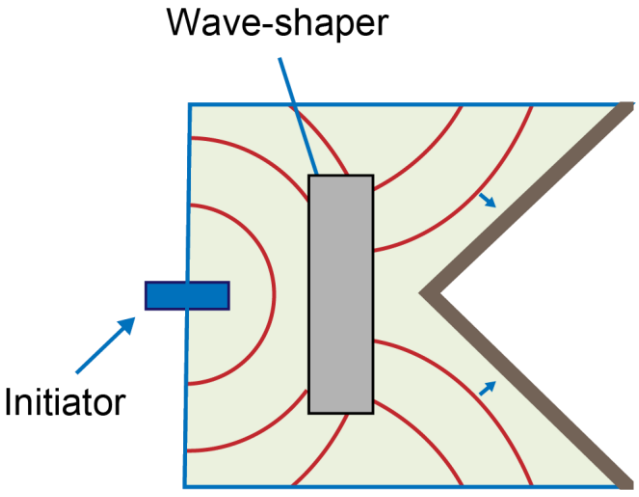


Figure 7-29 Diagram illustrating a cross-section through a shaped charge warhead arrangement containing a wave shaper / insert (detonation waves emanating from the initiator indicated in red)

Another example of a wave shaper is that of the explosive-metal ‘air-lens’. This is essence a shaped charge-like device. However, it employs a dish rather than conical linear and, rather than generating a jet to attack a target, is instead designed to exploit the reduction in wave velocity which will occur as the detonation wave meets the metallic liner. Essentially, the detonation wave will collapse the liner across the air gap leading to a reduction in wave velocity at the far side. Suitable linear geometric / material combinations can thus be used to modify the initial pulse into a more useful form, e.g. in the case of Figure 7-30 a plane-wave.

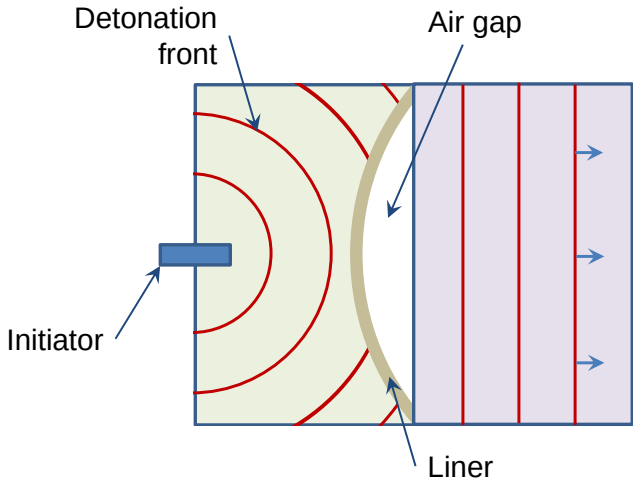


Figure 7-30 Illustration of an air-lens explosive metal wave shaper

7.4.4 Cored Charges

Approaches to modify detonation front shapes such as explosive lenses and wave shapers have a significant limitation in that in order to produce a desired output wave their construction is often complex and, consequently, expensive. One solution which allows formation of a quasi-planar wave is the cored charge. This construct, illustrated schematically in cross-section in Figure 7-31, comprises of a cylinder of explosive with a relatively low detonation velocity fitted into a surrounding bored-out larger diameter cylinder of higher detonation velocity explosive. Essentially, with such a device a hemispherically-fronted detonation wave will slow on entering the central lower wave velocity core, with outer elements of the wave then being able to catch-up / over-run the central elements. Consequently, careful design can allow the output at the far end of the device to correspond to a nominally planar front.

7.4.5 Surface (External) Wave Shaping

In an analogous manner to the way in which the internal wave shaping approaches discussed in Section 7.4.1 exploits differences in detonation velocity to modify propagating wave front geometries, it is possible to utilise the lower resultant velocity of a shock at an explosive / air boundary to create tailored wave front structures. The practical application of this effect, which

exploits the development of phenomena known as ‘Mach disturbances’, is illustrated schematically in

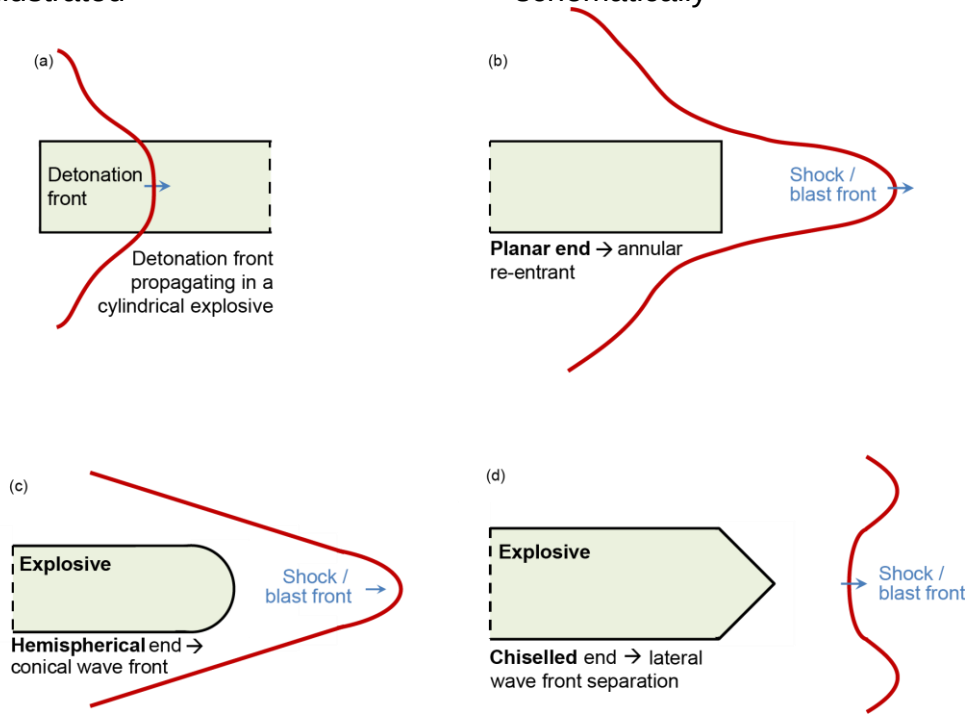


Figure 7-32. The hemispherical detonation front apparent in

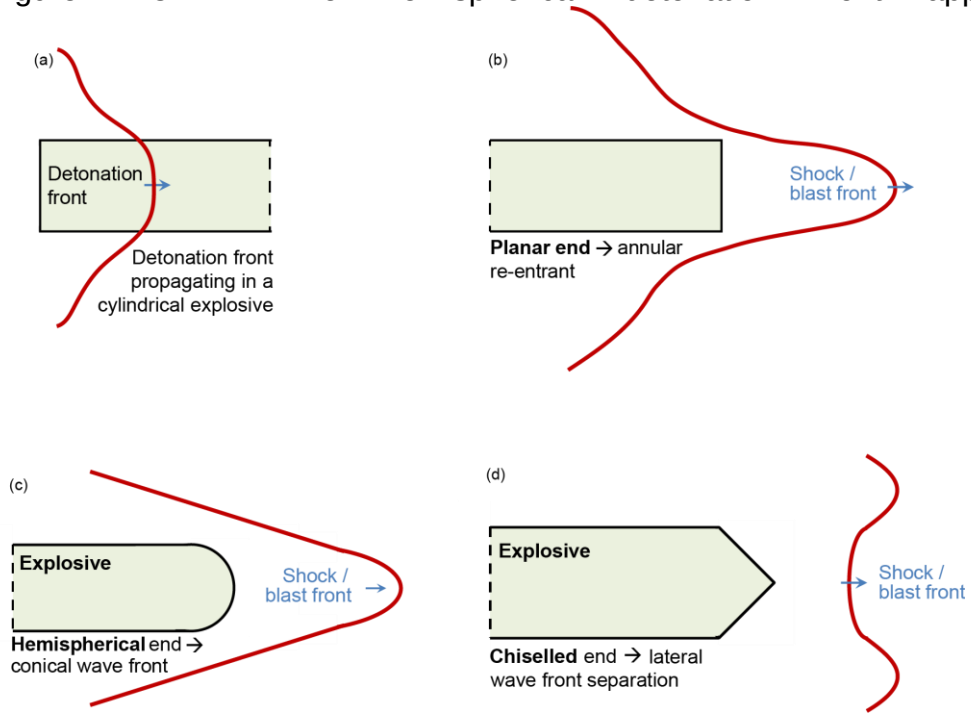
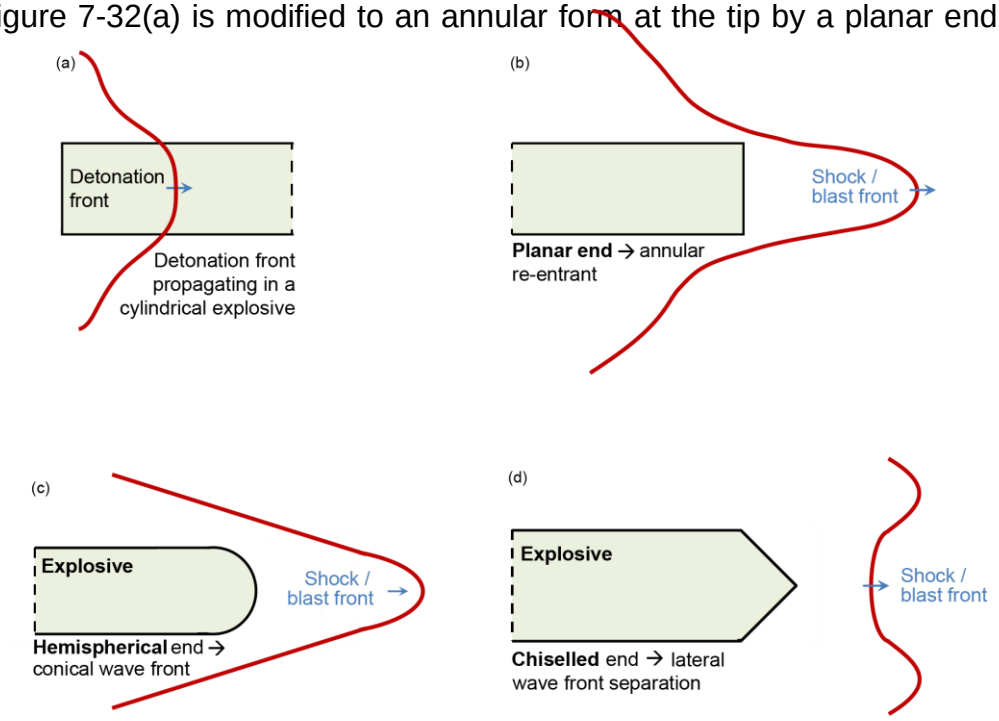


Figure 7-32(a) is modified to an annular form at the tip by a planar end section



in Figure 7-32(b); whereas in

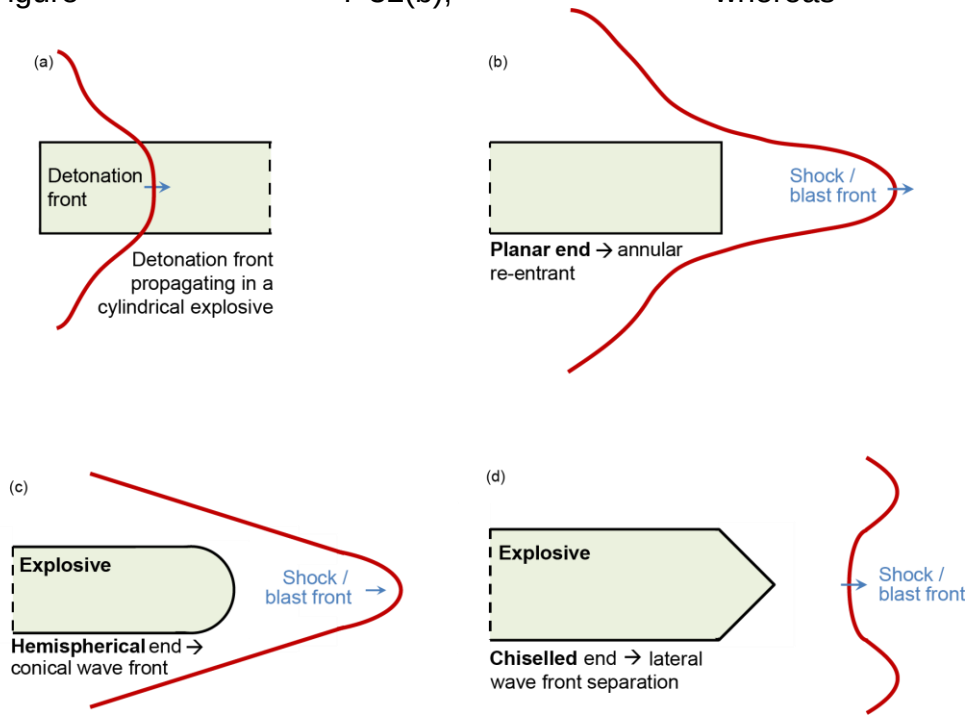


Figure 7-32(c) a hemispherical tip to the explosive leads to a conical shock / blast front, while in

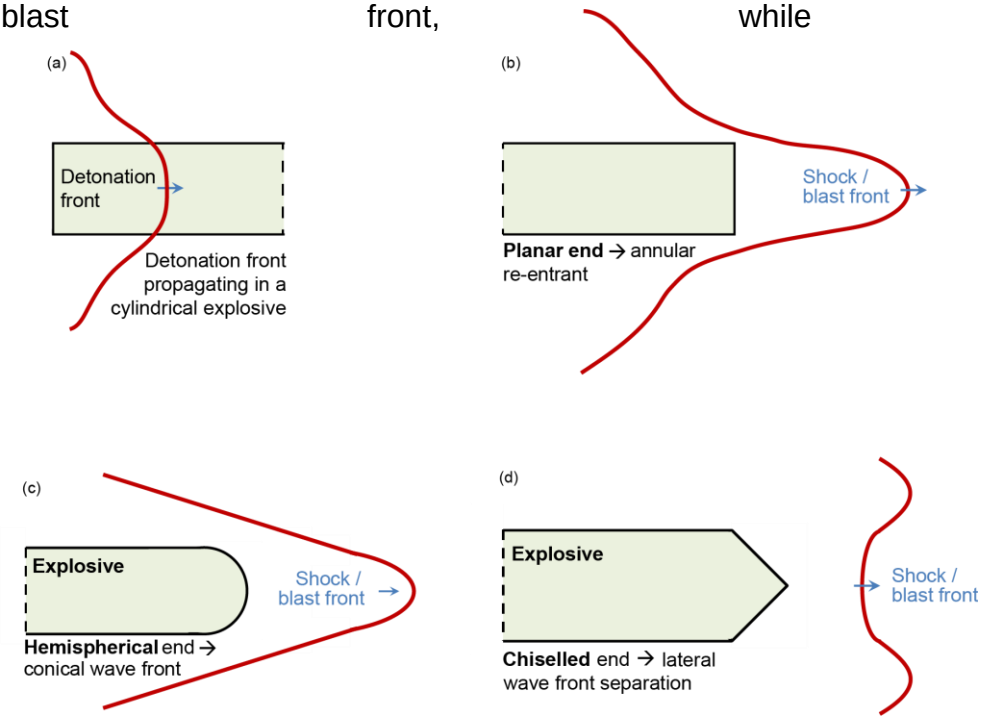


Figure 7-32(d) a wedge-shaped end section results in a laterally divergent front.

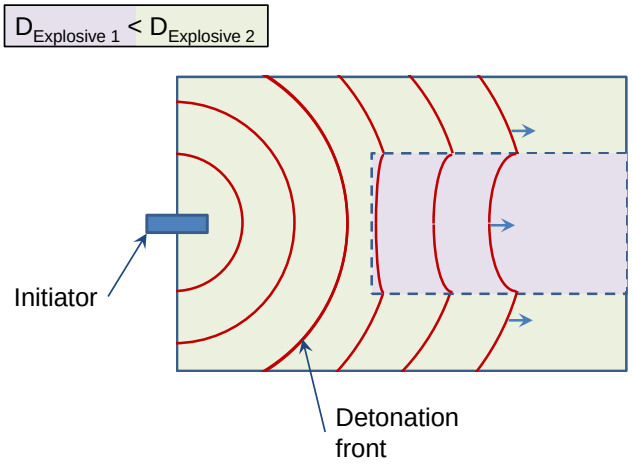


Figure 7-31 Cross-sectional illustration of a cored charge

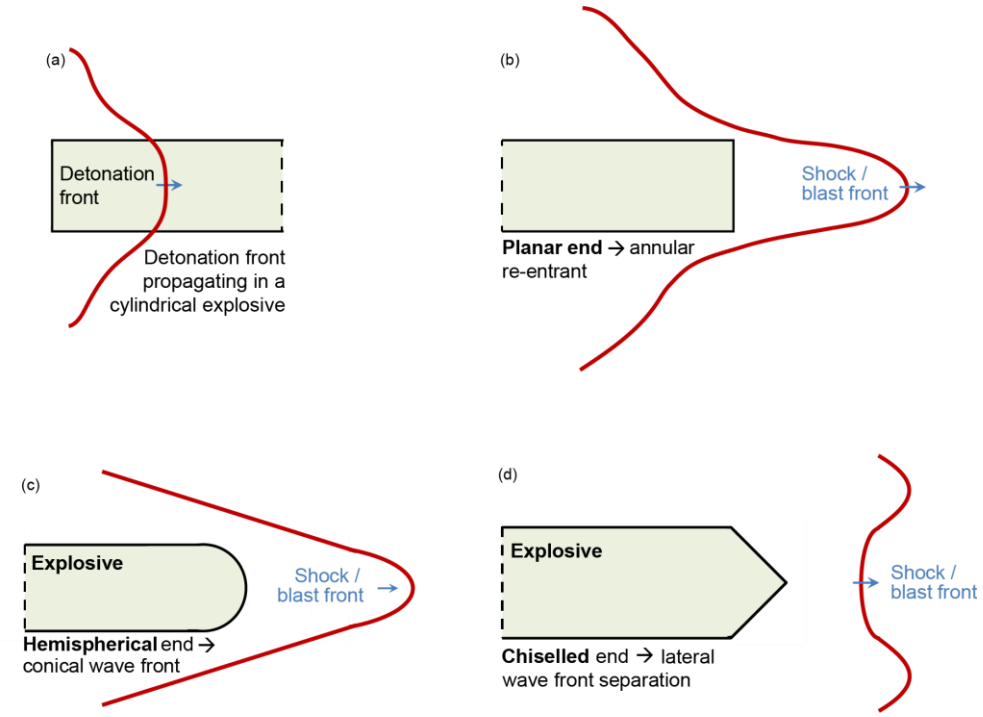


Figure 7-32 Schematic illustration of the effects of surface wave shaping (initially hemispherical detonation front in cylindrical explosive section exiting into air)

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CHAPTER 8
DETONATION EFFECTS ON METAL

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8 DETONATION EFFECTS ON METAL

Authors – G Appleby-Thomas and C A Couldrick (Cranfield University)

8.1 AWARENESS SUMMARY

8.1.1 Fragmentation

If an explosive is detonated inside a metal tube the walls of the tube are subject to intense pressure from the detonation shockwave and high pressure gas products. The strain produced on the tube causes it to plastically deform and expand. Depending on the properties of the metal such as ductility this expansion can increase the tube diameter up to 50 % before the strength is overcome and structural failure occurs. Once fractures occur the high pressure gases will begin to leak through the spaces and relieve the internal pressure. At some point the acceleration of the tube wall will cease and the metal will have a terminal velocity, the casing will separate in to fragments with this initial velocity.

This is often called primary fragmentation producing relatively small high velocity fragments (**Figure 8-1**) that can be lethal many hundreds of metres from the explosion. Initial velocities can be in excess of 2000 m s^{-1}. If a tube is filled with a deflagrating explosive such as black powder and this is initiated the tube will fragment but under these circumstances the fragments will be large and of relatively low velocity (Figure 8-2). Even so at close range these can be lethal. Metal driven by a deflagration will not be considered further.



Figure 8-1 Fragments from the detonation of an artillery shell



Figure 8-2 Metal tube following a deflagration type explosion

8.1.2 Controlling Fragment Mass and Size

Controlling the size of fragments from a warhead is critical to its lethality. To be effective they need to impact the target and so to increase the likelihood it is preferable to have a large number. However, the smaller the fragment the quicker it will decelerate and begin to lose target lethality. Increasing the mass of a fragment that has the same volume can be achieved using denser metals such as tungsten over steel and this will maintain velocity for greater distances although it also will reduce the initial fragment velocity.

8.1.2.1 Natural fragmentation

Natural fragmentation is where the explosive is confined and in contact with a metal casing where there are no features to assist in controlling where case fracture will occur. A typical example is an artillery shell as shown in Figure 8-3. At any point along its length the cross section is cylindrical and the ratio of explosive mass to metal mass together with the material properties of the metal will determine how it fragments including size and velocity. To produce small fragments use a case material of low ductility (low true fracture stress, low fracture strain) and thin wall, filled with an explosive with high detonation pressure. To produce large fragments use a case material of high ductility and thick wall filled with a lower detonation pressure explosive.

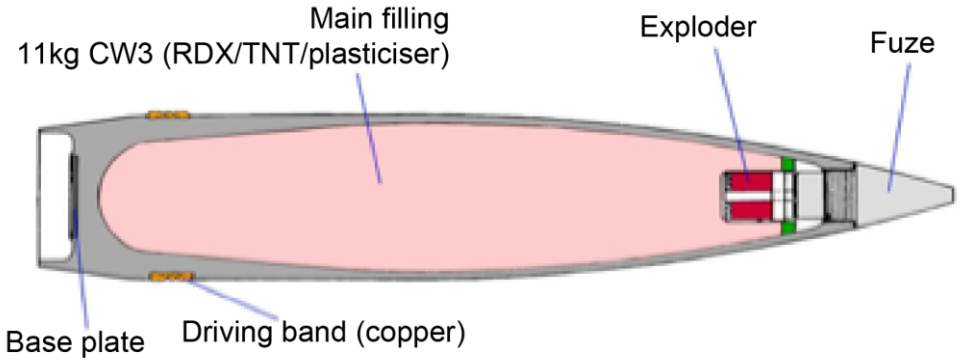


Figure 8-3 Longitudinal section of an L15 155 mm artillery shell

Natural fragmentation is used in ordnance because the munition casing is strong with no induced weaknesses, which is important to withstand the stresses of gun launch g-forces. It is also relatively straightforward to manufacture, which is important for a munition that is made in large numbers.

8.1.2.2 Controlled fragmentation

A means of improving the fragmentation efficiency is to introduce planes of weakness in the case which cause it to break up into fragments of an optimum mass. This is sometimes referred to as "fire-formed" fragmentation.

Consider a hexagonal bar of steel with a circular hole along its axis packed with high explosive. When the explosive is detonated one might expect the gases to burst through the confinement at its thinnest point along the centre of the faces. In reality, an intense shock wave passes through the metal and is reflected as a rarefaction wave from the surface as shown in Figure 8-4. The waves reflected from adjacent surfaces reinforce one another along the planes defined by the axis of the bar and the vertices, and it is at these planes that tensile failure occurs. By using various means to focus the shock waves within the case it is possible to exert useful control over the size and shape of fragment produced.

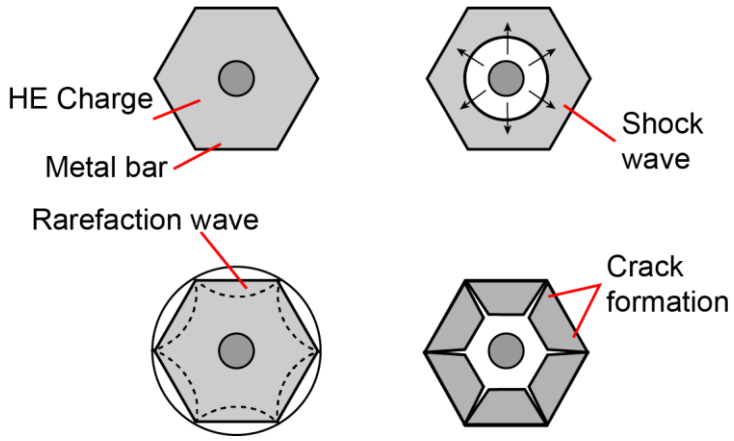


Figure 8-4 Fragmentation of a hexagonal bar (after Held)

There are 3 main ways that controlled fragmentation is achieved:

1. **Scored casing.** The case may be grooved internally or externally (Figure 8-5). It tends to fracture *between* external grooves and *at* internal grooves. Better control is achieved with internal grooves, although in practice they are more difficult and expensive to produce.
2. **Notched wire.** Cases may be constructed by brazing together internally notched metal annuli, or a coil of notched wire (Figure 8-5). The fragment size is defined by the cross-sectional dimensions of the metal and by the distance between notches, which is typically 1-1.5 times the case thickness.
3. **Grooves in the explosive.** It may be more convenient to groove the explosive by inserting a shaped liner between it and the wall of the case, or by using metal inserts (Figure 8-6). These focus the shock wave and

produce high local stresses in the case. The profiled liner is often referred to as a "Buxton liner".

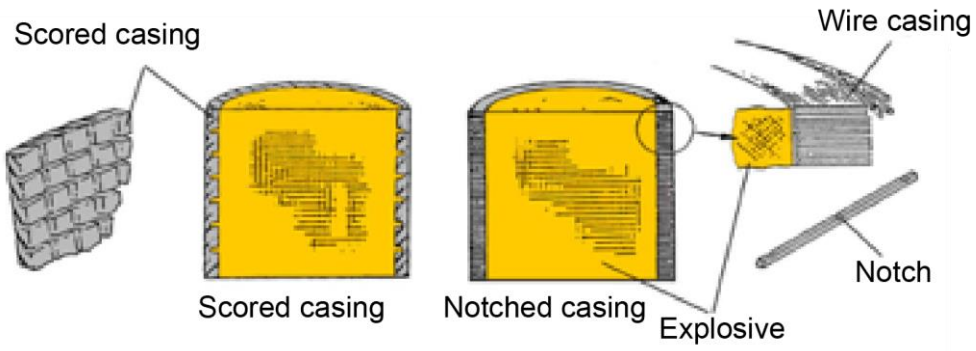


Figure 8-5 "Fire-Formed" fragmentation warheads (scored casing and notched wire)

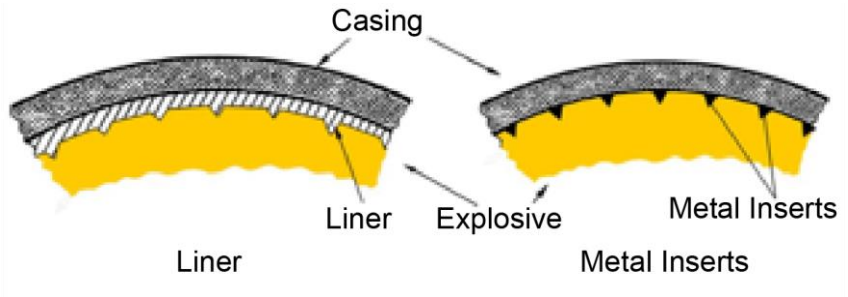


Figure 8-6 "Fire-Formed" fragmentation warhead (grooved liner)

Another technique relies on zone embrittlement of the case by treating it with lasers, electron beams or chemicals. As the shock wave passes cracks form preferentially in the treated regions.

8.1.2.3 Pre-formed fragmentation

Pre-formed fragments of optimum size, shape and mechanical properties for the intended target may be built into the warhead structure. They may be cubes, spheres, flechettes, etc. (Figure 8-7), and they may be pyrophoric as well as penetrating.

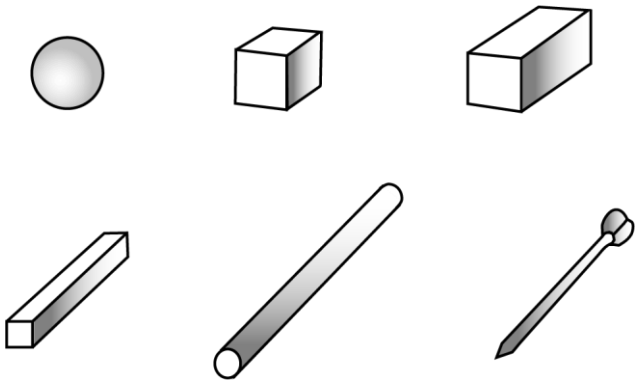


Figure 8-7 Pre-formed fragmentation

The disadvantages are increased manufacturing difficulty, the need for a parasitic structure to support the fragments and reduced fragment velocity, perhaps up to 10 %, resulting from early gas leakage between fragments during acceleration. To counteract this, the fragments usually are assembled around an internal liner sufficiently ductile to accelerate the fragments to near full velocity before rupturing and leaking gas.

8.1.3 Conical shaped charge

A shaped charge is a device that uses the energy of a detonating explosive to collapse a metal cone to its axis at which point a proportion, about 20 %, forms a forward directed jet with the remainder forming a slug of metal moving in the same direction. Figure 8-8 shows a cross section of a shaped charge warhead and Figure 8-9 a flash x-ray showing jet and slug formation.

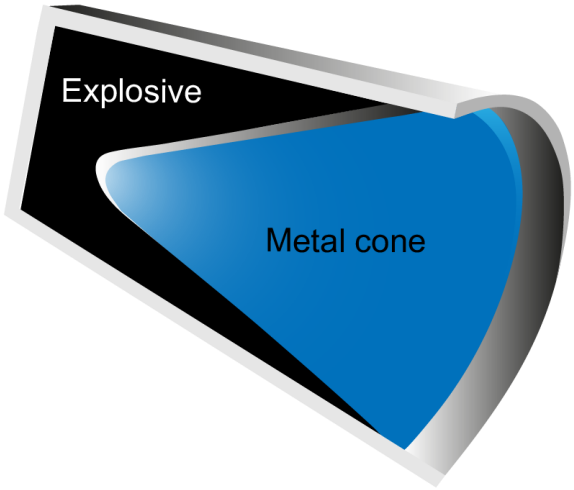


Figure 8-8 Cross section of a shaped charge warhead

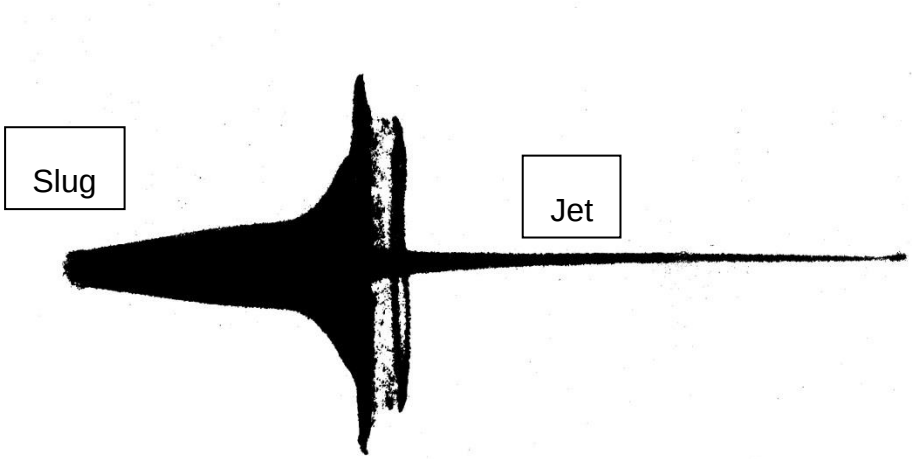


Figure 8-9 Flash x-ray immediately following detonation

The jet has a velocity gradient along its length with the tip travelling at around 8 km s^{-1} and the tail 2 km s^{-1}. This results in the jet stretching in flight to a point where the jet fragments. The jet when it impacts armour overcomes the strength of the target material, which flows allowing the jet to penetrate the target. The metal of the jet coats the cavity wall and so is consumed as the jet penetrates.

For optimum penetration the jet should impact the target before it fragments but has significant length as penetration is directly proportional to jet length. This requires a 'stand-off' distance between the shaped charge and target when it detonates. Typical values will be between 2 and 5 times the diameter of the cone. Also, the metal must have reasonably high density and be able to flow under the intense pressure of the detonation shock wave. Although other metals such as steel have been used the universal choice is copper. A shaped charge warhead with the optimum stand-off, very high detonation pressure explosive and high quality copper cone will penetrate eight times the cone diameter in to armour. Figure 8-10 shows a typical cavity in a steel target created by shaped charge jet penetration.

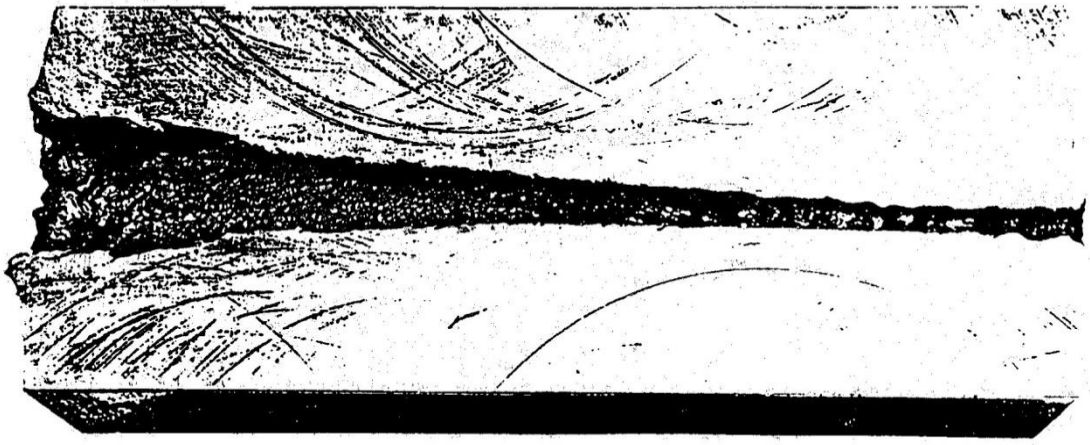


Figure 8-10 Cross section of a steel target penetrated by a shaped charge jet

8.1.4 Linear shaped charge

A conical shaped charge collapses the metal liner such that it produces a point impact on a target. If a metal liner with the geometry shown in

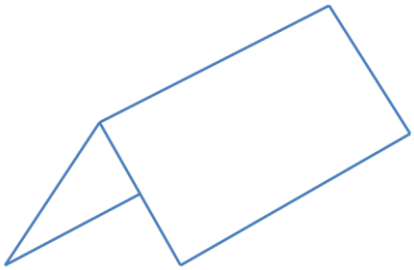


Figure 8-11 is backed by explosive then a planar jet is produced that can cut a line in a target. Early types had a rigid metal liner making the linear shaped charge difficult to employ other than on flat surfaces. However, demolition accessories now include a flexible version using a flexible liner constructed from copper powder and a binder as shown in Figure 8-12. Linear shaped charges usually have a smaller stand-off than conical shaped charges of around 1 × throat width and penetration of no more than 1.5 throat widths in to steel.

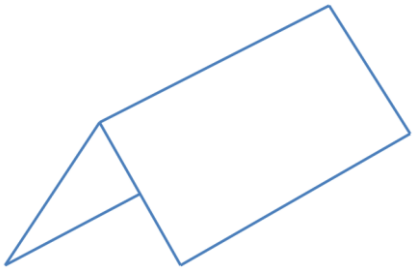


Figure 8-11Linear shaped charge liner

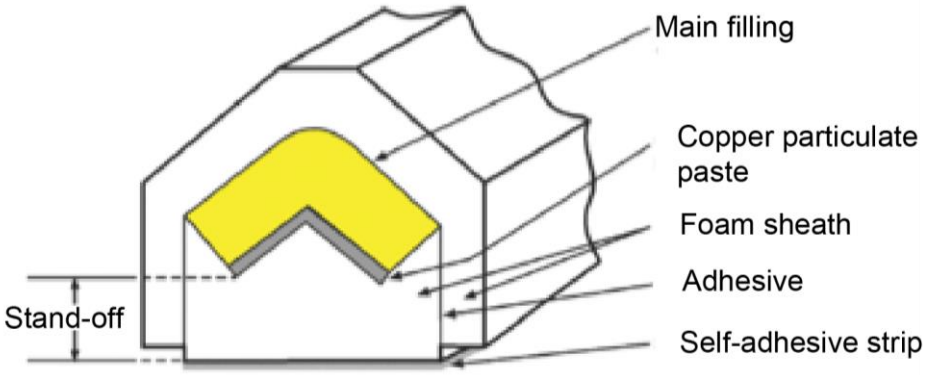


Figure 8-12 Cross section of a flexible linear cutting charge

8.2 FRAGMENTING WARHEADS

8.2.1 Fragment Initial Velocity

8.2.1.1 The Gurney equations

During World War II Gurney considered that the energy available from the explosive is partitioned between the kinetic energy of the detonation products and the kinetic energy of the fragments of the case and derived equations giving the fragment velocity for several simple geometries(1). He assumed that detonation occurs instantaneously, that all the products are gas, and that the geometry is such that only one dimensional flow occurs.

The process may be applied to simple geometries. If the geometry has a centre or plane of symmetry including sphere, cylinder and symmetrical sandwich, then the derivation is particularly simple because only one boundary velocity is unknown and only the conservation of energy equation is required. The gas velocity is zero at the element of symmetry.

If the plates are of unequal mass as for an unsymmetrical sandwich two unknown velocities result, and two equations are therefore required. The second equation is the statement of conservation of momentum. The form of the Gurney equation for various geometries is given in **Table 8-1**.

It must be remembered that the derivation of the Gurney equations assume that the flow is one dimensional. The measured fragment velocity for, say, a very short cylinder is much lower than calculated, because much of the flow is not radial, and Gurney's assumptions are no longer valid. For a cylinder, the length should be at least twice the diameter, and the fragment velocity at the ends is less than that at the centre. For light confinement, when *M*/*C* <~1/3, Gurney underestimates the fragment velocity due to a greater contribution of shock processes which improve the efficiency of the acceleration.

It must be understood that the Gurney equation takes no account of the mechanical properties of the case material, and makes no judgment on the size, and therefore of size distribution, of the fragments resulting from the detonative dispersal of the case. Gurney predicts the same velocity for a case that flies apart in two pieces, or as a powder. These differing fragments obviously have widely differing lethality. We note also that the Gurney equation gives a single velocity, whereas in reality the velocity varies along the length of the case being reduced at the ends where there is less confinement.

Table 8-1 Gurney Equations for Various Geometries

Cylinder	$\sqrt{2E}\left(\frac{M}{C}+\frac{1}{2}\right)^{-1/2}$	**(8-1))**
Sphere	$\sqrt{2E}\left(\frac{M}{C}+\frac{3}{5}\right)^{-1/2}$	**(8-2))**
Symmetric sandwich (*M* is the total mass of the metal)	$\sqrt{2E}\left(\frac{M}{C}+\frac{1}{3}\right)^{-1/2}$	**(8-3))**
Open sandwich	$\sqrt{2E}\left[\frac{1}{3}\left(\frac{4M}{C}+1\right)\left(\frac{M}{C}+1\right)\right]^{-1/2}$	**(8-4))**
Unsymmetrical sandwich (plate masses, M_A, M_B and velocities V_A, V_B).	$V_A=\sqrt{2E}\left[\frac{1+Z^3}{3(1+Z)}+\frac{M_B}{C}Z^2+\frac{M_A}{C}\right]^{-1/2}$	**(8-5))**
	and $V_B = ZV_A$ where $Z=\frac{1+2M_A/C}{1+2M_B/C}$	**(8-6))**

8.2.1.2 Properties of explosives

It has been shown by Cooper[2] from an analysis of the results for many military explosives that a useful engineering estimate for the Gurney constant is $\sqrt{2E} = D/2.97$ where *D* is the velocity of detonation (mm μs^{-1}) of the explosive. It should be noted, however, that values of D/√2E ranged from 2.81 to

3.09 mm μs^{-1}. Table 8-2 gives examples of Gurney constant values[2,3] for a range of explosives of given density and Velocity of Detonation.

Table 8-2 Examples of Gurney Constants

Explosive	Density ($kg\ m^{-3}$)	Detonation Velocity ($mm\ \mu s^{-1}$)	Gurney Constant ($mm\ \mu s^{-1}$)
Composition B	1720	7.92	2.71
PETN	1760	8.26	2.93
Composition C-4	1520	8.37	2.18
LX-14	1835	8.83	2.80
Pentolite 50/50 % w/w cast	1640	7.52	2.30
HMX	1890	9.11	2.97
RDX	1590	8.25	2.45
TNT	1630	6.73	2.09
Octol 75/25 % w/w	1810	8.48	2.80
Cyclotol 75/25 % w/w	1.75	8.25	2.79

8.2.2 Fragment Initial Direction

8.2.2.1 Taylor equation

The velocity at which the case is driven outwards depends upon the explosive used and on the ratio of the mass of explosive to the mass of case. The direction of motion tends to be normal to the surface, but modified by the direction of the incident detonation wave as indicated schematically in Figure 8-13.

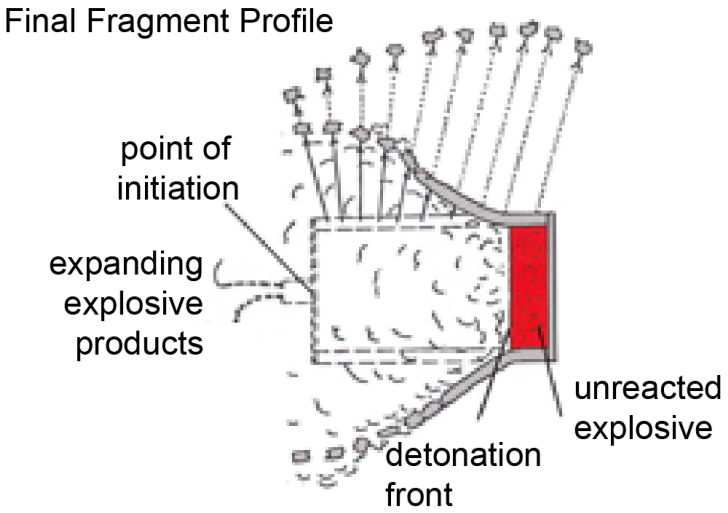
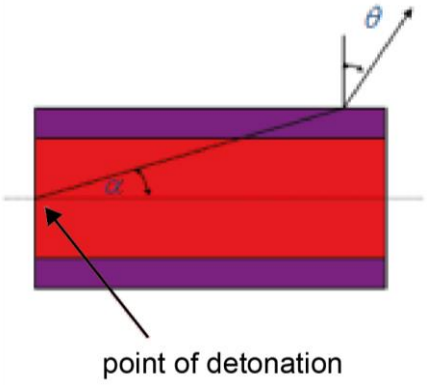


Figure 8-13 Fragment direction from single point, end initiation of a cylindrical charge

Taylor[4] calculated the ejection angle from the assumption that as the detonation wave passed the case is subject to a pure rotation and the fragment is then accelerated instantaneously. The angle of incidence varies with the relative positions of the point of initiation and the part of the case under consideration and in the simple case of a cylinder the relative positions may be defined as inFigure 8-14. Since $V_0/2D$ does not vary greatly between explosives, at constant geometry changing the explosive has little effect on the ejection angle.



$\theta = \sin^{-1}\{(V_0 \cos\alpha)/2D\}$

Where:
V_0 is static initial fragment velocity (from Gurney)
α is angle shown
D is VoD of explosive

Figure 8-14 Taylor angles for a centrally end initiated cylindrical charge

8.2.2.2 Beam angle

The fragments of a warhead tend to travel outwards in a nearly perpendicular direction to the surface of its casing. The total angle which includes all the fragments from the warhead is called the *beam width or beam angle*, and is a useful characteristic for the analysis of the likely effectiveness of the warhead. For a simple cylinder, it is simply the sum of the two extreme Taylor angles.

In the example warhead given above (Figure 8-14), we can calculate the beam angle and observe how it varies as the point of initiation is moved along the axis of the warhead from one end to the centre.

For initiation at one end, and a fragment from the other,

$\alpha = \tan^{-1}(0.1/0.4) = 14.04°$

If the VoD of the explosive is 7890 m s^{-1},

$\theta = \sin^{-1}(2407 \times \cos 14.04°)/(2\times7890) = 8.5°$

Since the fragments at the initiation end travel normal to the case ($\theta = 0°$), the beam angle is 8.5°.

For initiation at the centre, and a fragment at either end,

$\alpha = \tan^{-1}(0.1/0.2) = 26.56°$

$\theta = \sin^{-1}(2407 \times \cos 26.56°)/(2\times7890) = 7.8°$

Since fragments at opposite ends depart with the same inclination from the normal, but both away from the initiation point, the beam angle is 15.6°.

Figure 8-15 shows the calculated values along the length of the example warhead assuming initiation at one end. Figure 8-16 shows the effect of initiating at one end, centrally and at both ends of a cylindrical charge.

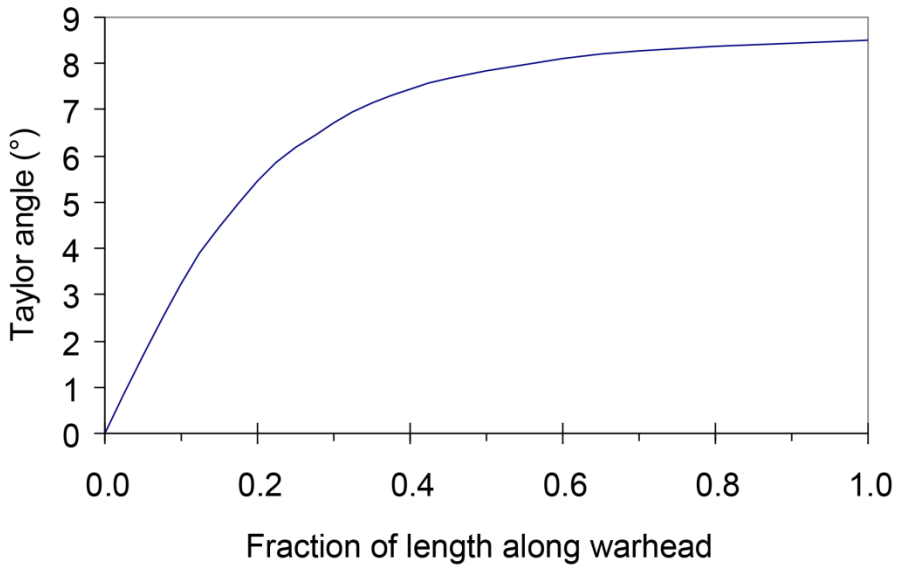


Figure 8-15 Variation of Taylor angle along a warhead

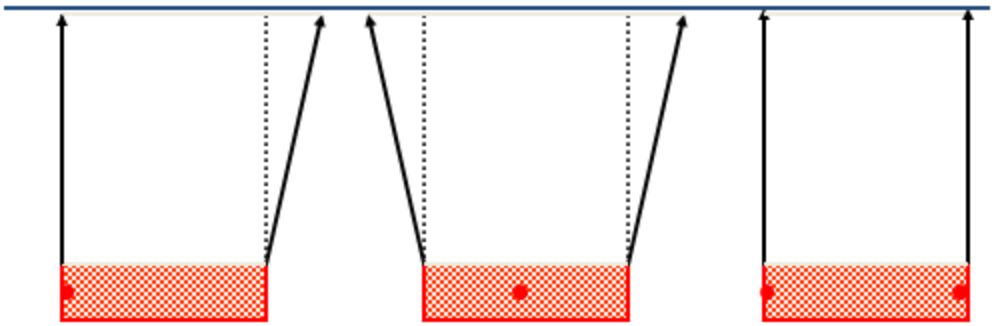


Figure 8-16 Warhead beam width for single end, central and two end initiation

Beam width also is a function of the warhead shape and the position of the point of detonation in the explosive charge. Some case profiles and fragment patterns resulting from central initiation are shown in Figure 8-17.

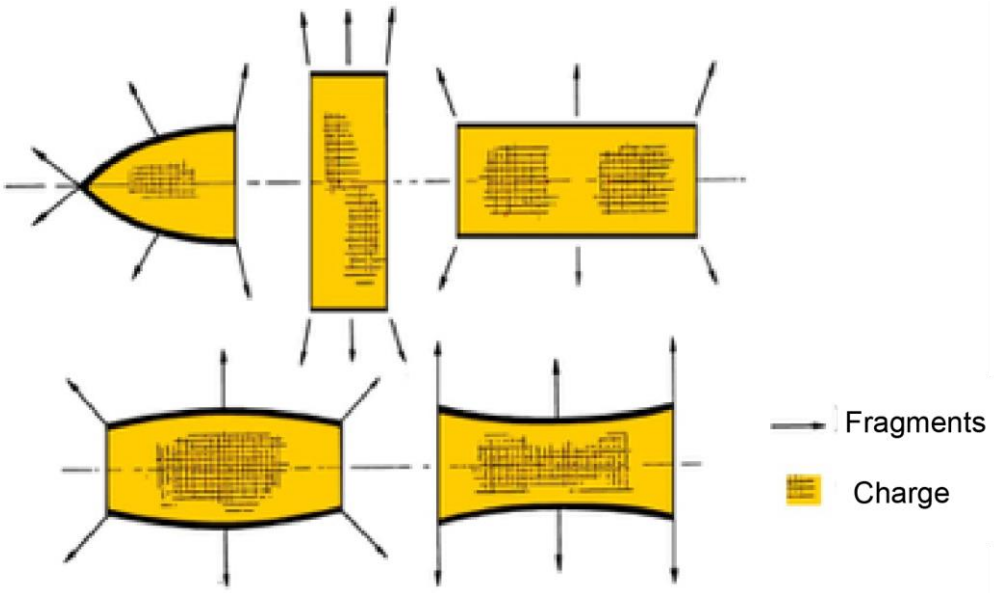


Figure 8-17 Effect of warhead shape on fragmentation patterns

8.2.3 Fragment Dynamic Velocity – the Effect of Warhead Velocity

Many warheads when they detonate such as missiles or air burst artillery shells have forward velocity, which will contribute to the overall velocity of the fragments. The static velocity of a fragment as can be calculated applying the Gurney equation, V_0, combines vectorially with the forward motion of the warhead, V_m at the moment of detonation to produce the dynamic velocity V_d. This is shown in Figure 8-18 for the front and rear fragments of a cylindrical warhead initiated at the rear.

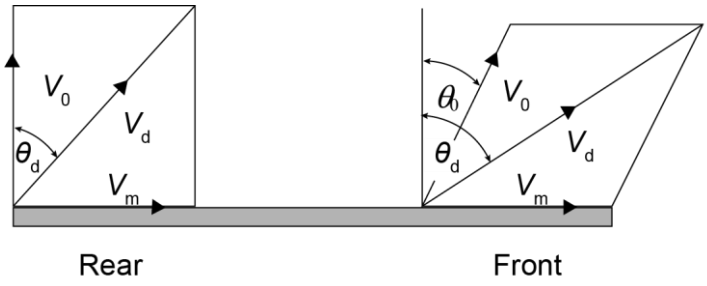


Figure 8-18 Vectorial combination of initial fragment velocities and warhead velocity

The Gurney velocity of each fragment is V_0 and for rear initiation the Taylor angles are 0° (rear) and θ_0 (front). The *dynamic fragment velocity*, V_d and *the dynamic ejection angle*, θ_d may be calculated by simple vectorial addition of the velocities.

$$V_d = \sqrt{V_0^2 + V_m^2} \quad \textbf{(8-7)}$$

Rear fragment

$$\theta_d = \tan^{-1}\left(\frac{V_m}{V_0}\right) \quad \textbf{(8-8)}$$

$$V_d = \sqrt{V_0^2 + V_m^2 - 2V_0V_m\cos\alpha} \quad \textbf{(8-9)}$$

Front fragment

$$\theta_d = \sin^{-1}\left(\frac{V_m}{V_d}\sin\alpha\right) + \theta_0 \quad \textbf{(8-10)}$$

Where $\alpha = (90 + \theta_0)°$

8.2.4 Fragment Slow-down

Once a fragment has ceased to be accelerated by the explosive, it slows down as it travels through air (or any other medium) according to drag as given in the following equation:

$$V_s = V_d \exp\left[\frac{-C_d r_a A s}{2m}\right] \quad \textbf{(8-11)}$$

Where V_d = initial dynamic velocity of the fragment relative to the medium ; V_s = velocity (m s^{-1}) after travel of s *(m)* distance in air ; C_d = drag coefficient of the fragment in the medium ; m = fragment mass (kg) ; A = cross-sectional area of the fragment (m^2) ; r_a = density of air (kg m^{-3}) through which the fragment moves.

8.2.4.1 Fragment density

Conventional fragments have a constant mass (m) and size (A) as defined in the section on controlling fragment mass. These depend upon their shape but also upon the material. If a fragment is made of a denser material (e.g. tungsten rather than steel), it will have a smaller ratio of A/m and so will maintain its velocity and hence its kinetic energy to a greater distance.

Figure 8-19 shows the drop in velocity and kinetic energy density for 5 mm steel and tungsten cubes travelling with an initial velocity of 2,400 m s^{-1} in air. Note how the velocity drop is greater for steel than tungsten and how the tungsten fragment always has greater kinetic energy density (KED) at any given range due to the smaller ratio of A/m. KED is a measure of how penetrative a fragment may be when impacting a target and depends on fragment velocity and cross sectional area: KED = $mV^2/2A$

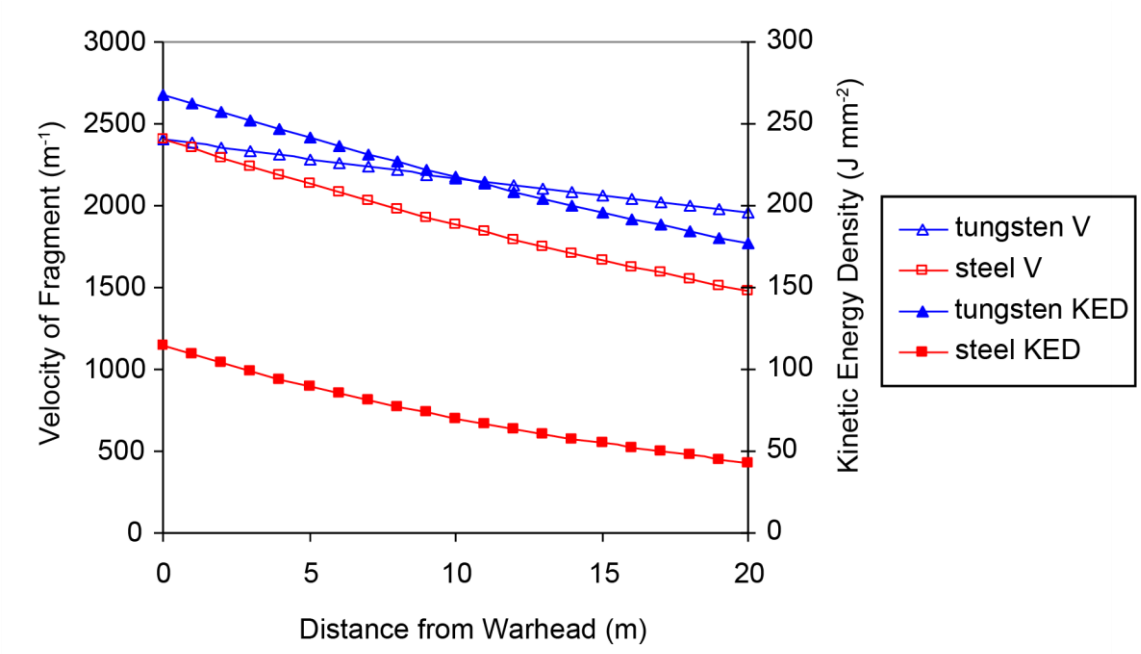


Figure 8-19 Effect of drag on velocity and kinetic energy density

8.2.4.2 Drag coefficient and fragment shape

Most fragments of interest to warhead designers have velocities which are comfortably supersonic, which is very convenient for the application of the drag equation because in this region the drag coefficient is essentially constant, and the values in Table 8-3 may be used. If more accurate calculations are required, variations in drag coefficient with respect to velocity as represented by Mach number, the velocity divided by the speed of sound in the medium, are available[5]. Examples are shown in **Figure 8-20**.

Table 8-3 Typical Drag Coefficients for Simple Shapes

Shape	Drag Coefficient (C_d)
Sphere	0.9
Cube (edge-on, tumbling)	1.1
Cube (face-on, tumbling)	1.6
Cylinder (end-on)	1.7
Cylinder (side-on)	1.2

The drag coefficient values given demonstrate that some shapes are more aerodynamic than others and will maintain velocity and kinetic energy to a greater distance. For example, spheres will travel further than cubes.

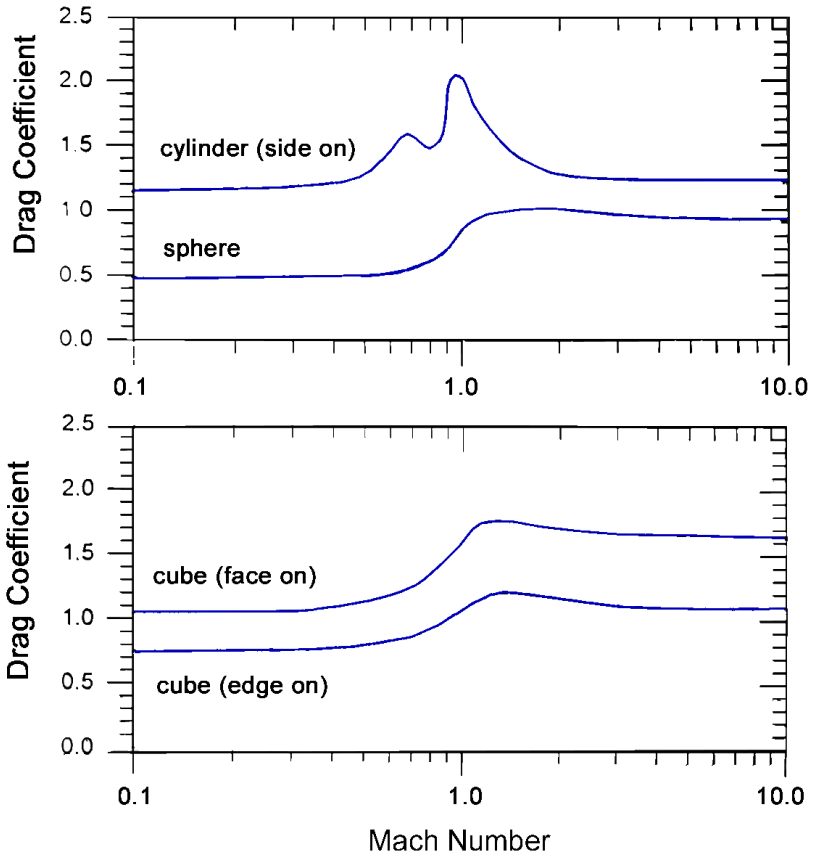


Figure 8-20 Aerodynamic drag coefficient versus Mach number

8.2.4.3 Air density and altitude

Air density varies with altitude and also is dependent on temperature and humidity at a given altitude. Example figures for air density at different altitudes are given in Table 8-4. It is clear from the equation for fragment slowdown that fragments lose velocity much more slowly at low density and therefore high altitude. This is of particular value to the lethality of missiles that attack air targets.

Table 8-4 Variation of Air Density with Altitude

Altitude / m	Example Air Density / kg m^{-3}
0	1.206
1,000	1.098
5,000	0.746
10,000	0.425
20,000	0.092
30,000	0.019

8.2.4.4 Lethal range

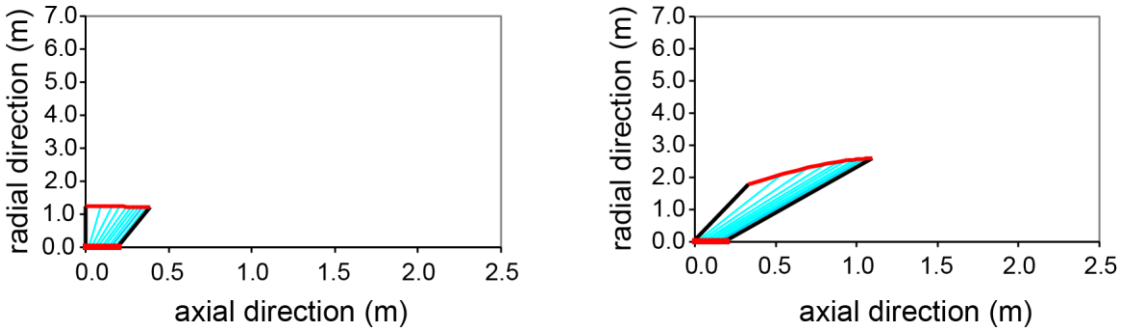
An initially lethal fragment slows down until it becomes sub-lethal at a sufficient distance. That distance is the *lethal range* and can be assessed. There will be a minimum critical velocity at which a given fragment will just defeat a target. This critical value is inserted into the fragment slow down equation and the resultant critical distance is the lethal range.

The lethal range is increased if:

- The fragment initial dynamic velocity is increased (increased initial static velocity or increased engagement velocity for a forward-projected fragment).
- The fragment mass is increased (via natural, controlled or pre-formed fragments) although this will also increase drag.
- The fragment density is increased (e.g. tungsten rather than steel).
- The fragment drag coefficient is reduced (e.g. spheres rather than cubes).
- The air density is reduced (e.g. at higher altitude).
- The target is weaker (e.g. due to a lack of ballistic protection).

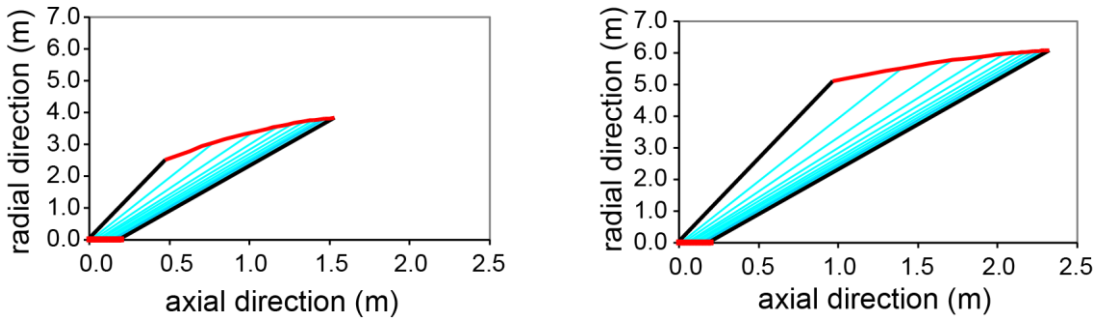
8.3 THE DAMAGE VOLUME

Damage volume is the volume surrounding a fragmenting device which, for a given target and engagement scenario, is lethal. Looking at a cross-section of the damage volume for a rear-initiated, cylindrical warhead attacking a stationary target (Figure 8-21), the effects of forward velocity of the warhead is clear. As the warhead gets faster, the beam angle narrows and the lethal range increases. If the target is approaching, the beam angle stays the same but the lethal range increases with velocity of the target (Figure 8-22). These effects alter the likelihood of hitting a target and of defeating it.



(a) stationary warhead (b) warhead velocity 500 m s^{-1}

Figure 8-21 Damage volume of a warhead (Stationary Target)



(a) Target approach angle 0° (b) Target approach angle 45°

Figure 8-22 Damage volume of warhead with velocity of 500 m s^{-1} (target approaching at 300 m s^{-1})

8.4 DIRECTED EXPLOSIVE ENERGY

8.4.1 Introduction

In 1885 Charles Edward Munroe, an American explosives chemist, noted an important effect during tests involving guncotton (nitrocellulose). Letters indented on the explosives surface were replicated on the target post-detonation, with corresponding raised marks occurring if embossed letters existed. This crucial observation with the phenomena subsequently termed the 'Munroe effect' provided the first tangible evidence of ability to focus detonation waves.

Figure 8-23 schematically illustrates this effect:

a. An explosive detonated against metal with a planar interface produces a shallow crater.
b. If the explosive has an indentation in the face contacting the target a deeper cater is formed.
c. If the explosive has a protrusion on the face contacting the target a raised structure is formed.

In all cases the explosive would be in intimate contact with the target.

The phenomena demonstrated in Figure 8-23**Error! Reference source not found.** involves focusing of the detonation front thus producing '*directed explosive energy*'. A hollow at the output end of an explosive concentrates the detonation wave, focusing it in a manner akin to a convex lens, leading to a greater resultant crater depth; in corollary, a raised structure at this explosive / target interface will lead to detonation wave divergence (analogous to a concave lens). This concept is illustrated schematically for the hollow interface case in **Figure 8-24**.

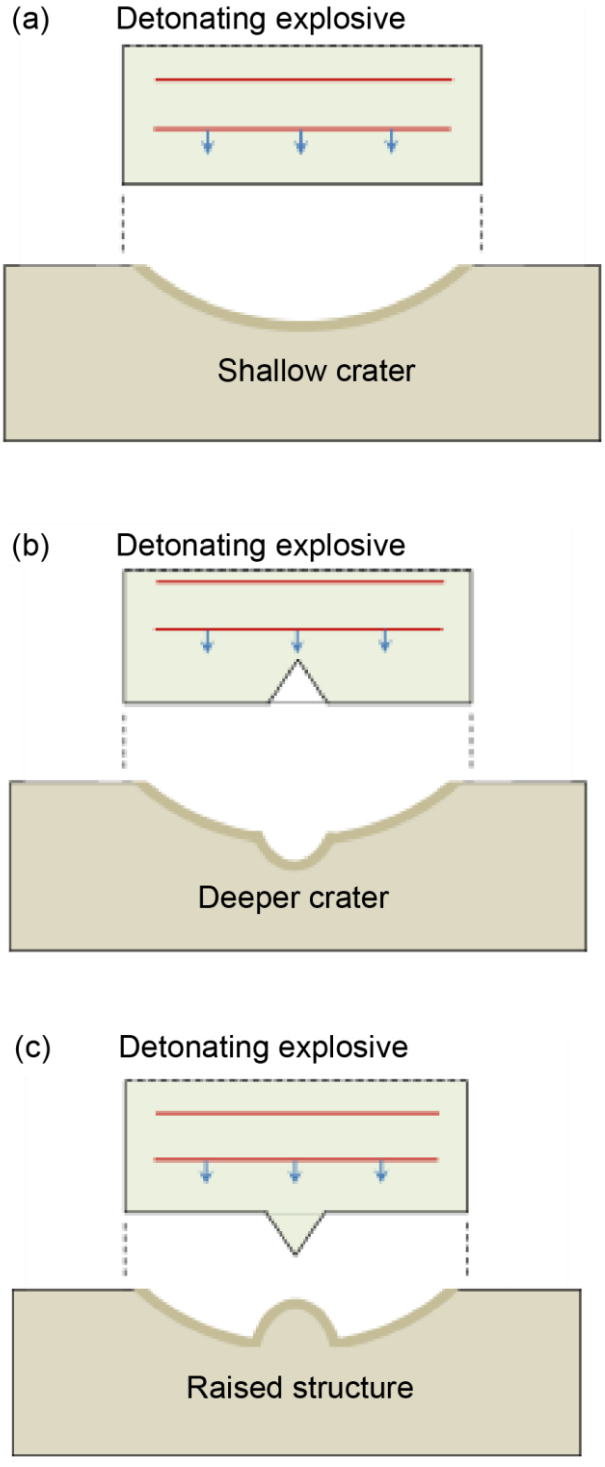


Figure 8-23 Schematic illustration of the Munroe Effect

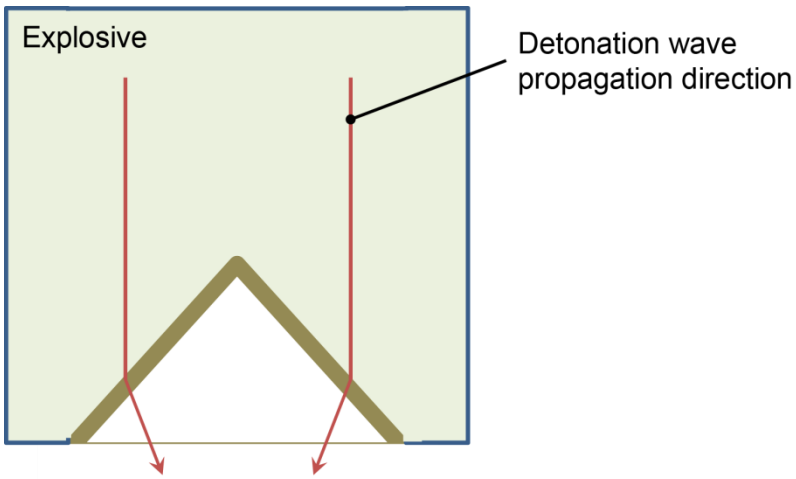


Figure 8-24 Illustration of the production of a converging detonation shockwave via the hollow charge effect

This effect, exploited in the hollow charge warhead can be tailored via control of the cavity shape and through the introduction of a metal liner, which enhances the penetration. Broadly speaking, the effect follows the shape of the cavity in the explosive. Consequently, a wider, shallower cavity at the explosive / target interface will lead to a corresponding wide, shallow crater, whereas, narrower, deeper cavities lead to deeper, but narrower, penetrations and eventually perforation of the target. This is universally known as the shaped charge effect and the term 'shaped charge warhead' used for weapons that exploit it. The complex physics and details of the shaped charge phenomenon can be found in Walters and Zukas[6].

8.4.2 Shaped Charge Warheads

8.4.2.1 Mechanism

The shaped charge warhead, as shown schematically in **Figure 8-24**, comprises a hollowed-out explosive head with a metallic liner. This hollow, and the corresponding liner, normally have a conical section. Initiation of the explosive head leads to a detonation front which propagates through the device until it reaches the apex of the conical liner. The pressure exerted by the detonation front is so great that it exceeds the shear strength of the liner material. This consequently flows in a hydrodynamic manner, that is, in a fluid-like state, despite the fact that the material remains in the solid phase, something confirmed via X-ray diffraction experiments[7]. Collapse of the liner subsequently proceeds with material accelerated inwards towards the central axis of the cone. The resultant structure consists of two elements. Typically around 20 % of the linear material will be deflected forwards to form a jet with the rest forming a slug which travels behind. In general, the proportion of material in the slug will increase with the presented angle of the shaped charge liner. The jet tip possesses a substantial velocity of the order of 8-12 km s^{-1}

whereas the slug is ballistic in nature typically moving at less than 1.5 km s^{-1}. The process of jet collapse is illustrated in the flash X-ray radiograph presented in **Figure 8-25**[6] showing two exposures on a single film and illustrating the progressive collapse of a copper liner. The lower image shows the early stage of cone collapse and the upper image the jet stretching to the right with the slug forming behind. As illustrated by this figure, a shaped charge jet takes a finite amount of both time and space to form. Consequently, a space or 'stand-off' from the target is required in order to allow for full jet formation. In addition, a white dashed ring include on the later time (upper) of the two exposures highlights a perturbation in the jet, likely a function of microstructural imperfections in the liner or alternatively a slightly asymmetric collapse.

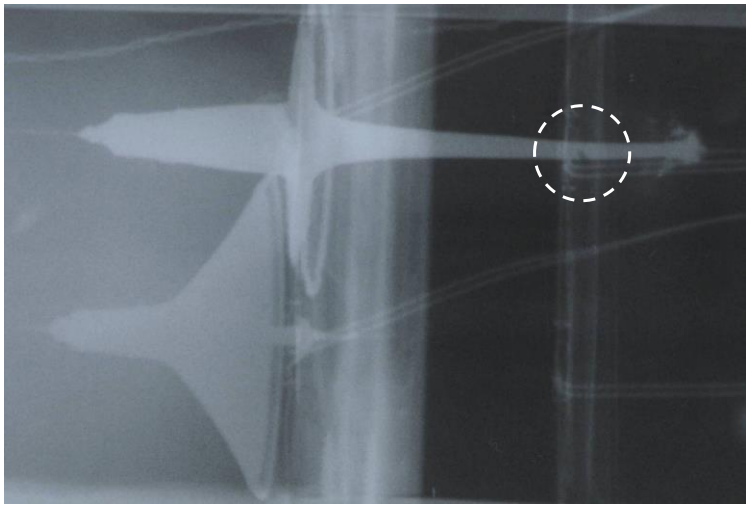


Figure 8-25 Flash X-ray radiographs illustrating collapse of a shaped charge liner

As shaped charge jets have very high on-axis momentum, such perturbations act to disrupt the jet as it develops, limiting the stand-off at which shape charge warheads can act. Further, as shown below, to a first-order, subsequent penetration (P) by the jet is velocity independent and a function only of target (ρ_T) and liner (ρ_P) densities and jet length (L):

$$\mathrm{P} = L\sqrt{\frac{\rho_P}{\rho_T}} \qquad \textbf{(8-12)}$$

A shaped charge jet will typically form in ~40 μs and given a resultant tip velocity of around 8-12 km s^{-1}, which implies accelerations in the order of 25×10^6 g or 25 Mega-g. As the jet forms it stretches due to a velocity gradient along its length caused by the increase in metal mass being driven by decreasing explosive mass as the cone collapses. The jet tail will have a velocity of ~1-2 km s^{-1} with the slug at 0.5-1.5 km s^{-1}. Ultimately, if left to stretch in free space the jet will fragment and not provide optimum target penetration.

When the jet tip impacts a metal target the pressure exerted is so great it overcomes the strength of the material such that it undergoes hydrodynamic flow. The jet still behaving hydrodynamically flows and lines the surface of the resulting hole. A typical shape charge penetration path is illustrated in **Figure 8-26** showing a series of sectioned 20 mm deep blocks penetrated by a copper shaped charge. Although the depth of penetration is independent of jet velocity the diameter of the hole does decrease as slower elements of the jet penetrate as the hole depth increases.



Figure 8-26 Photograph showing sectioned mild steel blocks penetrated by a small-scale shaped charge.

8.4.3 Factors Effecting Shaped Charge Jet Penetration

While the basis of a shaped charge warhead is intrinsically simple being a metal cone backed by a detonating explosive there are a wide range of variables that contribute to the performance of a shaped charge warhead. These are illustrated in **Figure 8-27** with detail below. Dimensions of a shaped charge warhead scale such that it is usual to consider stand-off, charge length and target penetration as multiples of charge diameter (CD).

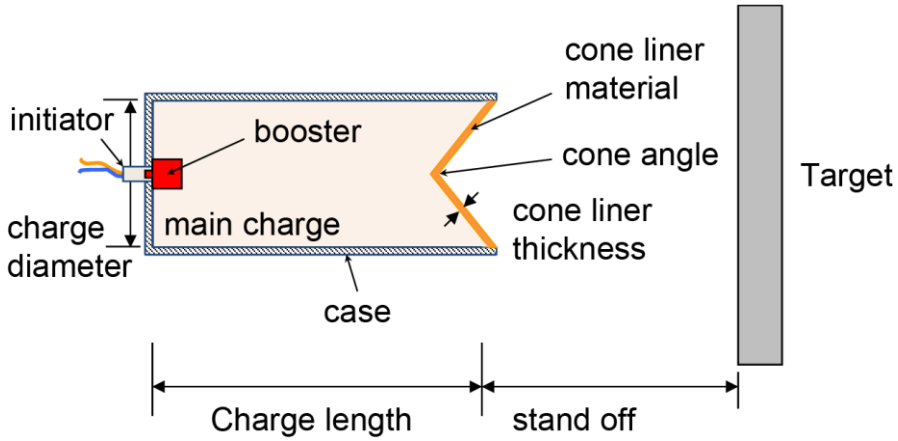


Figure 8-27 Schematic illustration of a simplified shaped charge warhead/target system, highlighting key variables.

8.4.3.1 Stand-off

This is a critical factor for a shaped charge warhead. Insufficient stand-off will not allow the jet to fully form as maximum target penetration requires a fully stretched jet that has not begun to fragment. Consequently, an appropriate triggering mechanism is required to ensure optimal stand-off. Too short and the jet has insufficient time to form; too long and inevitable perturbations will lead to

jet instability. Figure 8-28 shows this effect showing penetration in to steel for a particular design of shaped charge at varied stand-offs.

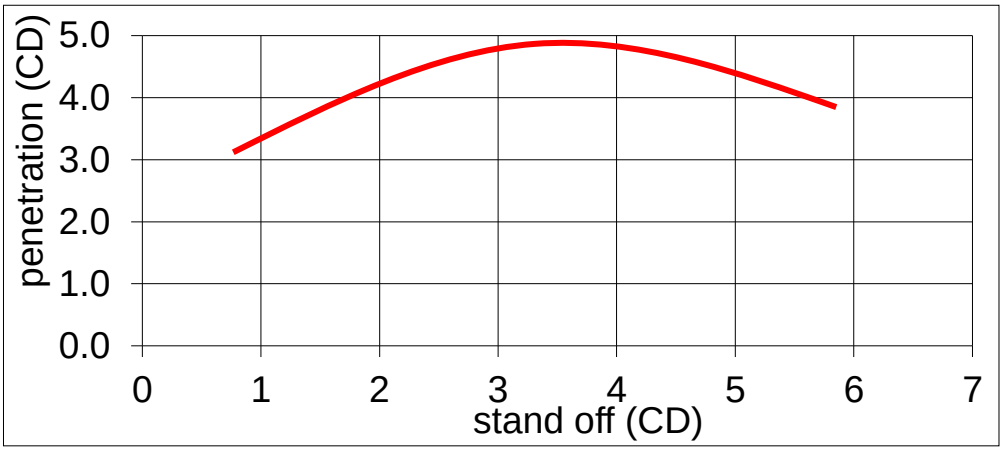


Figure 8-28 The effect of stand-off on penetration of a shaped charge warhead

A stand-off of between 2-5 CD is usually appropriate depending on other design factors. This is a challenge for weapon designers as impact fuzes will require a probe on the front of the warhead as found in infantry anti-tank weapons. For larger warheads sensors can be employed, however, these would be in the nose of the warhead and can affect the jet formation.

8.4.3.2 Charge length

The detonation wave from a centrally initiated warhead as shown in **Figure 8-27** needs to be fully formed and axially symmetrical once the apex of the cone is reached. Only minimal performance gains are found for charge lengths greater than one CD. It is now common practice in shaped charge design to utilise wave shapers to manipulate the detonation shockwave such that shorter warheads can be produced with improved penetration. Figure 8-29 shows how a waveshaping element set in to the explosive forces a centrally initiated shockwave to travel to the periphery of the charge and then converge on to the apex of the metal liner.

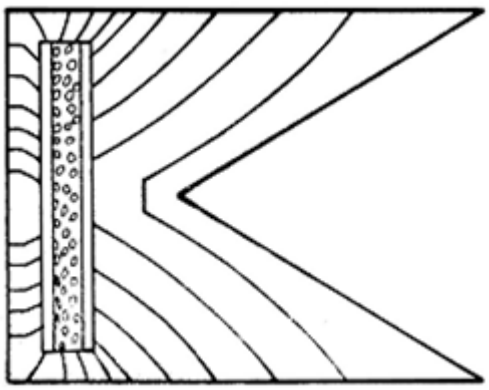


Figure 8-29 Shaped charge warhead with waveshaper

8.4.3.3 Explosive

Explosives with very high detonation pressures optimise metal driving and so it is usual to find shaped charge warheads with explosive fills with high HMX content.

8.4.3.4 Cone liner material

In line with equation (8-12), use of a higher density liner material will lead to a corresponding increase in subsequent penetrative ability of the warhead provided the selected material is able to demonstrate sufficient high strain-rate ductility to flow in an appropriate manner.

As a comparison, Table 8-5 illustrates the relative potential effects of varying liner material density for a selection of common materials compared to copper. The figures are theoretical as the material must have the ability to flow and form a jet. Tungsten would appear to be a suitable material, potentially 47 % more penetrative than copper but due to its material properties it does not form jets. Some unlikely materials, however, do form jets such as glass. Improvised shaped charges have been constructed from wine bottles that have a deep, almost conical, indentation in the base as found in champagne and red wine bottles.

In practice the material commonly used worldwide is copper for anti-armour warheads due to its relatively high density and high strain-rate ductility linked to an ability to recrystallize under high strain-rates. It is not expensive, easy to fabricate and by careful control of the microstructure will provide penetration of up to eight time the diameter of the cone. However, there is evidence that aluminium performs better than copper against concrete.

Table 8-5 Relative Resultant Penetration Calculated Based on Equation Error! Reference source not found.2) for a Nominal Shaped Charge Warhead as a Function of Cone Liner Material

Cone liner material	Relative penetration (CDs, normalised to copper)
Depleted Uranium	1.45
Tungsten	1.47
Copper	1.00
Steel	0.94
Aluminium	0.56
Glass	0.53

8.4.3.5 Cone angle and cone geometry

The angle of the metal cone at its apex has a major impact on penetrative performance of a shaped charge as shown in Figure 8-30. Most shaped charge warheads will have a cone angle between 45° and 60°. A narrower cone angle will produce a faster, but narrower, resultant jet and vice-versa.

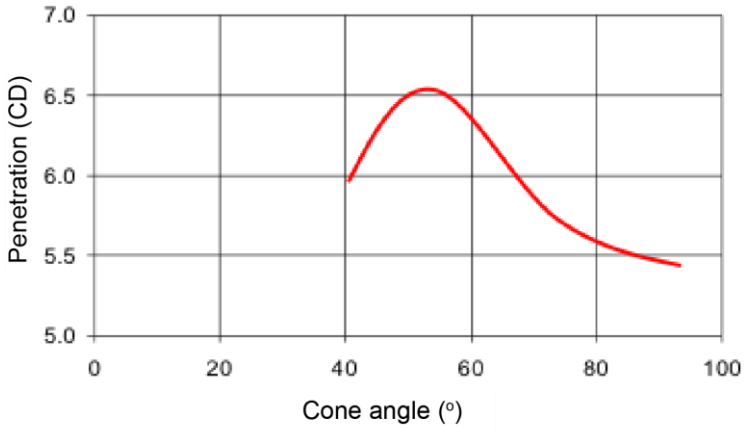


Figure 8-30 the effect of cone angle on penetration of a shaped charge warhead

Other cone geometries do exist for example, trumpet-shaped liners that have a continually changing cone angle from apex to base. However, these are more difficult to manufacture and are not commonly found.

8.4.3.6 Cone/charge diameter (CD)

If the diameter of a shaped charge is doubled this will double its penetration in to steel or armour. As shaped charges and their effects scale by dimension this will require the stand-off also to be doubled.

8.4.4 Explosively Formed Projectiles (EFPs)

Explosively formed projectiles in essence represent a limiting case of a shaped charge in which the presented angle of the liner is such that all of the material in the liner forms the slug. In general, this occurs once the presented angle of the cone is around 120° – 140°. However, for an EFP the liner often made of high-purity iron is more typically replaced with one with the form of a hemispherically divergent dish rather than a conical section. Figure 8-31 shows how the dish liner collapses to form a single slug, which is fully formed in to its aerodynamic shape in around 40 µs.



Figure 8-31 Computer model of an EFP dish forming a slug

Via careful design, the resultant projectiles with a ballistic velocity in excess of 1 km s^{-1} are aerodynamically stable and able to penetrate targets over a hundred cone (dish) diameters from the detonating warhead. This makes such EFPs suitable for stand-off weapons such as off-route mines or top attack area mines. A recovered EFP is shown in **Figure 8-32**. It is placed in a cross section of the hole it would produce in an aluminium target.



Figure 8-32 Recovered EFP projectile placed in a penetrated aluminium target

8.5 LINEAR CUTTING CHARGES

The physics underlying shaped charge formation can be exploited to produce a planar jet, useful for cutting through hard targets for demolition purposes. As shown schematically in **Figure 8-33**, this comprises of a box whose upper half is filled with an appropriate explosive composition, while the lower half consists of a metal liner and a built-in spacer to provide a stand-off.

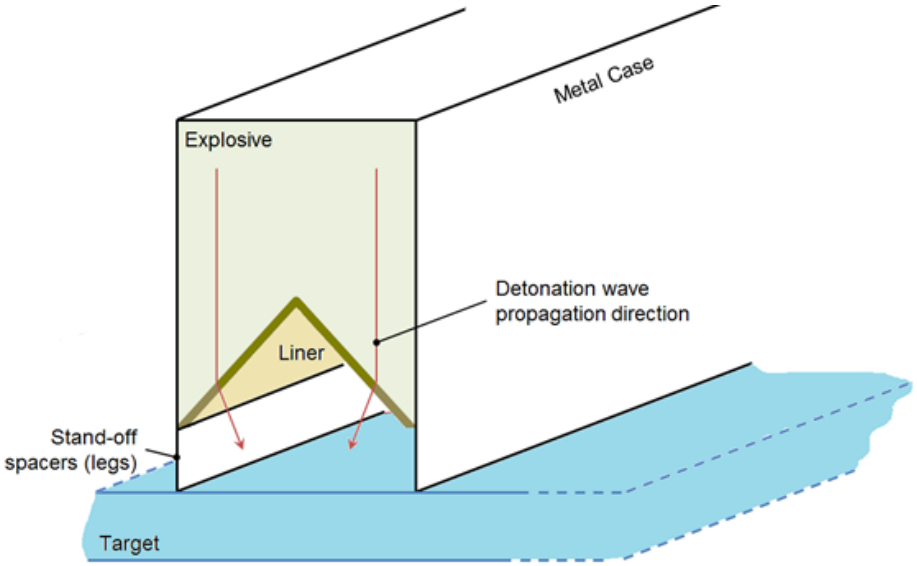


Figure 8-33 A linear cutting charge

Large charges of the type shown in **Figure 8-33** are used for rapid bridge demolition. These have rigid metal liners; however, for smaller applications a more flexible design uses a lead liner made by filling a lead tube with explosive and then pulling through dies to give the necessary size with a ‘v-shaped’ groove along one side providing the focusing element for the charge. Fillings typically comprise a powdered high explosive such as RDX or PETN, with the systems flexibility making it ideal for demolition tasks involving cutting through metal plates, girders, etc. More recently this lead type of linear cutting charge is being replaced by foam sheathed extruded explosive with a flexible liner manufactured from copper powder and polymer a shown in Figure 8-12.

In addition to the linear cutting charges detailed above, it is possible to exploit the influence of material impedance on shock propagation to fracture or cut a target. Essentially, if a diamond shaped charge is placed on a target and detonated at opposing corners the interaction of the resultant shock waves in the target, in particular, their reflection as tensile release waves from the un-confined rear-surface, will lead to fracture along the diamonds plane of symmetry. This process exploiting the phenomena of material spallation is illustrated schematically in **Figure 8-34**. It has been successfully employed in both ‘Fracture Tape’, which comprises a series of nominally diamond shaped individual charges which are initiated at their extremities, and in ‘Shock

Refraction Tape' – which instead uses wave shapers to achieve a comparable effect from a continuous strip of explosive material.

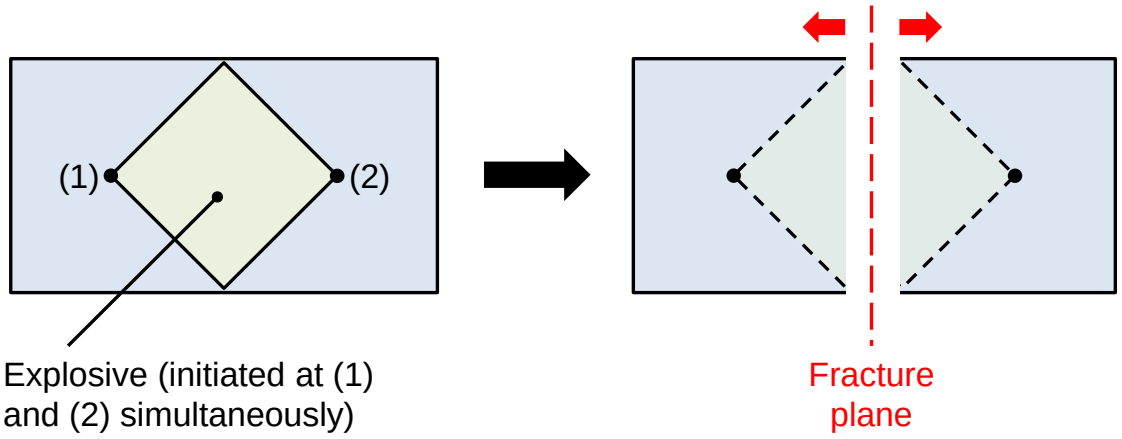


Figure 8-34 Schematic illustration of the effect of metal cutting using a diamond shaped charge (top-view)

8.6 EXPLOSIVE WELDING

Explosive welding essentially involves the use of an explosive to accelerate one metallic material into a dissimilar metallic material, creating a region of extremely high pressure. This high pressure acts for a sufficient time for material bonding and subsequent cooling to occur leading to a welded interface. In the process of accelerating one material into the other, a jet is formed ahead of the welding front analogous to the formation of a jet from a collapsing shaped charge liner. This jet acts to clean the interface between the materials, resulting in a very strong bond. The major advantage of the approach is the ability to bond materials which would otherwise not conventionally weld for example, titanium to steel, copper to aluminium and aluminium to steel. This process, described in more detail elsewhere[2], is illustrated schematically for a planar geometry in **Figure 8-35**.

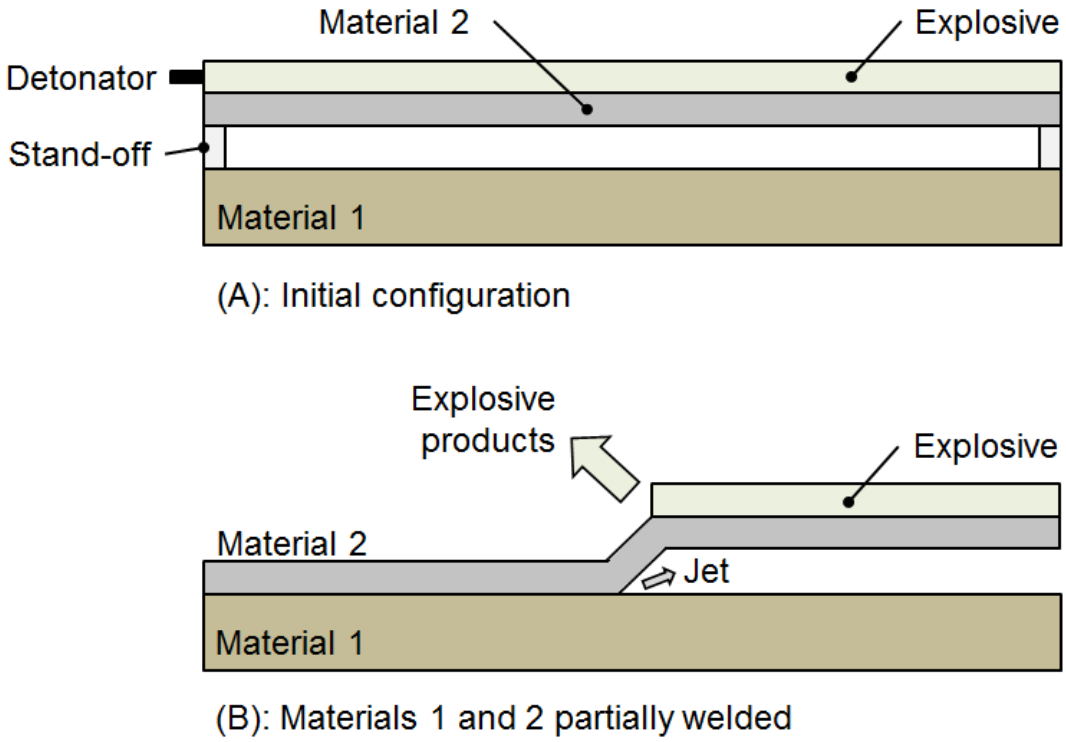


Figure 8-35 Schematic illustration of the explosive welding process

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CHAPTER 9
EXPLOSIONS IN AIR AND WATER

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9 EXPLOSIONS IN AIR AND WATER

Authors – C Knock and S G Murray (Cranfield University)

9.1 AWARENESS SUMMARY

Explosions in air and water are often considered together as one of their primary damage mechanisms is caused by expanding gases, which in air creates the blast effect and in water the bubble pulse effect. As can be seen in Chapter 11, High Explosives, weapons that wish to maximise either blast or bubble pulse damage will generally use the same type of explosive, which maximises the energy in the expanding gases.

9.1.1 Explosions in Air

9.1.1.1 Blast waves

When an explosive detonates in air it generates a shock wave, an intense pressure wave travelling faster than the speed of sound in air (approximately 330 - 340 m s^{-1} at sea level depending on temperature). A point some distance from the explosion will experience an instantaneous rise in pressure that within milliseconds falls back to ambient pressure and then creates a negative pressure as shown in

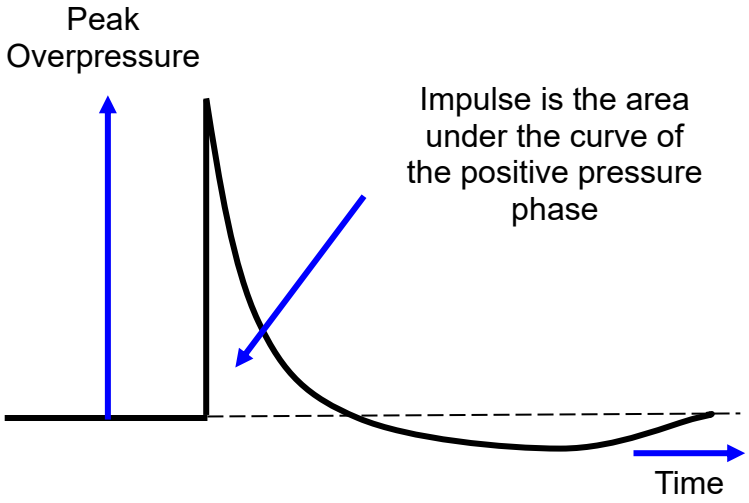


Figure 9-1 where the dotted line is ambient air pressure.

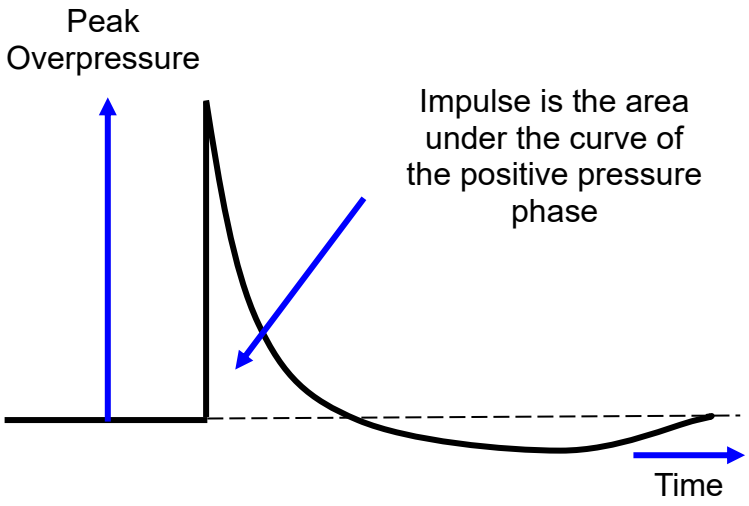


Figure 9-1 Blast overpressure vs. time

The peak pressure of a blast wave is called the peak overpressure, which is the pressure above ambient air pressure and is often used as a measure of damage potential of that blast wave. This is a convenient way to consider damage potential although it is more correctly assessed by knowing the impulse, which depends not only on the peak overpressure but also on the duration of the positive overpressure.

The negative pressure phase for most explosions, unless they are very large such as from nuclear weapons or kiloton explosive accidents, does not have the potential to cause damage but is important to understand the after effects of damage caused by the positive phase. For example when a blast wave impacts a building and breaks windows much of the fragmented glass will be accelerated forwards and enter the building. However, as the negative phase is a suction effect some will be caught and sucked back out of the building and fall to the street below. This has been seen on many occasions when a terrorist vehicle bomb has been detonated in a city.

9.1.1.2 Factors that affect blast damage potential

There are a number of things that can affect the size of blast from an explosion, the most important being:

- Size of the explosive charge
- Type of explosive
- Distance from the explosion

Other factors include:

- Casing on the charge (the greater the weight of casing the less will be the blast)
- Altitude (as altitude increases blast values decrease)

9.1.1.2.1 Size of the explosive charge

Increasing the size of an explosive charge does not increase the blast effectiveness by the same amount. If a charge weight is doubled this will only increase its effectiveness by around 13 %. To double the effectiveness such as having twice the blast pressure at a given distance from an explosion will require 8 times as much explosive and to triple the effectiveness requires 27 times as much.

9.1.1.2.2 Type of explosive

Some types of explosive can produce better gas expansion effects than others and are formulated for this purpose. Details are given in Chapter 11, High Explosives (see 11.3). It is common to take TNT as a standard when considering blast performance and compare others by using a TNT equivalence value. This means that if an explosive type has a TNT equivalence of 1.2 then a given charge weight, say 1 kg, will produce the same blast effect as 1.2 kg of TNT. These values will usually be in the range of 0.8 (e.g. ANFO) to 1.2 (e.g. Torpexes). One kg of ANFO will produce the same blast effects as 0.8 kg of TNT.

9.1.1.2.3 Distance from the explosion

Peak overpressure from an explosion falls off very rapidly with distance as shown in Figure 9-2. Doubling the distance reduces the blast overpressure to one quarter and tripling it to almost one tenth. This demonstrates the effectiveness of barriers that control how close vehicles can approach a building when protecting from terrorist attacks.

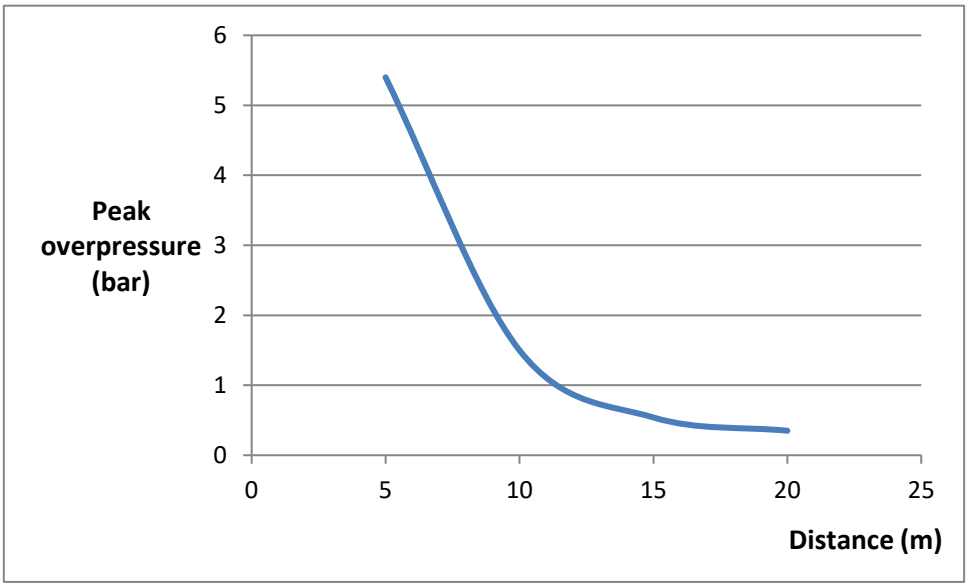


Figure 9-2 Overpressure vs. distance for a 50 kg TNT explosion

9.1.2 Explosions in Water

9.1.2.1 Primary shockwave

When an explosive detonates underwater an intense pressure pulse called the primary shockwave travels away from the explosion at a velocity faster than the speed of sound in water, which is approximately 1500 m s^{-1}. Water is a good medium to transmit shockwaves and pressures measured in hundreds of bar (10s MPa) may be produced within the first 50 metres from a large charge such as a depth charge and still many tens of bar (>1 MPa) at over 100 metres. In contrast a charge of similar size detonated in air would produce a blast wave with a peak overpressure no more than 0.2 bar (20 kPa).

If this primary shockwave hits a ship it has the potential to damage sensitive equipment and if close to the explosion damage even robust equipment. The shockwave accelerates the structure, which then interacts with anything in contact. This can include the ship's crew and has been known to cause ankle fractures.

9.1.2.2 Bubble pulse

After the primary shockwave has left the explosive charge a high pressure sphere of gas explosion products then begins to expand as a bubble in the water. This expansion continues due to inertia to a point where the pressure inside the bubble becomes lower than the pressure in the surrounding water. The surface of the bubble then begins to move back and the bubble shrinks. Again due to inertia as the bubble collapses it reaches a point where the pressure inside the bubble is greater than the surrounding water and so begins to expand again. At this point it releases a pressure wave in to the water of much lower pressure than the primary shockwave but with a much longer duration. This expansion and contraction can cycle many times each time producing a pressure wave.

For the bubble pulse pressure waves to be damaging the process must occur in close proximity to the target as is often the design intent of underwater weapons. The overall effect of detonating a large explosive charge of a few hundred kilograms under the keel can break the back of the ship.

9.2 GAS EXPANSION EFFECTS FROM EXPLOSIONS

Expanding hot gases produced by an explosion can perform work on the surroundings. This is the mechanism by which explosives can be employed to produce a number of effects:

- Lifting and heaving
- Cratering
- Creation of airblast
- Production of underwater bubble pulses

9.2.1 Work Capacity

In air the energy of the detonation shock wave from an explosion is quickly dissipated as heat and is collected by the gaseous explosion products as they expand. Nearly all the intrinsic energy of the explosive (the Heat of Explosion, Q) is therefore available for work. The maximum available work (A) is expressed by the work integral shown in Equation (9-1).

$$A = - \int_{v_i}^{v_f} p\,dv = - q \qquad \textbf{(9-1)}$$

Where: v_i is the initial volume of the gaseous explosion product; v_f is the final volume of the gaseous explosion product; p is the gas pressure; q is the heat content of the gases in their final state.

Usually v_f is very much greater than v_i so that the mechanical efficiency of an explosion is very high.

In CHNO explosives where all the products of reaction are gaseous, A is generally within 7 % of Q. For explosives which produce condensed or solid materials in the reaction products, thermal equilibrium between the gas and solid phases may not be maintained during the gas expansion stage, the solid phase retaining a significant proportion of its energy. Many explosives generate appreciable quantities of solids or liquids in their reaction products. TNT produces free carbon and black-powder produces potassium salts including oxide, carbonate, sulphide and sulphate. Explosives containing aluminium yield solid aluminium oxide. For TNT, about 20 % of the heat of explosion is contained in the solid explosion products, of which only half becomes available to do useful work.

9.2.2 Force, Power and Strength of Explosives

In practical situations it is rarely possible for the work integral to be evaluated since the value of v_f when no more useful work is being done on the surroundings cannot be determined. The performance of an explosive through gas expansion is therefore expressed in practical units of force, power or strength.

9.2.2.1 Force Constant

The chief performance parameter for a gun propellant is its 'force constant', the maximum amount of work which can be done by a unit mass of propellant. A more practical measure is the pressure produced by unit mass of propellant when contained in a fixed volume, so that

$$\text{Force Constant (F)} = nRT_d \qquad \textbf{(9-2)}$$

Where: n is the number of moles of gas per unit mass of explosive; R is the molar gas constant; T_d is the temperature of detonation.

For example, RDX has a value of 0.041 mol g^{-1} for n and 4255 K for T_d. The molar gas constant has a value of 9.31 J mol^{-1} K^{-1} given a Force Constant for RDX of 1434 J g^{-1}.

In general, explosion products of low molar mass favour high values of n. They also tend to have lower heat capacities, resulting in higher temperatures of gaseous products.

9.2.2.2 Power Index

Although Force is a valid parameter for use with high explosives it is more usual to employ a parameter called the 'Power Index'. Power is related to the amount of gas produced and the amount of heat available to expand the gases. When used in connection with explosives the word 'power' does not refer to the general definition of power, that is the rate of doing work, but rather to the total work output. The 'Power Index' is obtained by comparing the value of [Heat of Explosion (see 4.4.2) (Q J g^{-1}) x Gas Volume (see 4.4.3) (V cm^3 g^{-1})] for an explosive as a percentage of that of a standard explosive, picric acid though this is no longer used as a practical explosive.

The use of Power Indices to compare explosive for their potential to perform work through gas expansion can be justified as follows. The most accurate way to assess individual explosives is by applying its Force Constant (F) as shown in Equation (9-2). Since one mole of an ideal gas occupies the same volume, 22.4 dm^3 at standard temperature and pressure and n has the units moles g^{-1} then n is directly proportional to V. Temperature of detonation (T_d) is related to Heat of Explosion (Q) as shown in Equation (9-3).

$$T = \frac{Q}{\sum \bar{c}} \qquad \textbf{(9-3)}$$

$\sum \bar{c}$ is the mean molar heat capacity of the gaseous products and this value will depend on the ratio of CO, CO_2, H_2O (g), H_2 and N_2. Clearly this will differ for every explosive; however, for military explosive formulations they are quite similar. Therefore it is acceptable to say that T_d is proportional to Q and that F is proportional to Q x V.

As an example the Power Index of RDX is given by:

$$Power\ Index = \frac{Q_{RDX}\ x\ V_{RDX}}{Q_{\ Picric\ Acid}\ x\ V_{Picric\ Acid}}\ x100 \qquad \textbf{(9-4)}$$

Q values: RDX 5125 J g^{-1}, Picric acid 3745 J g^{-1}

V values: RDX 0.908 $dm^3\ g^{-1}$, picric acid 0.780 $dm^3\ g^{-1}$

Therefore:

$$Power\ Index = \frac{5125\ x\ 0.908}{3745\ x\ 0.780}\ x100 = 159$$

9.2.2.3 Strength

Commercial explosives manufacturers express the performance of their products in terms of strength. This is measured by comparing the work done by an explosive with that done by either an equal weight (weight strength) or an equal volume (bulk strength) of a standard explosive. The standard chosen is often blasting gelatine; however, other commercial explosive standards are sometimes used. Care must be taken when considering a strength value for a particular product as the standards can be quite different in strength.

9.2.3 Measurement of Power and Strength

Many methods have been developed for the measurement of the maximum power output of explosives. A typical method consists of detonating the explosive in a water-filled quarry and estimating the total energy liberated by measuring the pressure in the shock waves produced, the gas bubble size and frequency of oscillation. The practical value of these methods is limited by the inconvenience of the experiment and the fact that the efficiency of explosives in real situations is rarely ideal. Methods which may be used in a laboratory are more useful.

9.2.3.1 Trauzl lead block test

This classical method of measuring 'power index' was established at the International Congress of Applied Chemistry in 1903. The test provides a ready means of measuring the relative power of an explosive though the result provides an index of brisance as well. A cylindrical block is cast from pure lead, its dimensions being 200 mm for both length and diameter. The cylinder has an axial hole 25 mm in diameter and 125 mm in length. Ten grams of explosive wrapped in tin foil and fitted with an electric detonator are inserted to the bottom of the hole and tamped with graded dry sand until the hole is full. The charge is fired and the hole enlarged to a pear shape by the explosion as shown in Figure 9-3. The new volume of the hole is measured by filling it with water and the increase in volume obtained by subtracting the original volume (61.5 cm^3). A parallel test with the standard explosive picric acid is also carried out and the 'Power Index' obtained by comparing the relative crater volumes.

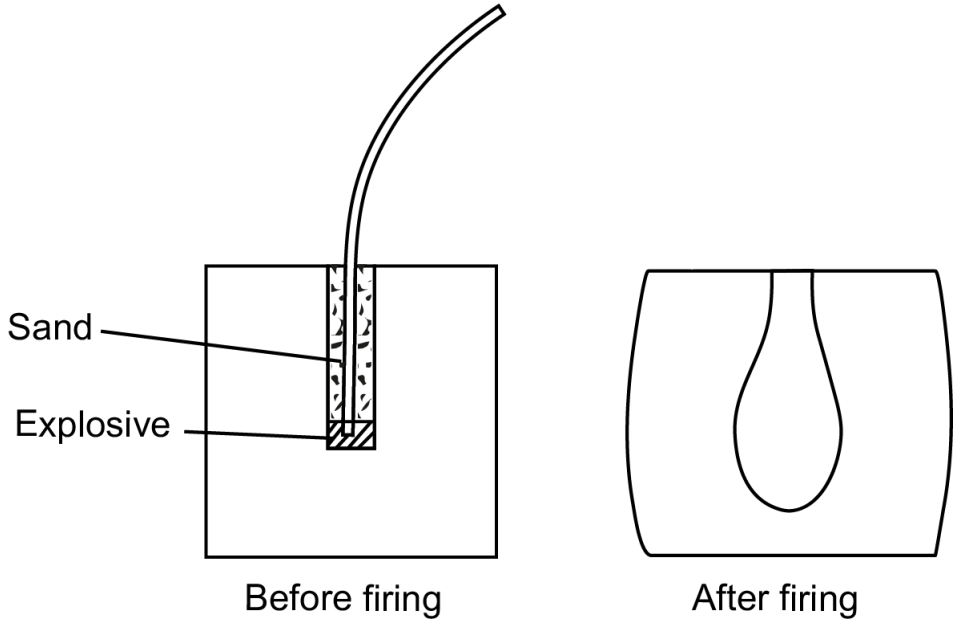


Figure 9-3 Lead block test

Criticisms of the test include the fact that the results depend on the starting temperature of the lead block, the number of times the lead has been recast and the nature of the tamping material. Though the test is no longer employed, accepted results exist for most explosives and are still commonly used (Table 9-1). It is still of value in studying weak explosives which are unsuitable for measurement in the ballistic mortar.

Table 9-1 Calculated and Experimental Power Index Values

Explosive	Calculated	Trautzl lead block	Ballistic mortar
Nitroglycerine	171	175	200
PETN	161	165	179
HMX	160	160	-
RDX	159	170	194
Torpex-2 (RDX/TNT/A1)	158	155	-
Amatol 80/20 (% w/w)	126	135	128
RDX/TNT 60/40 (% w/w)	138	125	-
Tetryl	123	120	132
Pentolite 50/50 (% w/w)	129	115	-
TNT	117	95	86
Lead styphnate	21	39	-
Lead azide	13	37	-

9.2.3.2 Ballistic mortar

Various mortars have been designed but an internationally accepted standard has been agreed by the International Committee on the Standardisation of Tests on Explosives, Sterrebeck, Belgium (1962) and the European Commission for the Standardisation of Explosives Testing, and rests on a design by the American company, DuPont. The principle of the mortar is illustrated in Figure 9-4. A 3 m long pendulum is fitted with a bob weighing 333 kg. A hole in the bob is fitted with a shot 12.37 cm in diameter, weighing 16.6 kg and having a clearance of 0.08 mm. Ten grams of explosive are wrapped in tin foil and fired using a plain detonator. The explosive ejects the shot which is captured on rubber matting or by a mound of sand. The recoil of the bob is measured on a scale and is a measure of the work done by the explosive on the system. The mechanical efficiency of the system is low but the results are reproducible and suitable for comparative work.

9.2.3.3 Other tests

The ballistic mortar and Trauzl tests use only 10 g of explosive. Some explosives are too insensitive or have critical detonation diameters which are too large to enable them to be tested by either of these methods. For these explosives, several kilograms may be exploded under water and the oscillation frequency of the gas bubble produced measured and used to calculate the power of the explosive. In a similar vein, another effect from explosive power is

air blast, which also can be used for comparisons. In this case the standard used is TNT and has led to explosives being assessed for blast potential being given a TNT equivalence and described in section 9.3.2.1.

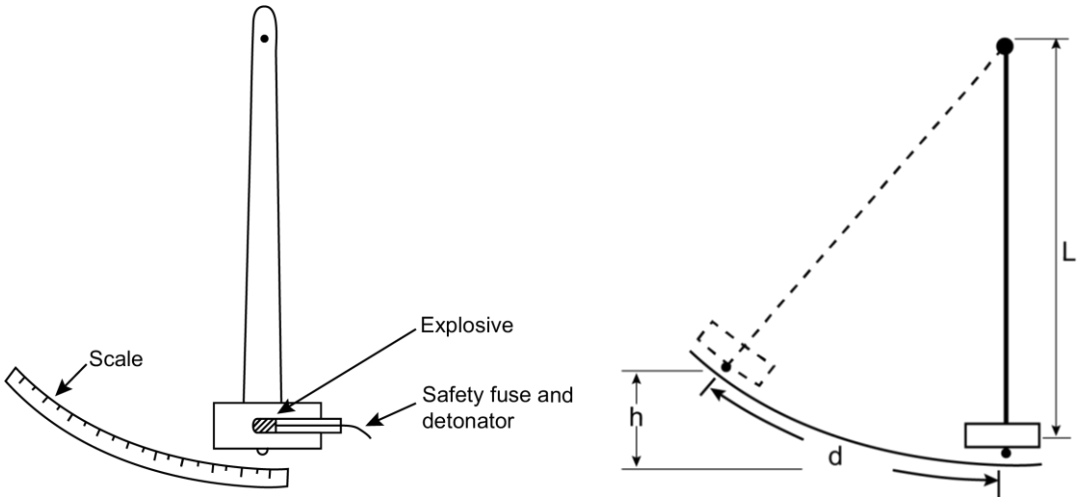


Figure 9-4 Ballistic Mortar

9.3 EXPLOSIONS IN AIR

9.3.1 Formation of Blast Waves

9.3.1.1 Primary shock wave

When an explosive charge is detonated in air the detonation shock wave passes through the charge at several thousand metres per second. When the detonation wave reaches the surface of the charge it is transmitted into the surrounding air. Once transmitted into the air, the detonation wave becomes known as the primary shockwave. No longer sustained by the chemical reactions within the explosive, the energy of the primary shockwave is rapidly dissipated through heating of the air and expansion over an ever increasing volume.

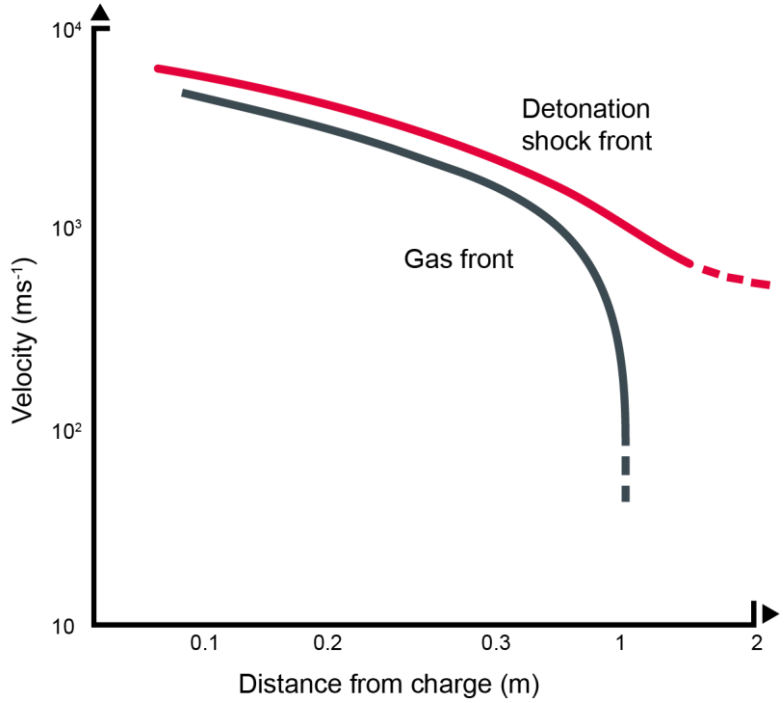


Figure 9-5 Detonation shock and gas front velocities from a 1 kg spherical charge of TNT in free air

9.3.1.2 Formation of the blast wave from expanding explosive gases.

Behind the primary shock wave is an area of high pressure and high temperature gas formed from the gaseous products of the explosion. The gas expands outwards and overtakes the primary shock wave in about 2 to 3 charge diameters picking up the energy deposited by the primary shock. As the gas expands further, the air surrounding the explosive gas is pushed away from the explosion and compressed forming a pressure wave, initially with a pressure profile shown at (a) in **Error! Reference source not found.**. Note that in Figure 9-5 the gas front from a 1 kg detonation has essentially stopped one metre from the explosive charge.

The speed of sound in air depends on its pressure, the greater the pressure the greater the speed of sound. Taking a wave of gas moving outwards, as in **Error! Reference source not found.**, the gas at point 'b' on the pressure curve is moving in air at a higher pressure than the gas at point 'a' and hence moves faster. So over time the gas at point b catches up with the gas at point a, as shown at (b) eventually forming a shock wave at (c). The actual shape of the initial wave has less effect on the eventual shape of the shock wave than the amount of energy released. This difference results in the formation a shock wave through this process called 'shocking up' and has an initial velocity of around 1000 m s^{-1}.

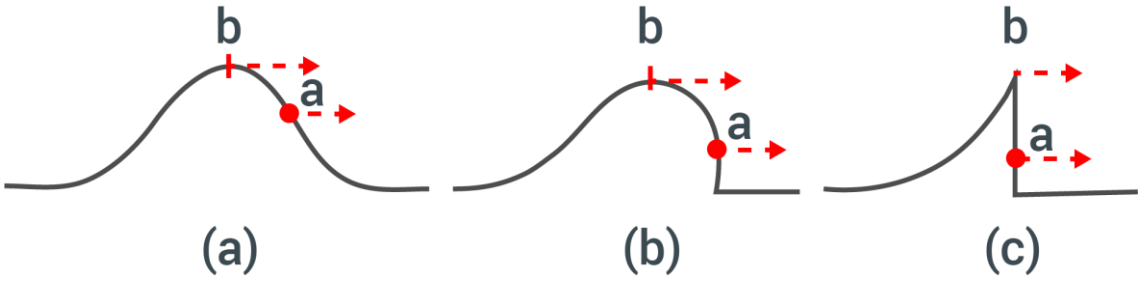


Figure 9-6 Formation of a blast wave

9.3.1.3 Ideal blast wave

For an idealised explosion a pressure transducer at some distance from the charge would record a signal similar to that shown in Figure 9-7**Error! Reference source not found.**. It takes time for the shock wave to reach the pressure transducer and so for some time after the explosion the transducer records the atmospheric pressure, P_o. The blast wave arrives at time t_a. At this time there is an almost instantaneous rise in pressure to the maximum pressure, known as the peak pressure, P'. The maximum overpressure, P_s, is the maximum pressure above atmospheric pressure and is given by $P_s = (P'-P_o)$.

As the pressure wave passes over the transducer the pressure decays with time. Eventually the pressure drops to atmospheric pressure at time t_d. However, due to inertia of the air molecules that are moving in the direction of the blast wave the pressure drops below the ambient atmospheric pressure producing a negative pressure phase before returning to atmospheric pressure at time t_f. The time (t_d - t_a) is the 'positive duration' of the blast wave and spans the 'positive phase' of the blast wave, that is when the pressure is above atmospheric pressure. The 'negative phase' of the shock wave is when the pressure is below atmospheric pressure and is from time t_d to t_f.

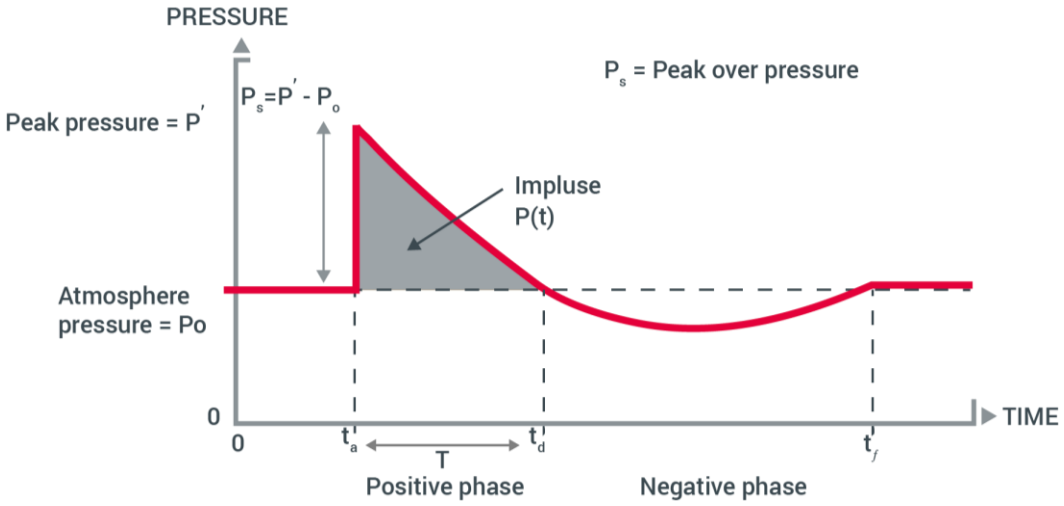


Figure 9-7 Ideal blast wave

The positive impulse, I, of a shock wave is a measure of the pressure multiplied by the duration of the pressure. It is defined as the integral of pressure over the duration of the positive phase of the blast wave as shown in Equation (9-5) where $p(t)$ is the pressure of the shock wave at time t. The impulse corresponds to the shaded area under the positive phase of the blast wave curve in **Error! Reference source not found.Error! Reference source not found.**. Compared to peak overpressure the impulse gives a more accurate method of assessment of the damage capacity of a blast.

$$I = \int_{t_a}^{t_d} (p(t) - p_o)\,dt \qquad \textbf{(9-5)}$$

As the blast wave travels away from the explosion, its energy is dissipated due to heat losses to the air medium in which it is travelling. As a result the energy density of the wave falls as the wave expands out to cover an ever larger volume. The blast overpressure is related to the energy density and hence it also decreases with distance as shown in **Error! Reference source not found.**9-8.

The front of the blast wave has a higher pressure and hence faster velocity than the later part of the blast wave. Hence the front of the shock wave travels faster. As a result the positive duration increases with distance.

Finally the velocity of the shock wave falls to the sonic velocity in air (approximately 330 m s^{-1} at standard temperature and pressure). The wave front becomes less steep and the 'negative phase' (rarefaction) becomes approximately equal to the 'positive phase' in amplitude. The blast wave then resembles an ordinary impulsive sound wave.

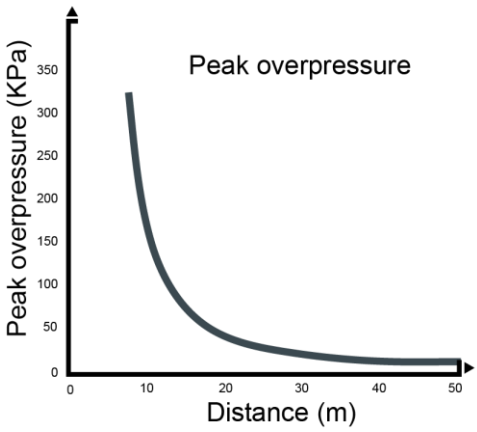


Figure (a)

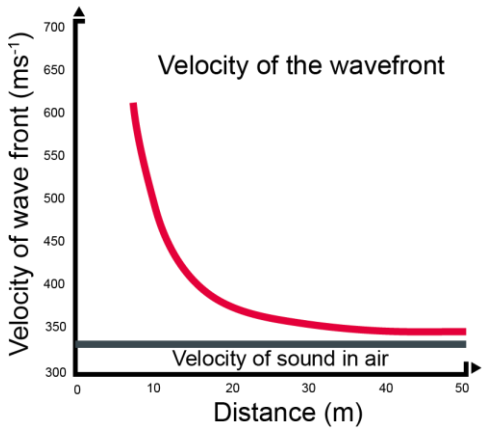


Figure (b)

Figure 9-8 Peak overpressure (Figure a) and velocity of the wavefront (Figure b) for 100 kg TNT

9.3.1.4 Shape of the blast wave

The decay of the pressure-time curve at a given location in space can be fitted by the Friedlander equation shown in Equation (9-6).

$$P(t) = P_s\left[1 - \frac{t}{T}\right]\exp\left\{-\frac{bt}{T}\right\} \quad \textbf{(9-6)}$$

$P(t)$ is the pressure at time t, P_s is the peak overpressure, t is time, T is the positive wave duration and b is called the waveform parameter and is a function of the peak overpressure. The waveform parameter is an adjustable factor selected to fit the curve to provide a method of obtaining the correct blast impulse.

The shape of the pressure/time curve also can be reasonably well fitted by the simpler equation due to Ethridge:

$$P(t)=P_o+P'e^{-ct} \quad \textbf{(9-7)}$$

Where c is a constant obtained from fitting the equation to the data. The equation is an oversimplification but will accurately fit many gauge records over much of the 'positive duration'.

Curve fitting using the Friedlander equation can be particularly useful when analysing blast records. Figure 9-9 shows the pressure vs. time recording from the detonation of a small explosive charge. To obtain accurate values for peak overpressure is not straightforward as the blast gauge takes time to react as the shockwave arrives. To calculate the impulse requires an accurate figure for the positive phase duration, which is usually masked by the pressure spikes overlaid on the true pressure measurement by gauge ‘ringing’. This is caused by the natural frequency of some part of the gauge mounting as it is struck by the blast wave. The early part of the decay after peak overpressure and before the first spike from gauge ringing gives accurate data points from which to apply the Friedlander equation.

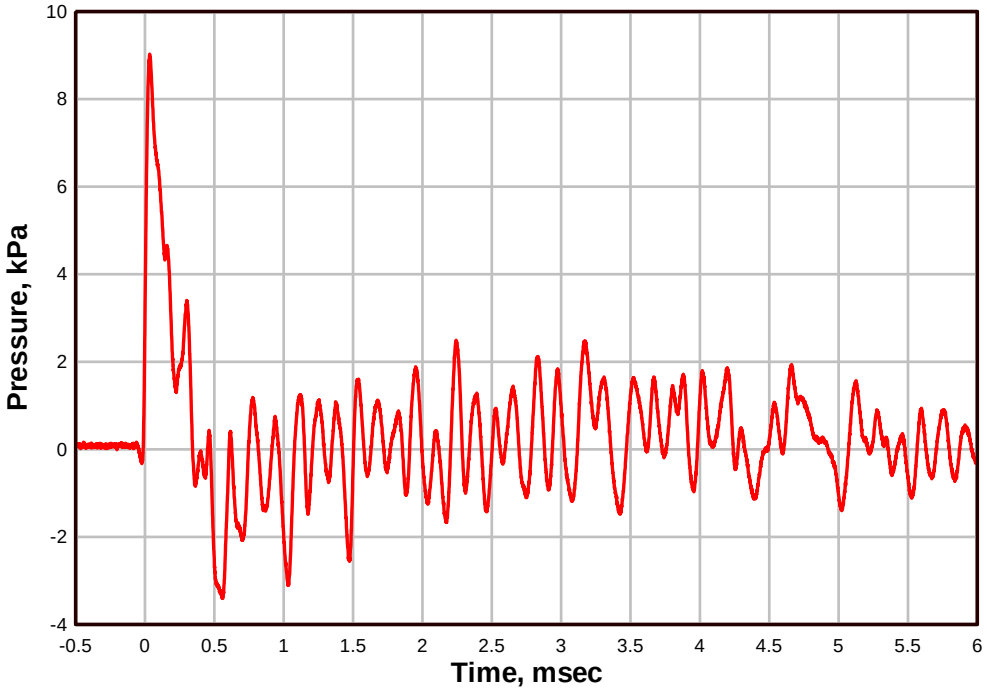


Figure 9-9 Actual pressure vs. time recording from an explosion

9.3.1.5 Velocity of the blast wave

For a simplified blast wave in an ideal gas the blast wave velocity, U_S, and the peak overpressure are related by Equation (9-8).

$$P_s - P_o = \frac{2\gamma\left(\left(U_s/a_o\right)^2 - 1\right)}{\gamma + 1} P_o = \frac{7\left(\left(U_s/a_o\right)^2 - 1\right)}{6} P_o \qquad \textbf{(9-8)}$$

For an ideal gas (pressures up to 500 kPa = 5 bar) it has been assumed that the ratio of specific heats = 1.4 and a_o is the speed of sound in air at standard atmospheric temperature and pressure. Rearranging gives a shock velocity as in Equation (9-9).

$$U_s = \sqrt{\frac{6P_s + 7P_o}{7P_o}}\, a_o \qquad \textbf{(9-9)}$$

In practice for shockwaves from explosions the irreversible heating of the air behind the blast wave at high overpressures makes the equations more complex.

9.3.1.6 Non-ideal blast waves

The shock wave in Figure 9-7 is for an ideal blast wave. Quite often the observed characteristics differ from the ideal profile. If the blast source is of low specific energy then the pressure pulse may travel some distance before 'shocking up'. If the blast source is a cased charge then the time/pressure profile may be quite 'spiky' in appearance. This is due to small pressure disturbances superimposed on the primary blast wave. These disturbances are ballistic shocks from casing fragments moving at supersonic velocities. Since the fragment velocities decay less rapidly than the blast wave velocity it is possible for the disturbances to be recorded before the blast wave arrives.

Non-spherical explosive charges, such as cylindrical and rectangular charges, will initially form non-ideal shock waves, often with multiple shocks, as discussed in Section 9.3.1.7. However over time and distance the energy distribution equalises around the shock waves and a single spherical shock wave is formed.

9.3.1.7 Non-spherical charges

Much of the theory for blast waves assumes an ideal blast wave from a spherical charge. In practice most military charges are either based on a cylinder due to the aerodynamic design of projectiles or occasionally cuboids such as plastic explosive.

Each face on an explosive charge will produce a shock wave. Figure 9-10 Shock waves from a cylindrical chargeshows the shock waves from a cylindrical charge. The strength of the shock wave depends on the presented area of the face from which the shock wave originates, the larger the presented area the larger the shock wave. Close into the charge this shock wave can be over double that from a spherical charge of the same mass.

As the shock waves expand out they collide. The angle of collision is such that Mach reflection occurs between the colliding shockwaves. This results in Mach stems (known as bridging waves in this instance) and the formation of reflected shock waves also known as secondary shock waves. The secondary shock waves expand out from the line of collision. For cylindrical charges a single secondary wave is observed. For cuboids, several secondary shock waves can be observed. As the shock waves expand, energy is transferred between the shockwaves and eventually a spherical shock wave is formed. Further information on shocks from non-spherical sources can be found in the literature[1-3].

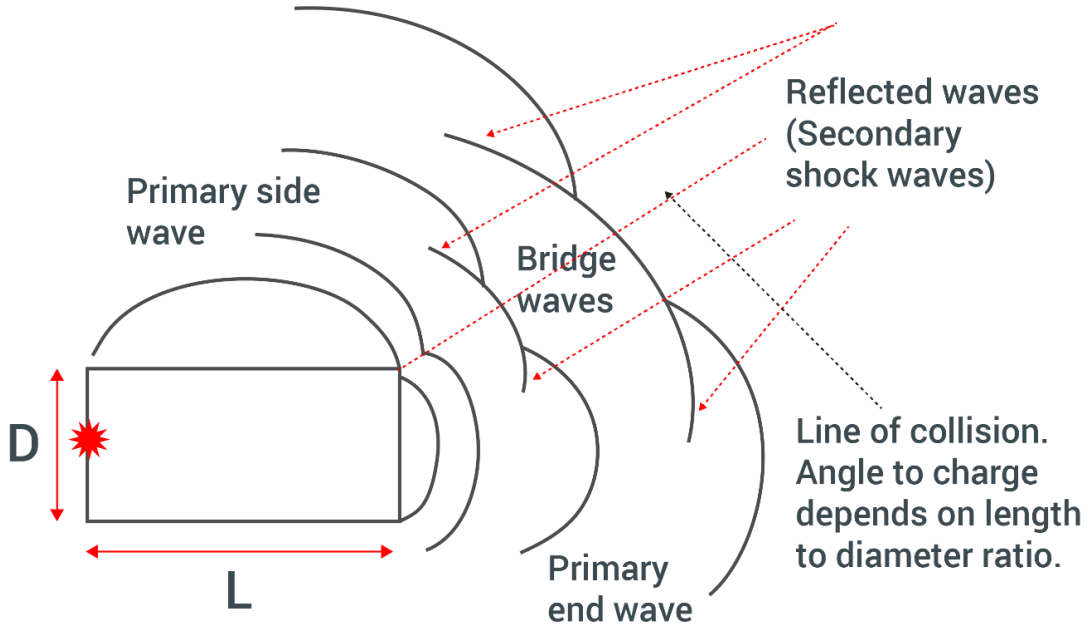


Figure 9-10 Shock waves from a cylindrical charge

9.3.2 Factors Affecting the Size and Shape of Blast Waves

A number of factors affect the magnitude of the blast overpressure; these include the power of the explosive used, the mass of explosive and the distance from the explosion.

9.3.2.1 Comparison of explosives and TNT equivalency

To compare the blast waves from different explosives TNT equivalency is used. This compares the properties, e.g. impulse, peak overpressure, and heat of explosion or power of a blast wave from a given explosive to that of TNT. For each property, TNT equivalence gives a constant that is the ratio of the property of a given explosive compares to that of TNT. For example, the TNT equivalence of Composition B for pressure is obtained from equation (9-10).

$$\text{TNT equivalence}_{pressure}(\text{Composition B}) = \frac{\text{Overpressure Composition B}}{\text{Overpressure TNT}} \qquad \textbf{(9-10)}$$

This is for the same mass and shape of explosive at the same distance from the explosion. For power the TNT equivalence of Composition B is obtained from equation (9-11).

$$\text{TNT equivalence}_{power}(\text{Composition B}) = \frac{\text{Power Composition B}}{\text{Power TNT}} \qquad \textbf{(9-11)}$$

Again this is for the same mass and shape of explosive at the same distance from the explosion.

It would not be unreasonable to consider that the TNT equivalence for a given explosive should be the same no matter how it is determined. However, the TNT equivalence of an explosive can be different for peak overpressure or impulse as shown in Table 9-2. Note that for a given explosive the values of TNT equivalence in the literature can vary depending on the way the data was obtained with values for RDX varying from 1.14[4] to 1.4[5]. More details on the issues of TNT equivalence can be found in the literature[6,7].

Table 9-2 TNT Equivalence for Peak Overpressure and Impulse for Some Explosives[8]

Explosive	TNT equivalence pressure	TNT equivalence impulse
ANFO	0.82	0.82
HMX/TNT (70/30)	1.06	1.06
RDX/ TNT (70/30)	1.14	1.09
Composition C4	1.37	1.19
Tritonal 80/20	1.07	0.96
TNT	1.00	1.00

9.3.2.2 Effect of distance

The blast wave from an explosion decreases rapidly with distance, d, as shown in Figure 9-2. How blast overpressure and other parameters such as impulse and blast wave arrival times are affected by the distance from an explosion can be demonstrated by applying polynomials derived from blast measurements[9,10].

There is some complexity as to the relationship between peak overpressure and distance where, depending on many factors, overpressure may vary proportionally with 1/distance or with 1/distance^2[11]. However, the most likely scenario where such a relationship has practical value is for surface burst explosions such as accidental detonation of stored ammunition or terrorist attacks using large vehicle borne devices. Data has been produced for a 50 kg TNT hemispherical burst allowing peak overpressure to be plotted against 1/distance and 1/distance^2. Figure 9-11 shows that peak overpressure for distances from 5 to 100 m does not have a linear relationship with 1/distance but when peak overpressure is plotted against 1/distance^2 there is a good linear relationship (R^2 = 0.9959) as shown in Figure 9-12. The linear fit is even better for ranges close to the charge, 5 to 10 m, with a regression value of 0.999 (Figure 9-13).

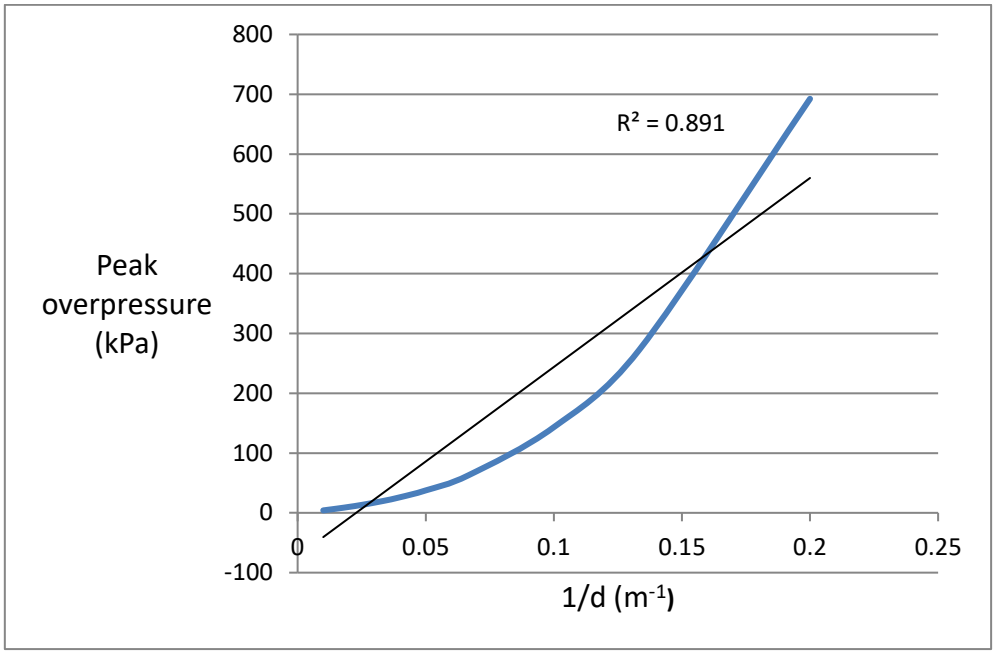


Figure 9-11 Peak overpressure vs. 1/distance for a 50 kg hemispherical TNT explosion from 5 to 100 m

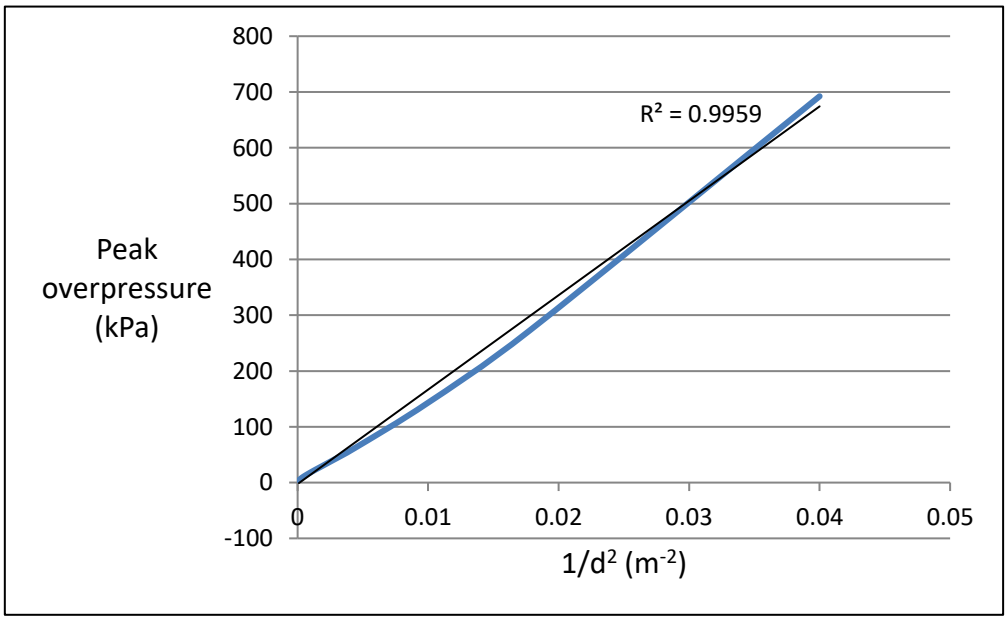


Figure 9-12 Peak overpressure vs. 1/distance^2 for a 50 kg hemispherical TNT explosion from 5 to 100 m

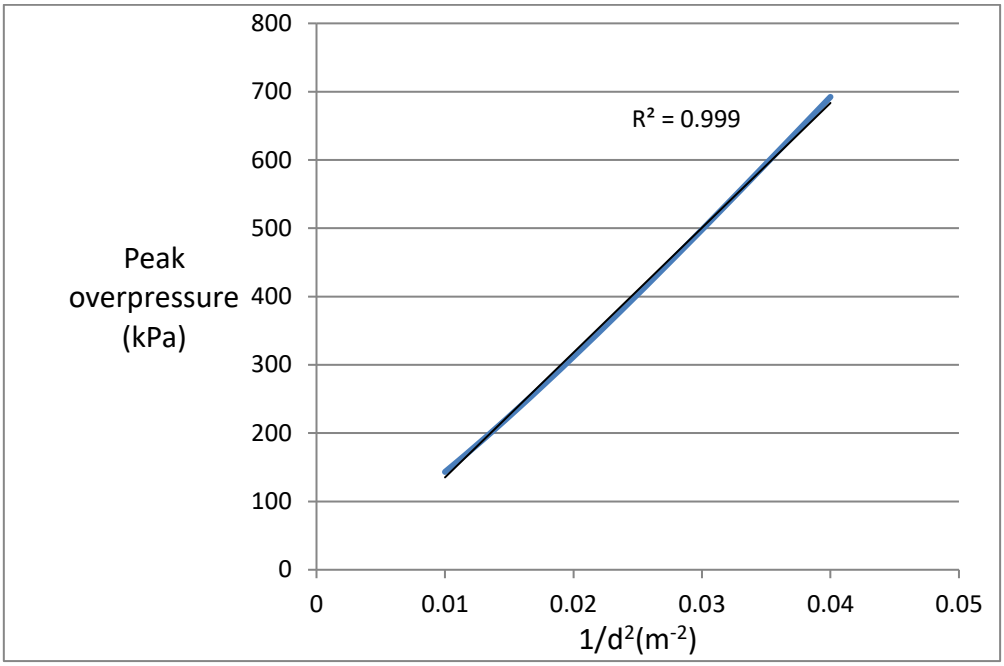


Figure 9-13 Peak overpressure vs. 1/distance² for a 50 kg hemispherical TNT explosion from 5 to 10 m

9.3.2.3 Hopkinson-Cranz scaling laws

Both Hopkinson[12] and Cranz[13] independently found that blast from explosive charges could be scaled by dimension. This is true provided that the charges have the same geometry, are detonated in the same atmospheric conditions and have the same charge to surface geometries. The relationship is known as cube-root scaling or Hopkinson-Cranz scaling as can be demonstrated using Figure 9-14.

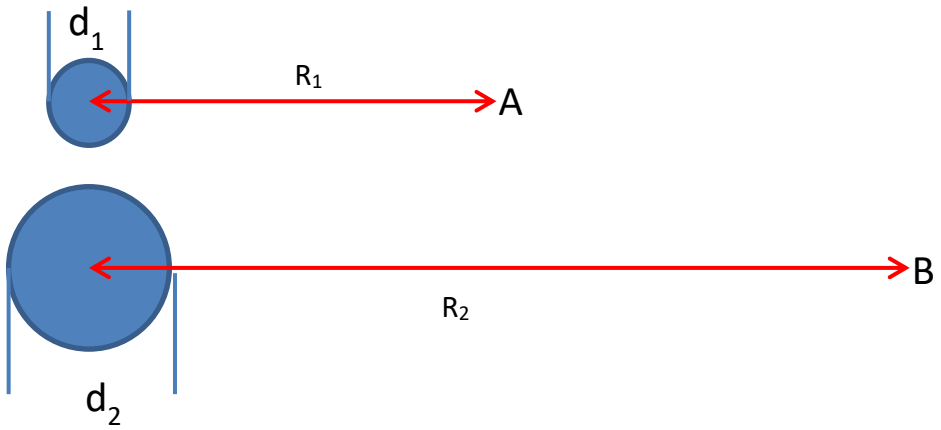


Figure 9-14 Example of Hopkinson-Cranz scaling

R2

In Figure 9-14 d_2 is 2 x d_1 and if R_2 is 2 x R_1 then the blast wave parameters recorded at points A and B are identical. The volume of a spherical charge is proportional to d^3 and so as d_2 is 2 x d_1 then the larger charge will be eight times the volume and if the explosive is the same in both then eight times the mass. From this scaled distance is a value at which the blast wave parameters will be the same for a range of charge weights and distances from the explosion as long as the scaled distance is the same. Scaled distance (Z) is calculated using equation (9-12) where R (m) is distance from the charge and $M^{1/3}$ is the cube root of explosive mass (kg).

$$Z = \frac{R}{M^{1/3}} \qquad \textbf{(9-12)}$$

Each value of Z will correspond to a particular peak overpressure and this is further demonstrated with data plotted for peak overpressure vs. distance using three charge weights as shown in Figure 9-15.

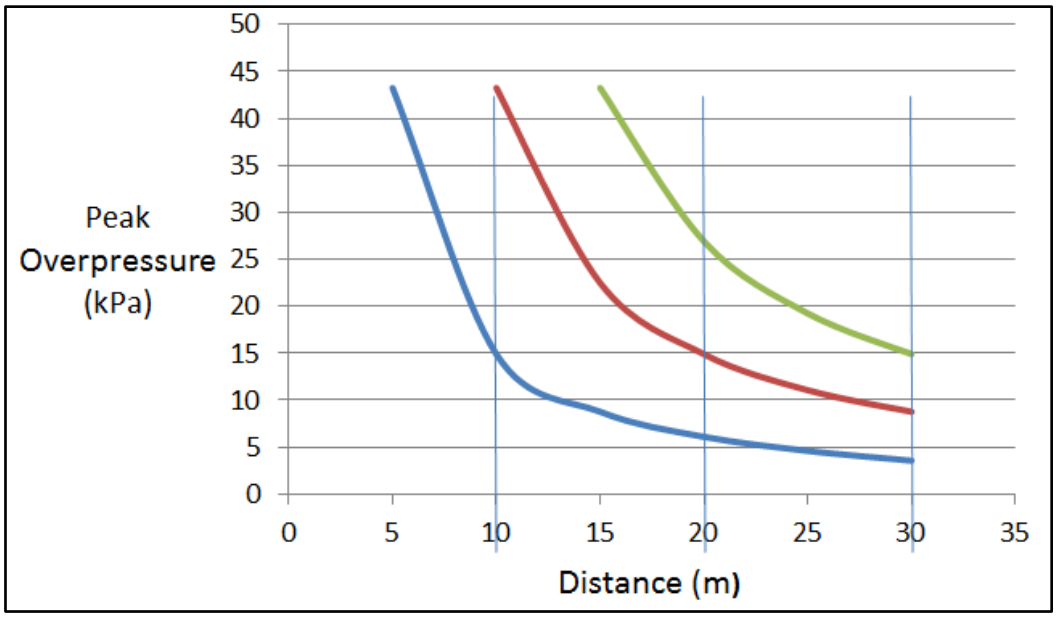


Figure 9-15 peak overpressure vs. distance for 1 kg (blue), 8 kg (red) and 27 kg (green)

It can be seen that all three charge weights give the same peak overpressure of 15 kPa at 10 m, 20 m and 30 m respectively. If peak overpressure is now plotted against $R/M^{1/3}$ then a single curve is produced. The 15 kPa point on each of the curves will become $10/1^{1/3}$, $20/8^{1/3}$ and $30/27^{1/3}$ all giving a scaled distance of 10. If this is carried out across all the data points in Figure 9-15 then the curve shown in Figure 9-16 is produced. To make this easier to use the data is presented with log/log scaling as shown in Figure 9-17.

Scaled distance for given peak overpressures is invaluable for calculating safety distances. For example, the horizontal line drawn on Figure 9-17 is at a peak overpressure of 5 kPa, the maximum peak overpressure that can be accepted to impinge on a building inhabited by the public for explosive licencing

purposes. From the curve the scaled distance is 22.2 and so the storage of explosives with mass explosion hazard can be regulated depending on distance to inhabited buildings and the quantity of explosives stored. By applying equation (9-12) the minimum distance allowed between a storehouse containing 1000 kg and housing occupied by the public is 22.2 x $1000^{1/3}$ = 222 m.

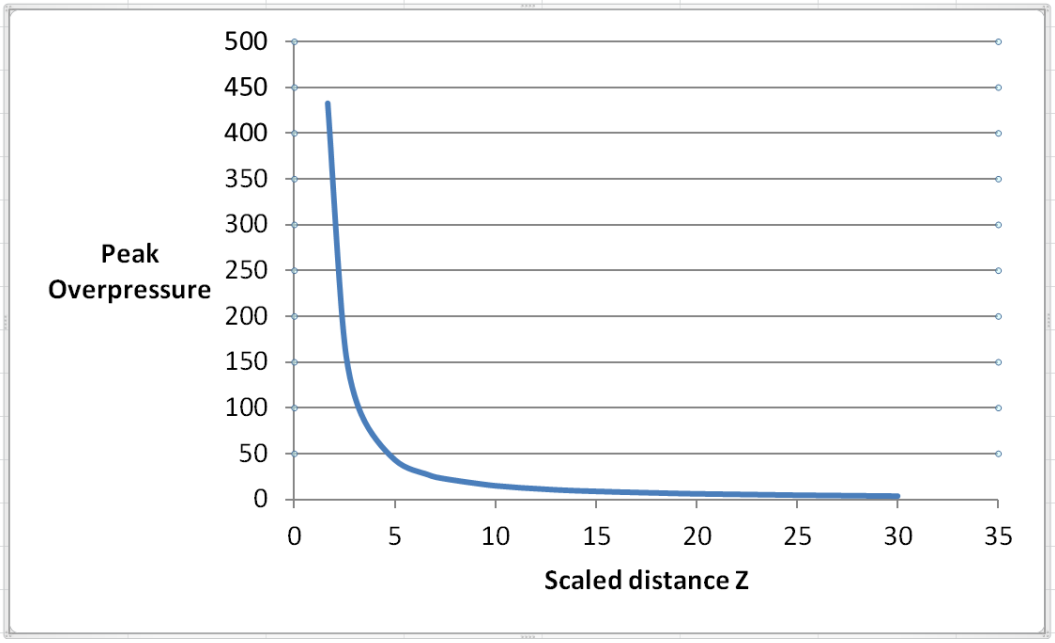


Figure 9-16 Peak overpressure vs. scaled distance from data in Figure 9-15

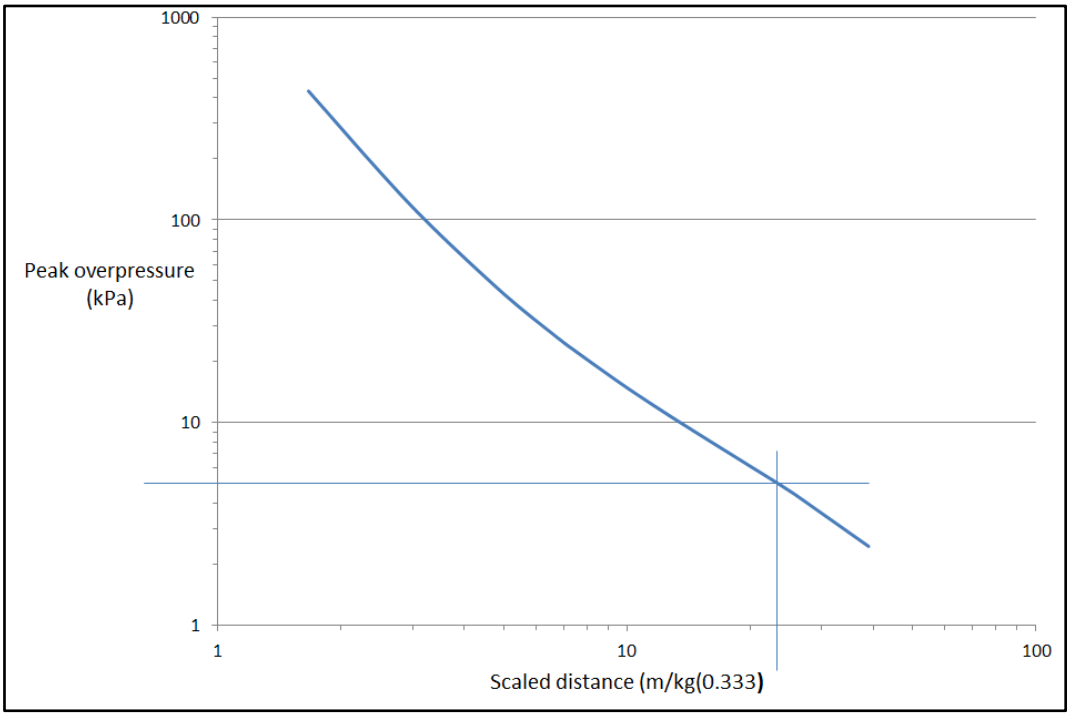


Figure 9-17 Log/log plot of peak overpressure vs. scaled distance

9.3.3 Equivalent Net Explosive Quantity (ENEQ)

The discussion so far assumes a bare charge of explosive. In practice most explosives are contained in some way. The explosives may be wrapped in wax paper, placed in a plastic box or stored in a brick building. Further, some types of ammunition have metal casing designed to fragment. When an explosive detonates, some of the energy goes into breaking up the casing and containment. As a result there is less energy in the blast wave, reducing the strength of the wave. Figure 9-18 shows the effect of casing on the blast waves from an explosion where C/M is mass of explosive charge (C) divided by total mass of explosive plus metal casing (M).

The Equivalent Net Explosive Quantity is defined as the amount of explosive that if the explosive was a bare charge, would give the shock wave observed. That is the amount of bare explosive required to give the shock wave observed after energy has been extracted breaking up the containment. Equivalent Net Explosive Quantity is also sometimes called the Effective Net Explosive Quantity.

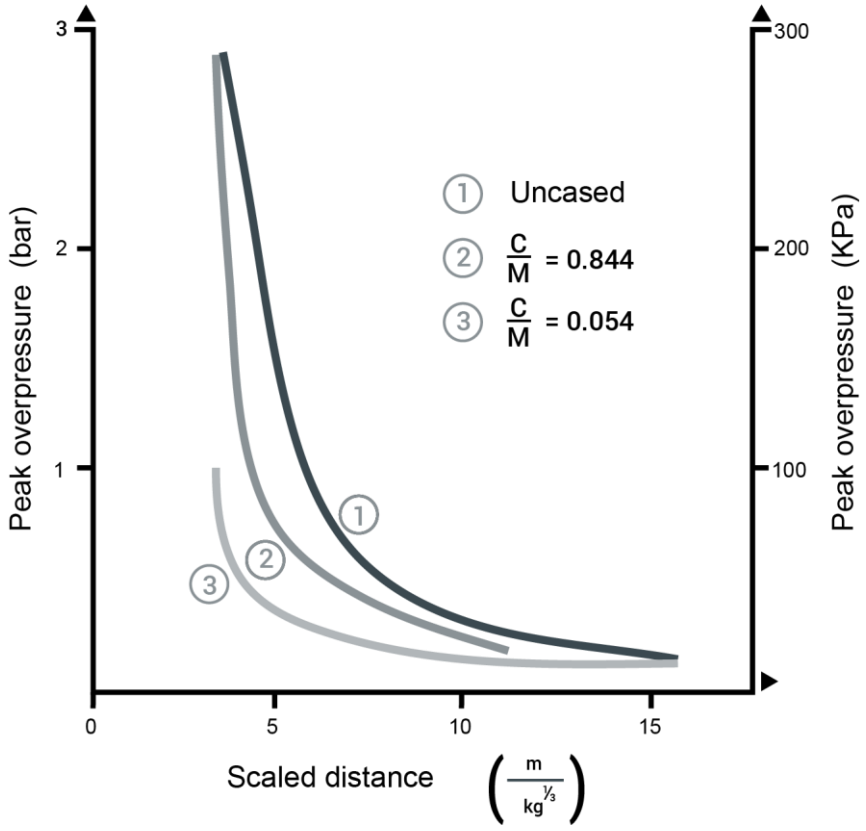


Figure 9-18 Effect of ratio of charge weight/total weight on peak overpressure for similar charge weights of HE in metal cases of different weights

9.3.3.1 TNT equivalency and ENEQ

Section 9.3.2.1 describes how explosives can be compared with TNT in regard to their ability to create blast. This also allows the application of ENEQ when

considering, for example, blast damage potential from stored explosives. If ANFO has a TNT equivalence of 0.82 then 1000 kg of ANFO would produce blast pressures equivalent to 820 kg of TNT. Safety distances, or more correctly safety peak overpressures, are related to a scaled distance as shown in section 9.3.2.3, where a scaled distance of 22.2 gives a peak overpressure of 5 kPa. This assumes the explosive mass used to calculate scaled distance is that of TNT. Therefore, it is not unreasonable to assess the blast damage potential by first converting the mass of explosive in question to that of TNT as shown above.

9.3.4 Reflection of Blast Waves

The above discussion of shock waves in air has assumed an explosion in free air, well away from any reflecting surfaces. It is more usual to be concerned with explosions at or near the ground, or near structures.

9.3.4.1 Explosion on the ground

When a charge explodes on the ground, the blast wave is not able to spread unobstructed in all directions. The blast wave is reflected from the ground into the air. A single hemispherical shockwave is formed. The proportion of the energy reflected depends on the nature of the ground but the increase in overpressure when compared with a free air explosion does not usually exceed a factor of two. Frequently an enhancement of 1.8 is used, allowing for the absorption of some energy into the ground[14]. The wave, once stabilised is similar in other respects to one in free air but expanding hemispherically.

9.3.4.2 Normal reflection

When a planar shock wave hits a surface at an angle of 0° as shown in Figure 9-19 the shock wave will reflect from the surface. When the shock wave reaches the surface, the air molecules in the shock wave come to a stop at the surface. The pressure, density and temperature increase above those of the incident shockwave. The gas molecules are then reflected from the surface.

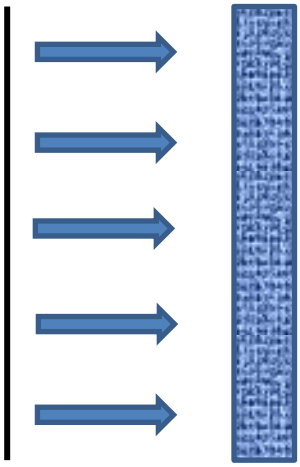


Figure 9-19 A blast wave that will undergo normal reflection

For a weak wave, the overpressure may be doubled by reflection normal to the surface. For a strong wave with a high temperature and pressure, the overpressure may increase up to 20 times or more[15,16], as shown in Figure 9-20. Damage criteria for hard targets are often quoted in terms of the reflected overpressure rather than incident pressure since it is the instantly reflected pressure which acts on the reflecting target.

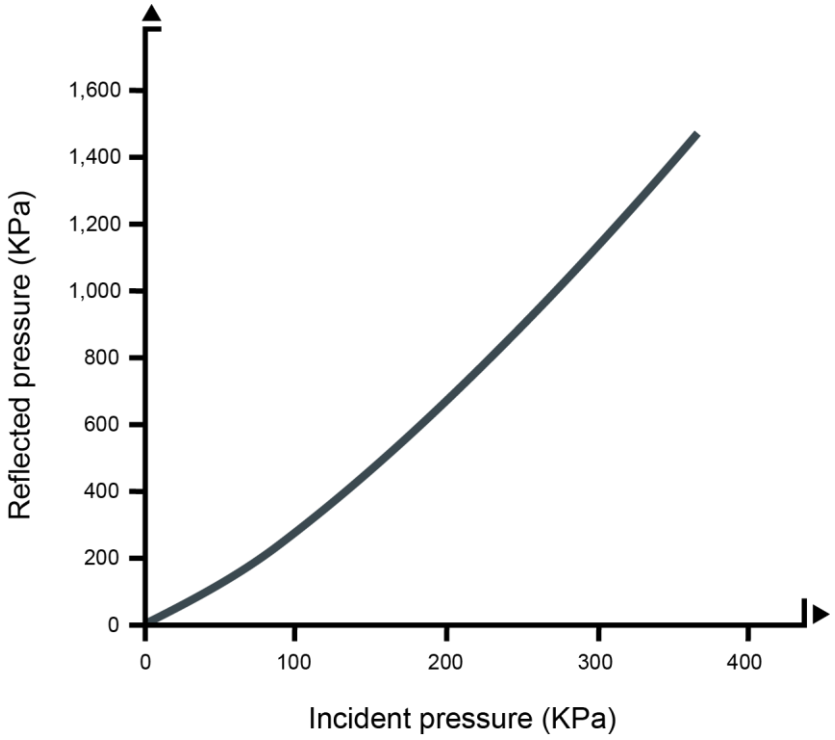


Figure 9-20 Peak reflected overpressure versus peak incident overpressure, for a theoretical target of infinite frontal area

9.3.4.3 Regular reflection

When a shock wave hits a surface at an angle between 0° and 39° regular reflection occurs where the angle of reflection, α_R, is less than the incident angle, α_I, as shown in Figure 9-21. As with normal reflection, the overpressure may be enhanced by regular reflection. The enhancement depends on the angle of incidence, see Table 9-3.

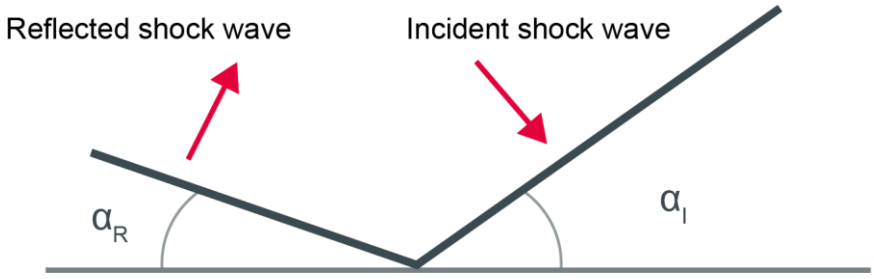


Figure 9-21 Angle of incidence, α_I, and reflection, α_R, of a shock wave hitting a surface

Table 9-3 Pressure Enhancement Due to Blast Wave Reflection at an Angle[17]

Angle of incidence of the blast wave α_I (degrees)	Enhancement factor
90*	1.00
80	1.48
70	1.95
60	2.43
39	2.80

***** At an angle of 90° the pressure measured is called the incident overpressure (see section 9.3.4.5).

9.3.4.4 Mach Reflection

When a shock wave hits a surface, e.g. the ground, at an angle greater than a critical angle of approximately 39°, then Mach reflection can occur. The actual value of the angle depends on, inter alia, the peak overpressure.

When a spherical shock wave hits a surface, the first part of the shock wave hits the surface normal to the surface. Normal reflection occurs and the shock wave reflects back normal to the surface, Figure 9-22, point 1. As the spherical shock wave moves across the surface the angle of impact increases and the shock wave hits the surface at an angle and regular reflection occurs, Figure 9-22, point 2. The reflected shock wave has a higher pressure and hence higher velocity than the incident shock wave. As a result the reflected shock wave catches up with the incident shock wave. The two wave fronts merge and form a single front called a Mach stem, Figure 9-22, point 3. The Mach stem is perpendicular to the ground and forms a cylindrical front, expanding outwards. The Mach stem has an increased overpressure and impulse. This is called a 'Mach reflection'. The point at which the incident wave, the reflected wave and the Mach front ('Mach stem') meet is called the triple point and is illustrated in Figure 9-22, point 4. The height of the Mach stem will increase as it moves outwards away from the initial point of impact with the ground.

The Mach reflection is exploited to increase the blast damage from nuclear weapons by optimising the height of burst above ground level. Also Mach reflections will occur when explosions occur in proximity to large buildings.

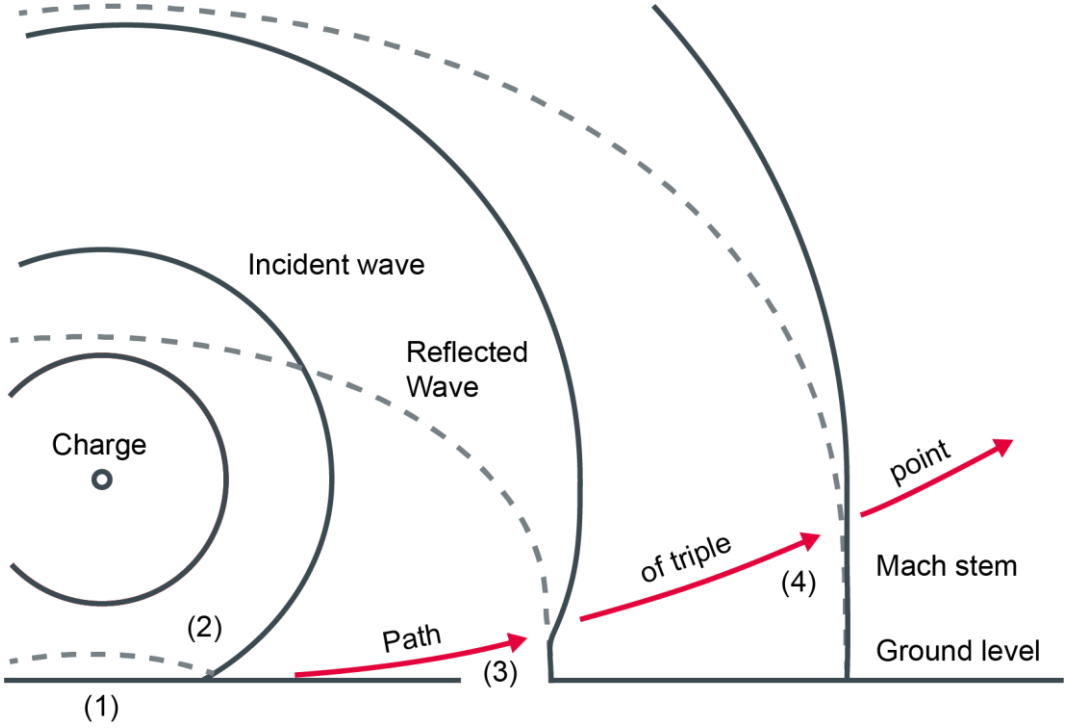


Figure 9-22 Mach Reflection

9.3.4.5 Incident overpressure

If α_i in Figure 9-21 is 90° then a pressure measured on a surface would be the incident peak overpressure. This is a blast wave travelling across a surface as shown in the Powerpoint slide Incident and reflected blast waves (go to Slide Show and click through the animation). Measurement and calculation of explosion blast effects are made to give baseline values for fully incident and fully reflected blast waves since, as has been demonstrated, the blast parameters will vary with reflected angle.

9.3.5 Effect of Altitude

As altitude increases, the density of air decreases and this reduces the effect of the blast wave. The decrease in blast strength with altitude is shown in Table 9-4, where A is the ratio of the charge weight, W_h, to produce a given overpressure at altitude, (h), and the charge weight, W_o, to produce the same overpressure at sea level. As an example it can be seen that at an altitude of 9,100 m, 1.2 times the amount of explosive is required than would be used at sea level to achieve the same blast. Scaling of blast waves at different altitudes can be carried out using Sachs scaling[18].

Table 9-4 Blast Attenuation at Altitude.

Altitude		Attenuation Factor
Feet	**Metres**	**(A)**
sea level	sea level	1.0
30,000	9,100	1.2
45,000	13,700	1.4
60,000	18,300	1.8
100,000	30,500	2.2

9.3.6 Explosions in a Confined Space

If an explosive detonates in a confined space, such as a room, two effects occur. First the blast wave is reflected from the walls, floor and ceiling of the room. This results in multiple reflected shock waves being experienced at any given position within the room. Secondly unless the pressure created by the production of hot gases by the explosion is vented immediately, e.g. through broken windows, blown out doors, etc. then there is a build-up of ambient pressure within the confined space called quasi-static overpressure. Where explosion accidents may occur such as in manufacture it is common practice to include blow-out panels in production rooms to assist in pressure release. Even so, on an explosive timescale the pressure release is not immediate and there always will be some quasi-static pressure effect that can last for hundreds of milliseconds. In the open a blast wave passes a given point in a few milliseconds and there is no further loading on a target.

If an explosion occurs within a tunnel where the blast wave cannot expand or escape then it will travel down the tunnel losing little energy from the shock front until it encounters side tunnels or branches such that the energy then can partition among the potential ways it can expand. Given the opportunity it may reflect back towards the source, which will take energy from the progress of the blast wave.

9.4 FUEL-AIR EXPLOSIONS

9.4.1 Creation of a Fuel-Air Explosion

A fuel-air explosion requires the pre-mixing of a fuel material, which can be in the form of a gas, liquid aerosol or fine powder, as a large volume cloud in air, which is a variant of the fuel-oxidiser mixture type explosive. These conditions, particularly with gases, can be created easily and have caused many explosion accidents both in domestic and industrial settings. Homes have been totally demolished by natural gas explosions due to gas leaks and the devastation of the Nyproplant at Flixborough, UK in 1974, which killed 28 people due to the

explosion of an estimated 36 tonnes of cyclohexane vapour in air, are both examples of the damage potential of fuel-air explosions.

9.4.2 Explosive Performance

The potential to produce damaging blast through a fuel-air explosion has been recognised by weapons designers. Conventional explosives such as TNT contain both the fuel and oxidiser elements within the explosive charge whereas a fuel-air warhead need only contain the fuel, as the oxidiser is oxygen in the air obtained at the point of initiation. A greater release of energy can therefore be achieved at the target for a weapon of given payload. It can be seen from Table 9-5 that the energy advantage can be as high as 10 times in ideal conditions compared to the heat of explosion of TNT at 4.2 MJ kg^{-1}. All but one, ethylene oxide also known as oxirane, are normally found in the gaseous state and not suitable for inclusion in a warhead. Oxirane has a boiling point of 10.5 ^{o}C and is a liquid if kept under modest pressure.

Table 9-5 Heats of Explosion of Some Fuels

Fuel	Heat of Explosion (MJ kg^{-1})
Methane	50
Propane	49
Acetylene	48
Ethylene	47
Ethylene oxide (oxirane)	28

At first sight the TNT equivalence would appear to be almost an order of magnitude, however, an efficiency factor must be considered. The explosive potential of a fuel-air explosion can be expressed as shown in Equation (9-13) where K is the efficiency of explosion, W_F is the weight of fuel, ΔH_F is the heat of explosion of the fuel and ΔH_{TNT} is the heat of explosion of TNT.

$$W_{TNT} = (K. W_F. \Delta H_F)/\Delta H_{TNT} \quad \textbf{(9-13)}$$

The full heat of explosion of the fuel is only realised when it is mixed with the stoichiometric quantity of oxygen. In any real fuel-air cloud there will be a wide range of concentrations so that the full energy output will not be achieved. Additionally, since air contains only 21 % of oxygen, for every unit mass of oxygen in the fuel-air system there will be 3.7 units of nitrogen which dilutes the system and absorbs heat. The explosive efficiency is therefore generally found to be less than 40 %. Nonetheless, this still equates to a potential TNT equivalence of ~4.

A fuel-air cloud will provide the optimum blast with a stoichiometric mixture as described above. If the mixture varies either to a fuel rich or fuel lean (poor) mixture it will still produce an explosion until it reaches certain limits called Upper Explosion Limit (UEL) and Lower Explosion Limit (LEL). Table 9-6 gives

some examples of these limits for an explosion caused by deflagration (burning) and within these are a narrower set of limits inside which the mixture is capable of detonation. Figure 9-23 shows how detonability varies with stoichiometry and initiation energy. The unusual fact that the UEL of acetylene is 100 % and has the potential to cause an explosion with no oxidiser present is through it undergoing a rearrangement of 3 acetylene molecules to form benzene with a large negative heat of reaction. For this reason acetylene cylinders do not contain compressed gas but contain acetylene dissolved in acetone solvent.

Table 9-6 Some UEL and LEL Values

Fuel	Explosive limits % vol/vol in air
Acetylene	2 - 100
Oxirane	3 - 80
Hydrogen	4 - 76
Carbon monoxide	13 - 74
Diethyl ether	2 - 48
Carbon disulphide	2 - 44
Ethylene	3 - 34
Methane	5 - 14
Propane	2 - 10
Gasoline	2 - 8

Initiation can be thermal (igniferous/flame), electric discharge (spark) or explosive shock (booster charge) and the initiation energy influences the Explosion Limits. As initiation energy increase the limits become wider as shown in Table 9-7 for the electric spark initiation of a methane-air mixture. The closer the mixture to stoichiometry and the greater the initiation energy the more likely the cloud is to detonate as shown in Figure 9-23.

Table 9-7 Explosion Limits for Spark Initiation of Methane

Ignition Energy (J)	LEL % vol/vol	UEL % vol/vol	Range % vol/vol
1	4.9	13.8	8.9
10	4.6	14.2	9.6
100	4.25	15.1	10.8
10,000	3.6	17.5	13.9

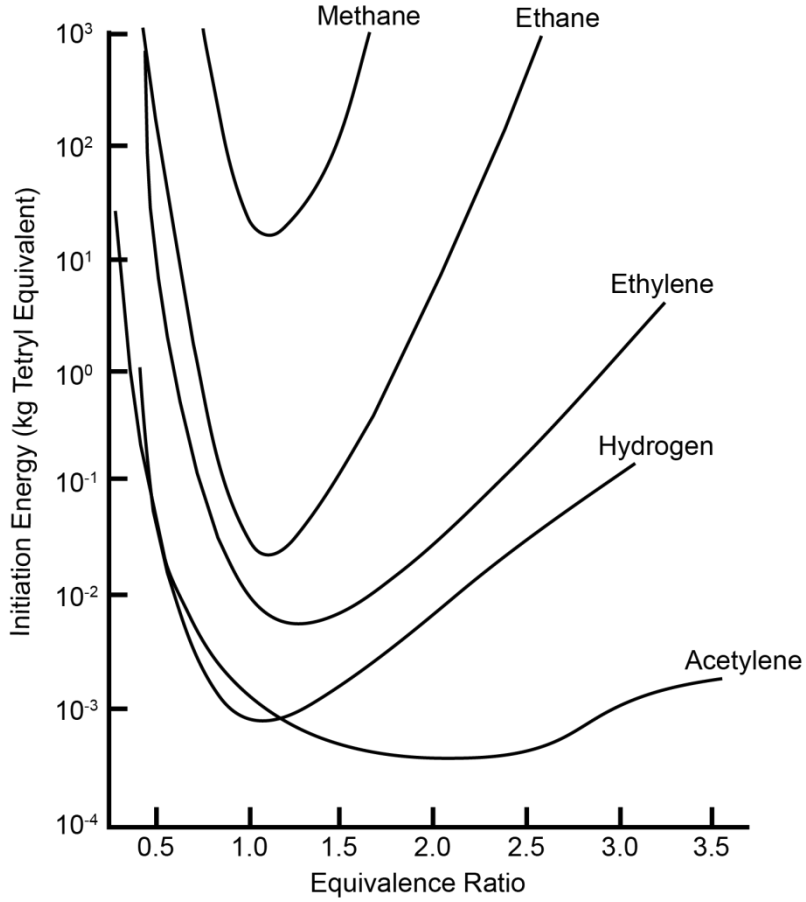


Figure 9-23 Detonability limits for some fuel-air mixtures

9.4.3 Fuel-Air Munition Effectiveness

9.4.3.1 Munition design and deployment

The basic design of a fuel-air munition is a cylindrical container filled with liquid fuel, examples being ethylene oxide or propylene oxide, which contains a central cylindrical burster charge filled with conventional high explosive. When the burster charge detonates the liquid is driven out in to a pancake shaped cloud of droplets and vapour creating the fuel-air mixture. The munition deploys a detonator or detonators for redundancy inside the cloud and when the fuel-air cloud is fully formed these initiate detonating the cloud. Vapourisation of the droplets primarily takes place when they are heated by the arrival of the shockwave or flame front following initiation of the fuel cloud.

The mass of the burster charge to fuel ratio have little effect on cloud dimensions once the ratio exceeds 1:40. The delay time between dispersion and cloud initiation of a few hundred milliseconds means that local meteorological conditions have little effect on cloud formation. Cloud sizes for

the dispersion of various quantities of propylene oxide (methyloxirane) in vertically aligned cylindrical drums fitted with central burster charges with a charge to fuel ratio of 1:20 are shown in Table 9-8. The cloud height and diameter varies little between 100 m and 200 m after dispersion and fuel concentrations ranged from 56 g m^{-3} - 105 g m^{-3} (stoichiometric value 100 g m^{-3}).

Table 9-8 Dimensions of Methyloxirane Clouds

Fuel quantity (litres)	Cloud diameter (m)	Cloud height (m)
10	10.6	1.8
30	13.9	2.5
45	16.0	2.9
60	17.6	2.9
150	20.0	3.8
170	23.5	3.7
300	25.1	5.1

9.4.3.2 Blast Effects

For fuel-air clouds that detonate the detonation pressures and velocities within the cloud are much lower than those of condensed explosives with maximum values of 2000 k Pa (20 bar) and 1800 m sec^{-1} (c.f. TNT 19 MPa and 6950 m sec^{-1}) so they have little brisant or shattering effects against hard targets. The value of a fuel-air warhead is to be found in the propagation of airblast. When a condensed explosive charge detonates it may be regarded as a point source of energy. The blast overpressure associated with the explosion falls rapidly with increasing distance from the charge. By contrast the source for a fuel-air explosion is in the form of a large cloud which, as an example, for a 30 kg charge, may be 15 m in diameter.

Therefore, if a fuel-air warhead is detonated at ground level there will be a blast pressure of up to 2000 kPa (20 bar) under the whole cloud. In comparison, if a 30 kg TNT warhead is detonated at ground level the blast peak pressure will have dropped to ~2000 kPa at a distance of 2.5 m and at 7.5 m, the radius of the cloud described above, it will be 185 kPa. Furthermore, when the blast wave leaves the edge of the cloud the blast peak pressure decays less quickly than from a point source and overpressure duration will be longer maintaining impulse. Together these factors make a fuel-air warhead an extremely effective blast weapon.

9.4.3.3 Fuel-air weapons

Both the US and Russia have included fuel-air weapons in their arsenal. The US had particular interest in the use of such weapons to clear minefields such as Surface Launched Fuel Air Explosive (SLUFAE) and Catapult Launched Fuel Air Explosive (CATFAE) developed in the 1970s and 1980s. However, they proved not to be sufficiently effective at detonating mines or clearing wire obstacles and were withdrawn from service. Large air dropped bombs such as the 500 lb BLU-95 and the 2000 lb BLU-96 and cluster bombs CBU-55 and CBU-72 have all been withdrawn from service.

It is understood that Russia field a range of fuel-air weapons including air dropped bombs, cluster munitions, multiple launched rocket systems, helicopter launched missiles and aircraft missiles. The BM-30 Smerch is of particular note as probably the most effective fuel-air weapon. It consists of a 12 barrel 300 mm calibre multiple launch rocket system with a range of up to 70 km that, with a full salvo, covers a target area of over 0.5 km^2. This weapon has been sold to over a dozen countries worldwide.

9.4.3.4 Terminology

There has been some confusion regarding the names given to weapons that utilise oxygen from the air as an explosive component, which began with the introduction of the Russian shoulder launched missile known as RPO-A. This was called a thermobaric weapon and the term began to be used for both this new type of warhead and fuel-air warheads. Adding to the confusion was the use of the term ‘volumetric warhead’ and more recently ‘enhanced blast warhead’. These various terms are explained below:

- A **Fuel-air Warhead** is a container of liquid fuel with a central high explosive burster. The central burster is detonated and causes the fuel to mix with air in a pancake shaped cloud. A few hundred milliseconds later detonators thrown in to the cloud during initial functioning detonate the fuel-air cloud. This is clearly a 2 stage event.
- A **Thermobaric Warhead** contains an explosive charge consisting of an explosive capable of detonation but mixed with a large percentage of metal powder such as aluminium. Unlike the Torpex explosives where the metal content is limited the thermobaric explosive may contain a much higher percentage as this reacts with air as the detonation products expand adding to the heat content of the explosion. This is a single stage event as there is only one detonation although it does utilise oxygen from the air. RPO-A has in the past been labelled as a Flame Weapon even in its country of origin. This is likely to come from the fact that the RPO shoulder launched missile was truly incendiary in its effect. There is no doubt that RPO-A is a blast weapon.
- A **Volumetric Explosion** is one where oxygen from the air is a major contributor to the energy of explosion. A fuel-air explosion, therefore, clearly is ‘volumetric’, but there can be a case to say that a Thermobaric

Explosion is also volumetric to some degree. It is generally accepted that only a Fuel-air Explosion is truly a Volumetric Explosion.

- An **Enhanced Blast Warhead** is one designed to maximise the blast output. The term 'enhanced' would presuppose a baseline, however, it can be said that blast enhanced explosives have developed since the use of picric acid as a warhead filling changed to TNT as shown in Figure 9-24.

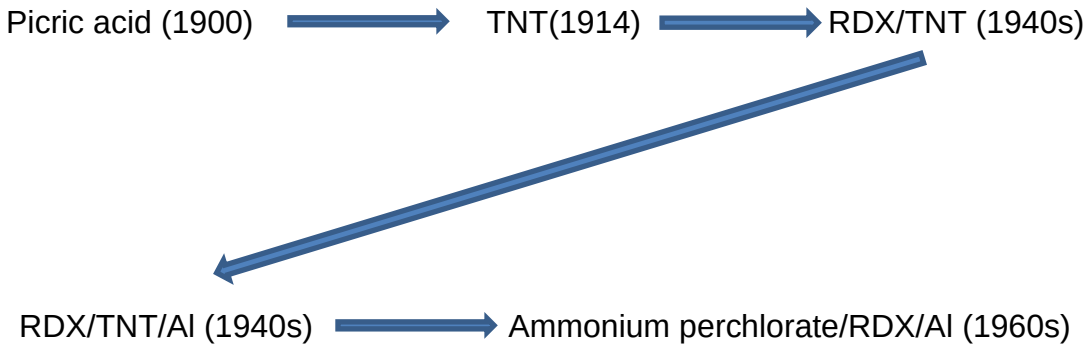


Figure 9-24 Development of blast enhancing explosives

Based on the information in section 9.4.3.2 it could be said that a fuel-air warhead was an Enhanced Blast Warhead. However, the current use of the term Enhanced Blast covers the use of formulations with large percentages of metal powder that react with oxygen in the air to increase the heat energy from the explosion and to an extent increase the duration of the blast pressure. Another name for these is Metal Augmented Charges (MAC).

Therefore, Thermobaric Warheads are Enhanced Blast warheads and vice versa. In the UK the term Enhanced Blast is used and not Thermobaric as the latter has humanitarian connotations with the unfounded but nonetheless popular believe that they are incendiary weapons. This type of warhead is particularly effective inside enclosed spaces such as buildings and tunnels. The UK employs such warheads in anti-structure munitions.

9.5 EXPLOSIONS UNDER WATER

9.5.1 Detonation Under Water

The detonation of an explosive in water is not fundamentally different from detonation in air or in any other compressible medium. In all cases the event involves the propagation of a primary shock from the explosive charge in to the surrounding medium followed by the slower expansion of the gaseous products of explosion. The way in which the total energy of the explosive charge is partitioned between them depends on the nature of the medium and on the properties of the explosive. The energy distribution can be calculated from

theory and in the case of water, it can also be determined experimentally because the separation of the two effects, primary shock wave propagation and gas expansion, is much more complete in water than in air. For an in depth understanding of explosions in water read the text by Cole[19].

9.5.2 Shock Wave Effects

In air, which is a medium of low density and high compressibility the primary shock wave is comparatively short-lived. It decays rapidly due to energy lost by irreversible heating of the air. As the hot, high pressure gaseous products expand immediately behind the primary shock wave that deposited heat energy is captured and contributes to the energy undertaking work compressing the surrounding air, which produces the blast wave. Thus beyond a few charge diameters from the explosion centre there is only one pressure wave to be considered.

In water the transmission of shock wave energy is much more efficient because water is some 800 times more dense than air and its compressibility is correspondingly much less. Even so, at the very high shock pressures initially produced on detonation, some energy is lost by inelastic compression of the water.

This efficient transmission of the shock wave allows it to detach and travel away from the expanding gases. When a spherical charge of high explosive, centrally initiated, detonates at moderate depth in deep water, the corresponding spherical shock front travels radially through the charge and into the surrounding water. The water at the interface with the explosive is violently compressed and accelerated. The shock wave thus formed is propagated through the water at up to 5000 m s^{-1}, becoming totally separated from the gas bubble which is expanding relatively slowly behind it. The velocity then decreases quickly to the sonic velocity in water of about 1500 m s^{-1}.

The shock pressure within the explosive charge may be more than 250 kbar but the acoustic impedance mismatch at the interface of the detonation products and the water causes a rarefaction wave to be reflected back into the detonation sphere. Because of this the initial shock wave pressure is approximately one half of the detonation pressure, say 125 kbar. The difference between shock pressures in air and water from identical explosive charges is shown in Figure 9-25.

Under reasonably good conditions an observer above the water surface can see the manifestation of these separate effects. The primary shock wave from the detonating charge can be seen fleetingly as a rapidly expanding ring of apparently darkened water, often called the 'slick'. This ring is caused by the reflected shock wave pressure momentarily flattening ripples on the surface. Directly above the explosion point, if it is not too deep, a dome of spray appears due to spalling of the water surface as the primary shock wave is reflected. Finally comes the plume of water thrown up by the gas bubble

venting at the surface. The shape and size of the plume varies with the depth of the explosion, and a charge at great depth does not create one. These observations will be difficult to separate if the explosion takes place in shallow water.

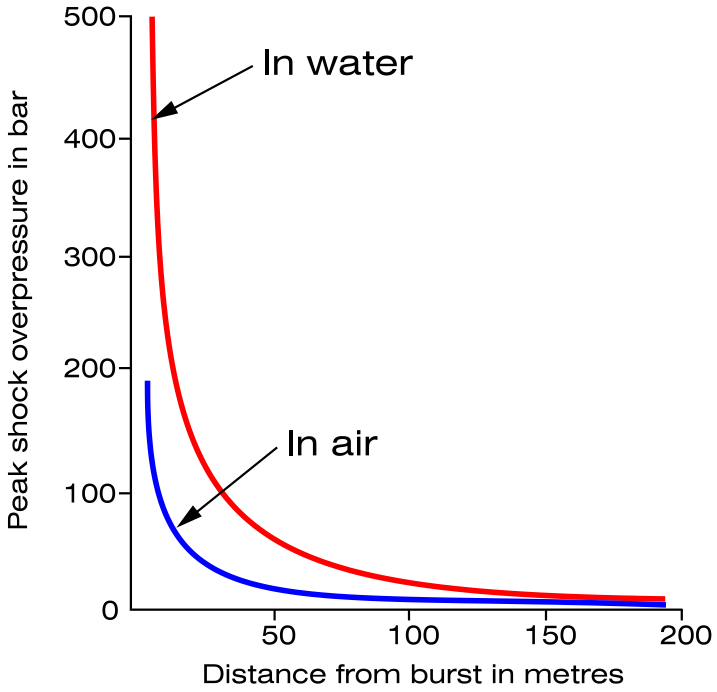


Figure 9-25 Peak shock pressure versus distance in air and in water for a spherical 136 kg charge

9.5.2.1 Shock wave pressure profile

The pressure of a shock wave in water decays rapidly over a time scale of about 1 ms. This decay time initially follows an exponential law so that at time, (t), after the arrival of the shock wave at a point of distance, (L) from the charge centre the shock wave pressure, (p), is given by:

$$p_t = p_{Max} . e^{(-t/\theta)} \qquad \textbf{(9-14)}$$

Where θ is the time decay constant (Figure 9-26). For a 136 kg TNT charge q was found to be 0.5 ms at a distance (L) of 6.1 m, and 0.9 ms at a distance (L) of 152 m; the corresponding values of p_{max} were 424 bar and 7 bar respectively. Explosives of higher detonation pressure than TNT (e.g. RDX and HMX compositions) give shorter time constants, indicative of a more rapid thermal dissipation of the shock wave energy by adiabatic and kinetic work on the water medium. Lower performance ammonium nitrate based explosives have longer time constants.

In a high pressure shock wave the dissipation of energy can be quite considerable. For example, a 300 kbar shock propagating through water loses

4.2 W for every cubic centimetre of water traversed, whereas at low shock pressures the losses are much less, only 0.12 W cm^{-3} for a 25 kbar shock. The energy density of the wave falls with distance from the charge due to its spherical divergence.

Primary shock wave pressures are virtually independent of depth and decay less rapidly than in air (Figure 9-26). It may be inferred from this that primary shock waves in water have a greater radius of effectiveness than shock waves in air. The positive duration of waterborne shock waves is, however, much less than for airborne shocks so that the impulse integrals are not excessive when compared with the same charge weight detonated in air at the same distance.

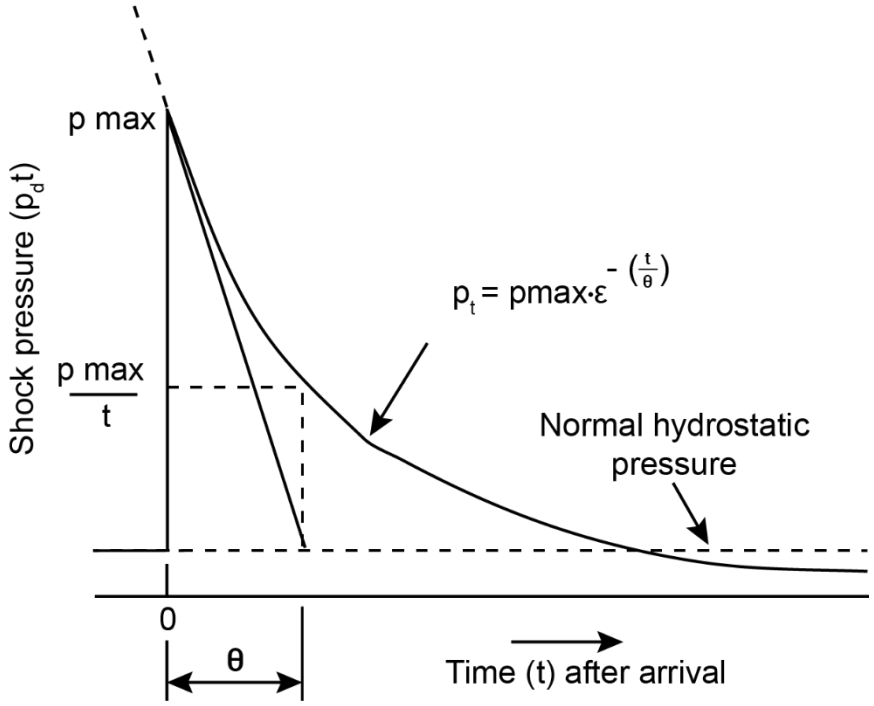


Figure 9-26 Shock pressure versus time, for an underwater shock wave

9.5.2.2 Scaling of shock parameters

The peak shock pressure and some other parameters of underwater shock waves obey the 'principle of similarity' known as Hopkinson's law.

9.5.2.2.1 Distance

The fall-off of peak pressure, p_{max}, with distance is very steep close to the detonating charge, approximating to an inverse cube relationship within 5 charge radii of the charge. A simple inverse relationship holds well however, between about 10 to 100 charge radii.

$$P_{max} \alpha \ 1/L \qquad \textbf{(9-15)}$$

9.5.2.2.2 Charge weight

Peak pressure is found to vary approximately as the cube root of the charge weight giving an overall empirical equation for the peak pressure of:

$$P_{max} = k \times (W^{1/3} / L)^{A} \quad \textbf{(9-16)}$$

A is an index which has the value of 1.16 for TNT and varies slightly for other explosives. k is a constant depending on the detonation parameters of the explosive and is usually expressed relative to the standard TNT (density 1.52 g cm^{-3}) for which it has a value of 510, giving P_{max} in bar. For other explosives, k_X may be found by:

$$k_x = k_{TNT} \times p_x / p_{TNT} \quad \textbf{(9-17)}$$

Where p_x and p_{TNT} are the respective Chapman-Jouguet (C-J) detonation pressures. The equation applies at short distances from the charge. At distances of a few charge radii outwards dissipation of the shock wave energy is such that the pressures are determined largely by the total energy of the charge, thus:

$$k_x = k_{TNT} \times Q_x/Q_{TNT} \quad \textbf{(9-18)}$$

9.5.2.3 Shock Impulse

Shock impulse (I), is obtained by integrating the shock pressure with respect to time:

$$I = \int_o^t p.dt \quad \textbf{(9-19)}$$

The impulse (and shock wave energy) integrals are conventionally taken to t - 6.7 q and may be expressed by:

$$I_{6.7} = k_I \times W^{1/3} \times (W^{1/3} / L)^{B} \quad \textbf{(9-20)}$$

Where B is 0.89 for standard TNT and K_I is 57.4 for a result in bar ms.

Figure 9-27 shows the time dependence of the pressure and impulse.

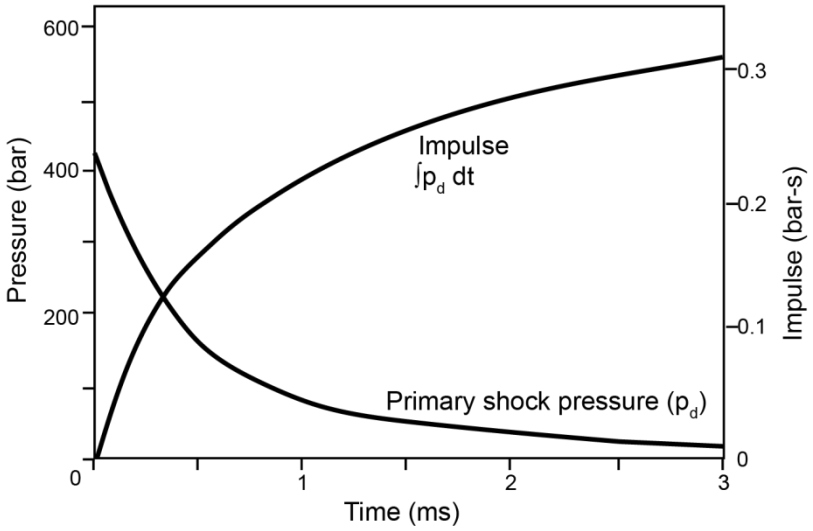


Figure 9-27 Increase in impulse from latter portion of shock wave, as recorded at 6.1 m (20 feet) from a 136 kg TNT charge

9.5.2.4 Shock-wave energy density

The shock wave energy density E_s is the (pressure)^2 - time integral and is directly related to the chemical energy Q of the explosive.

$$E_s = \int_0^t p^2 . dt \qquad \textbf{(9-21)}$$

It may be evaluated from the empirical equation:

$$E_s = k_E . W^{1/3} \left(W^{1/3} \left(W^{1/3} / L\right)^E \right. \qquad \textbf{(9-22)}$$

Where: E is 2.05 for standard TNT and k is 0. 0343 for a result in J m^{-2}.

9.5.3 Underwater Bubble Effects

A charge detonated under water creates a more or less spherical bubble of gas inside which the pressure immediately after the departure of the primary shock wave is very high. This high pressure causes the bubble to expand rapidly in spite of the inertia of the surrounding water, and is aided by the 'after flow' of the water in the wake of the primary shock wave. The pressure in the bubble falls as expansion occurs and as the temperature of the gas falls due to

adiabatic expansion. Because of the inertia of the water being displaced, the bubble continues to expand even though its pressure begins to fall below the hydrostatic pressure. Expansion soon ceases and a rapid contraction begins until the in-flowing water has compressed the bubble to a higher pressure than the hydrostatic pressure and so the cycle of expansion and contraction begins again.

In this manner a series of bubble oscillations of decreasing amplitude follows, numbering up to ten or so. Considerable flow of water accompanies the bubble oscillations and velocities as high as 100 m s^{-1} may be imparted to the water. The kinetic energy of this high velocity water is a potent source of damage to structures within two or three bubble radii.

Additionally, each bubble oscillation generates a quite separate pressure pulse which is set up at the point of maximum recompression of the bubble, when the water flow is reversing (Figure 9-28). The series of pulses grows successively weaker and only the first one or two are of significance.

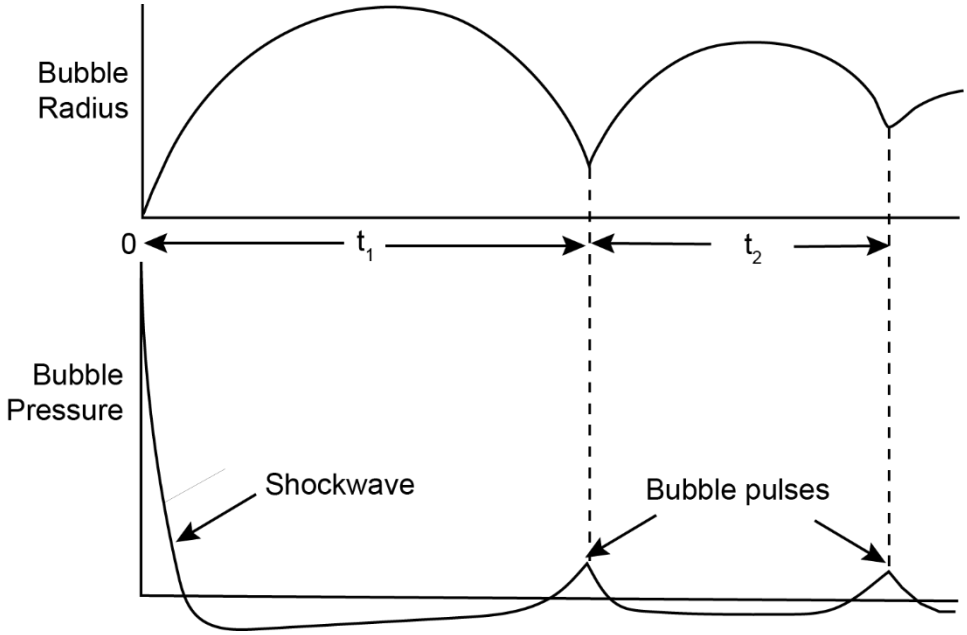


Figure 9-28 Gas bubble pulsation and pressure sequence

The timescale of the bubble period is long in relation to the duration of the primary shock wave. For example, a 250 g Tetryl charge detonated at a 91 m depth generates a bubble which reaches its maximum radius in 14 ms and its minimum radius in 28 ms. It is evident therefore that an interval of tens of milliseconds will occur between the primary shock wave and the first bubble pulse. The interval increases with distance from the charge due to the falling velocity of the bubble pulse with distance.

The peak pressure in a bubble pulse is very much lower than the peak shock pressure from the same charge at a given distance. For example, a 136 kg TNT charge at a depth of 20 m generates a primary shock wave pressure at a

distance of 18.1 m of 130 bar compared with a first bubble pulse of 5 bar at the same point. However, the longer duration of the bubble pulse enhances the magnitude of its impulse integral so that it can exceed that of the primary shock wave at some distances.

9.5.3.1 Mathematical formulae for the calculation of bubble parameters.

9.5.3.1.1 Bubble radius

Maximum bubble radius b_{max} depends on charge weight W, explosive power index, and hydrostatic pressure depth h (all dimensions in metres or kg) such that:

$$b_{max} = \frac{k_b \,.\, W}{(h + 10)^{1/3}} \qquad \textbf{(9-23)}$$

k_b is related to the explosive power index of the explosive by the formula:

$$k_b = \frac{power\ index\ of\ explosive}{power\ index\ of\ TNT}\ x\ 3.42 \qquad \textbf{(9-24)}$$

for a result in metres and kilograms.

9.5.3.1.2 Bubble period

The period of the first bubble oscillation t_1 (in seconds) for TNT is given by:

$$t_1 = 2.1 \times W^{1/3} / (h + 10)^{0.83} \qquad \textbf{(9-25)}$$

9.5.3.1.3 Bubble energy

The theory of underwater bubble behaviour shows that the total energy E_b, associated with the radial outflow of water due to bubble expansion is given by:

$$E_b \approx \frac{4}{3} \cdot H_o (b_{max})^3 \qquad \textbf{(9-26)}$$

Where H_o is the normal hydrostatic pressure (consistent units must be applied).

9.5.3.2 Bubble migration

Because an explosion bubble pulsates it does not rise to the surface steadily and vertically under the influence of its buoyancy. Instead, the varying resistance to motion that it experiences due to its changing size and the associated water flow around it will cause it to:

a. migrate towards any nearby rigid boundary (e.g. a ship, dam or sea wall)
b. to rise to the surface in an uneven manner

This behaviour is illustrated in Figure 9-29.

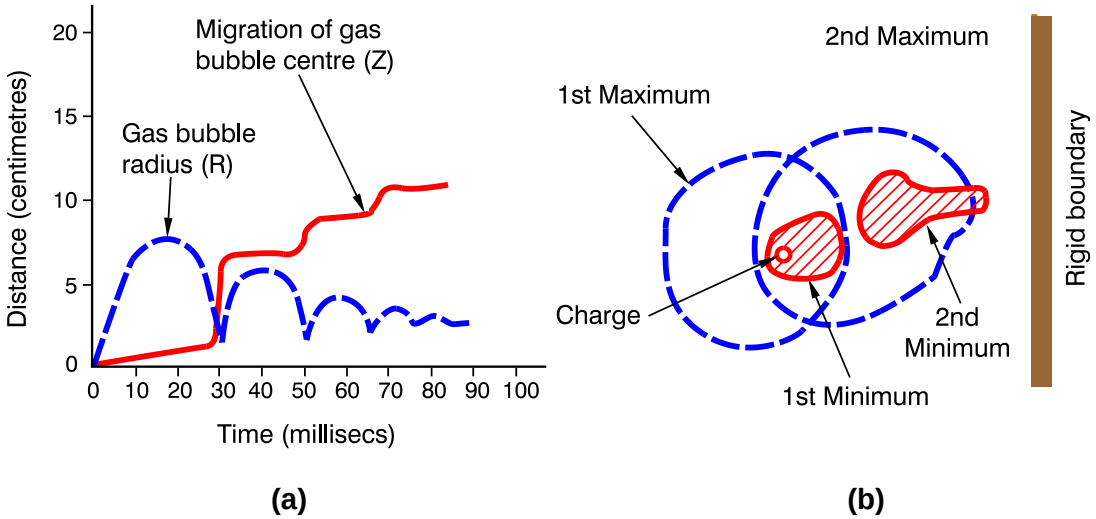


Figure 9-29 Migration of bubble upwards (a) in open water and (b) towards a rigid boundary

9.5.4 Damage by Underwater Explosions

The way in which damage is caused to underwater structures, particularly the hulls of ships and submarines, by explosive charges is a complex subject involving questions of materials science, engineering and fluid dynamics as well as the effect of incident and reflected shock waves in water. The topic is therefore largely outside the scope of the present work and is represented here by a few general remarks in conclusion.

The underwater attack of vessels by explosives usually involves the detonation of the charge virtually in contact with the hull, e.g. in the cases of torpedoes and sea-mines with contact fuzes, or limpet charges. Where this is so, the detonation pressure of the explosive is exerted almost undiminished on the plating, which is then likely to be fractured and to be further distorted by the rapid flow of water associated with bubble oscillation. Experience has shown, however, that greater damage is inflicted when there is an intervening stand-off distance between the charge and the hull. In this situation the effects of the primary shock wave and the bubble oscillations are separated by time and there is a question as to which of them is the deciding factor in damage capacity.

It is seen from Figure 9-30 that the shock wave energy available for inflicting damage is some 33 % of the total explosive energy (this applies to a short stand-off distance), whereas the first bubble pulse accounts for only 13 %. It would appear, therefore, a priori, that damage by shock wave is more likely than damage by bubble pulses. Account must be taken, however, of the kinetic

energy of the mass of moving water associated with the bubble oscillation. For a large bubble envelope moving at some 100 m s^{-1} the kinetic energy imparted to the target by this water flow can be very destructive, involving as it does an impact followed by a suction effect. The bubble oscillations also create pressure pulses of relatively long duration which cause additional stresses in the target material.

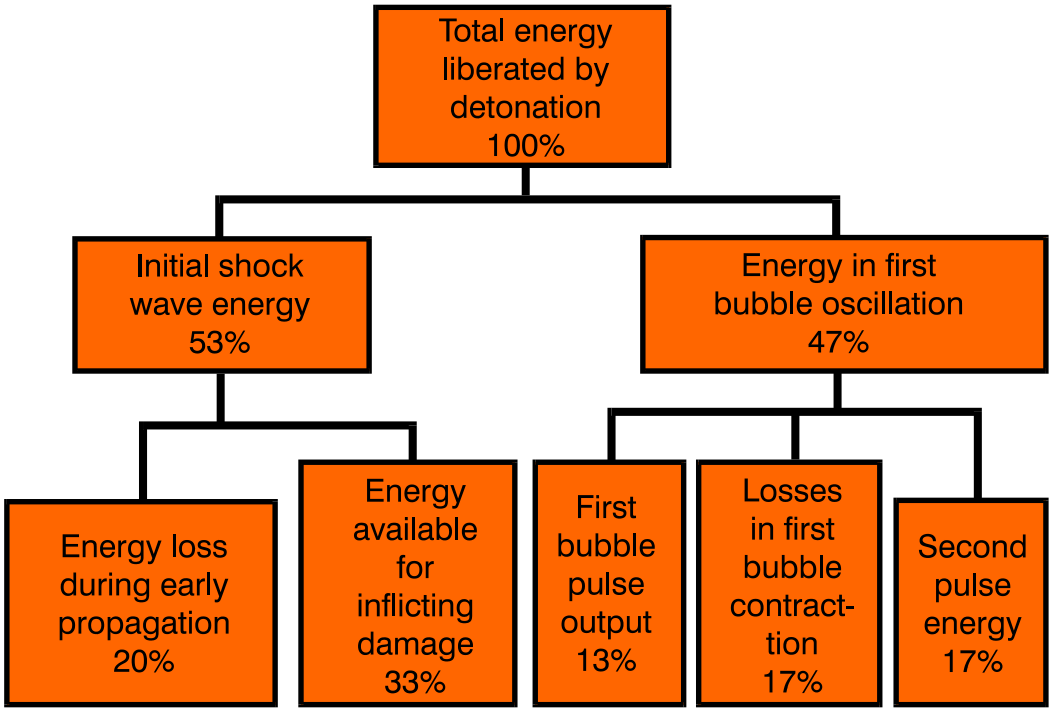


Figure 9-30 Typical distribution of the energy of an underwater explosion

The damage capacity of the shock wave depends, as in the case of airblast, on its duration as well as its maximum pressure, and this must be matched to the response time of the target, in this case plating backed only by air. The response time will depend on several factors, including the area of air-backed plating, which is effectively governed by the spacing of the supporting structure of the hull. The area of plating exposed to the shock wave at angles of incidence near to normal will be greater if the charge is detonated at some distance of stand-off, due to the radial progress of the wave. It is therefore generally true that, for large charges, the most effective position from which to attack a ship's hull is at an optimum stand-off depth below amidships. The damage done to an area of plating by the spreading of shock wave will then be exacerbated by the upward migrating bubble oscillating in contact with the damaged plating.

In the case of submarines the nature of the hull design produces a more resistant target. Moreover, the relative contributions to' damage infliction which are made by primary shock, bubble oscillation and bubble pulses at the depth of a ship's draught are considerably different at the greater depths where

submarines normally operate. Bubble effects are much reduced, and the damage capacity of the explosive charge depends much more on the primary shock which it creates. In one respect the vulnerability of a submarine is greater compared with a ship, since its hull structure is subjected to greater environmental stress at depth. These and other complicating factors make the generalised prediction of damage susceptibility even more difficult in the case of submarines than for ships.

For both ships and submarines, if the duration of the shock wave is much shorter than the deflection time of the plating, primary damage will not occur but there will still be a considerable vibration set up throughout the vessel. The plating can be accelerated at up to 10^5 g (10^6 m s^{-2}) and the structural members at a tenth of this figure. The vibration can last for some tens of milliseconds, depending on the duration and impulse of the shock wave. The rapid and irregular vibration thus caused can damage the delicate internal components on which a modern ship relies for its fighting effectiveness.

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Appendix A Units of pressure

The SI unit for pressure is the Pascal (Pa). Other units commonly used include the atmosphere, bar, psi (pounds per square inch) and for lower pressures, particularly from guns, the decibel. A list of the conversion factors is given in Table 9-9.

Table 9-9 Conversion of Pressure Units to Pascals

Unit	Value in pascals
bar	100,000
atmosphere	101325
psi (pounds per square inch)	6894.76
decibel (dB)	$\text{Pressure (Pa)} = 0.00002 \times 10^{\text{Pressure(dB)}/20}$

CHAPTER 10
THE MANUFACTURE OF EXPLOSIVE SUBSTANCES

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10 THE MANUFACTURE OF EXPLOSIVE SUBSTANCES

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10.1 AWARENESS SUMMARY

The manufacture of energetic substances is a wide-ranging subject of Materials Science, which encompasses the study of the relationships between the structure and the properties of an explosive material and how it is made; the aim is to develop new and/or common use energetics to meet engineering specifications and high performance.

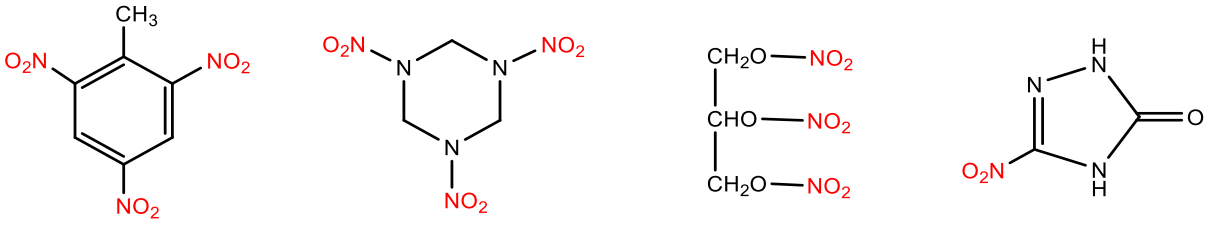
All manufacturing processes require a knowledge of the hazardous nature of both the process and the materials used including: starting materials, intermediates, desired products and any side products that might be found as impurities in reaction mixtures or final products. Many of the production processes require the use of highly concentrated acids which are hazardous chemicals in their own right.

In this chapter, the basic chemical principles and technology of commonly encountered explosives are outlined. The chemistry and the manufacturing processes for primary and secondary explosives will be discussed in detail. There has been no attempt to include commercially manufactured starting materials which can be purchased.

10.1.1 Nitration Reactions

10.1.1.1 General considerations

The most commonly used military secondary explosive materials contain nitro groups (NO_2) in their chemical structure (Figure 10-1). Nitration reaction plays a fundamental role in the preparation of explosives and it is explained in the paragraphs below.



TNT RDX NG NTO

Figure 10-1 Chemical structures of commonly used secondary explosives; nitro groups in red

Secondary high explosives are manufactured by two differently operated systems; batch processing and continuous processing. A batch process requires starting materials to be loaded into the plant and all are processed together. This produces a 'batch' of product at the end of processing. The plant can then be cleaned and readied for the next batch of materials. A continuous process has starting materials fed into the system and product removed throughout the production process. The

daily throughput of a continuous plant tends to be larger than that of a batch plant of the same size. The continuous process normally gives a smaller unit risk than a batch process (whole material charge), and there are savings in, for example, the use and storage of acids.

10.1.1.2 The nitration reaction

There are several methods of nitration; the most common method of nitration for the manufacture of explosives is the use of mixed acids. These are normally nitric and sulphuric acids (HNO_3 and H_2SO_4) in varying concentrations depending on the difficulty and degree of the nitration process. In the manufacture of the N-nitro materials such as RDX and HMX by the Bachman process, the presence of the sulphuric acid would result in the degradation of the explosive product; an alternative material is used with nitric acid. This is ethanoic acid (acetic acid CH_3COOH) and the anhydride of the acid to remove the water liberated during the process.

In both processes the general reaction is:

Fuel Moiety + Nitric acid → Explosive + Water

The second acid is required to form the nitronium ion (NO_2^+), which is the nitrating species and is also a solvent for the reaction.

Nitration can take place on carbon, nitrogen and oxygen atoms in the fuel molecule generating C-nitro compounds such as trinitrotoluene (TNT), N-nitro compounds such as 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX), and O-nitro compounds such as nitroglycerine (NG), respectively (Figure 10-2). The process details are covered in later sections.

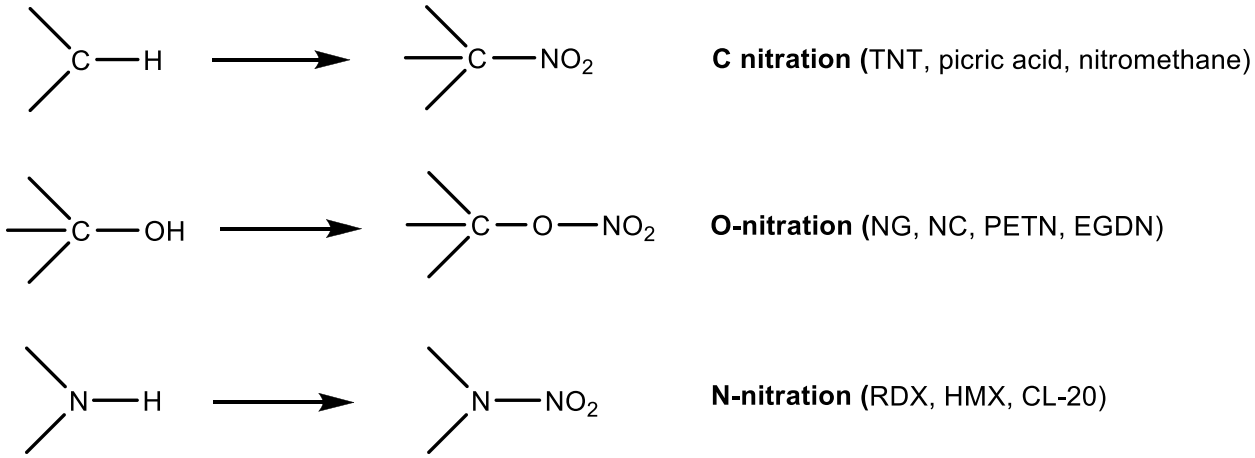


Figure 10-2 Types of nitration reaction

10.1.2 Primary Explosives

The sensitive primary explosives are produced in small batches due to their inherent hazards. Lead and silver azide employed in detonating explosive trains

can be readily synthesised mixing water soluble lead or silver compounds with sodium azide, itself also water soluble. However, care must be taken when manufacturing lead azide as it can precipitate in different crystalline forms, some of which are more hazardous than others with the potential to spontaneously detonate even when present as a water slurry.

Lead styphnate and lead dinitroresorcinate (LDNR) employed in igniferous explosive trains are readily synthesised, however, control of the crystal types is of importance depending on the specific application.

10.2 NITRATION CHEMISTRY

10.2.1 Nitration Involving Nitric and Sulphuric Acids

The best studied and most common method of nitrating is the use of mixed nitric and sulphuric acids. These variable mixtures are known as ‘mixed acids’ or ‘nitrating mixtures’. The key to the reaction is the formation of a positively charged nitronium ion, NO_2^+, which will react with areas of high electron density in a molecule. The overall equation for its formation is given below in Equation (10-1).

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2\,HSO_4^- \qquad \textbf{(10-1)}$$

In the nitration of benzene (I), for example, the initial reaction brings about the interaction of the benzene π-electrons, shown in Figure 10-3 as the double bonds, with the positive ion. This results in an unstable ion in which the benzene system is disrupted. Elimination of a proton yields the nitrated product, nitrobenzene (II).

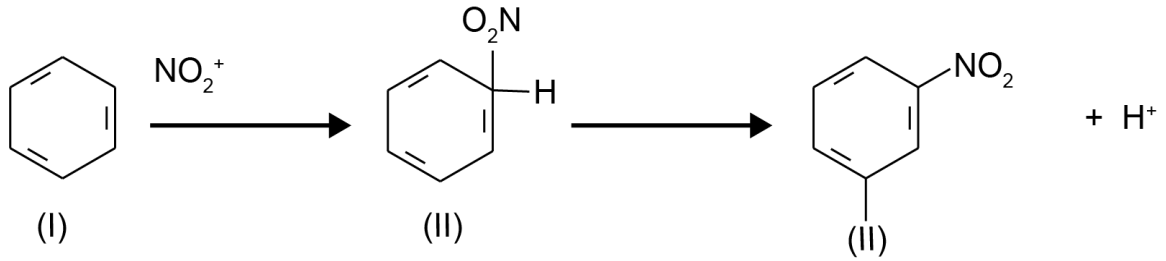


Figure 10-3 Schematic representation of nitration of benzene (I)

When toluene (methylbenzene) is used in place of benzene there are three different positions that may undergo nitration. These are the positions 2 and 6, 3 and 5, and 4 relative to the position of the methyl group. This is illustrated in Figure 10-4.

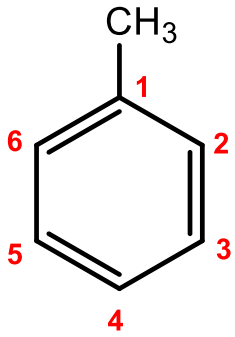


Figure 10-4 Chemical structure of toluene

The presence of the methyl group directs the positive nitronium ion into one of the 2-, 4-, or 6- positions by stabilizing an intermediate ion. Such stabilizing does not occur when nitration takes place in the 3- or 5- positions. This stabilizing is accounted for by the electron donating effect of the methyl group; that is to say, the methyl group pushes electron density towards the benzene ring. During the nitration, an unstable positive ion is formed as an intermediate step and this positive charge can 'move' around the ring. If this charge is capable of residing adjacent to the methyl group the electron donating effect will reduce the effective charge and stabilize the ion. This effect reduces the amount of methyl-3-nitrobenzene (3-nitrotoluene) to about 4 % compared with the 40 % expected on a purely statistical basis (2 locations in the 3 and 5 positions available for reaction) by providing a lower energy path to the 2-, 4-, and 6- positions. 2-nitrotoluene and 4-nitrotoluene then predominate in the product. Figure 10-5 illustrates the initial nitration steps for all three different isomeric nitromethylbenzenes (nitrotoluenes).

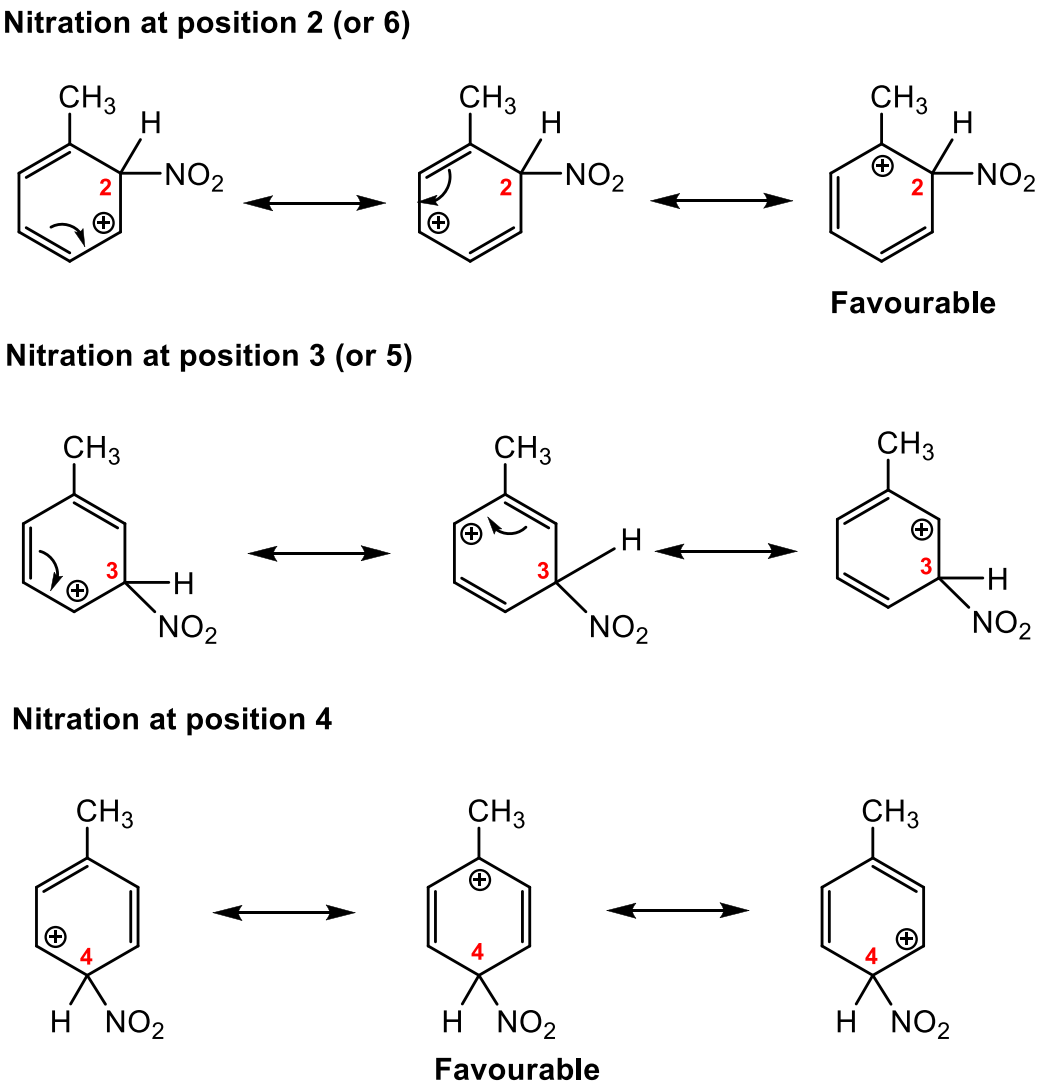


Figure 10-5 Schematic representation of nitration of toluene

10.2.2 Nitration using Nitrate Salts in Sulphuric Acid

A mixture of a nitrate salt in sulphuric acid will behave similarly to the nitric acid/sulphuric acid mixtures. The amount of water present has been reduced by the replacement of a nitric acid solution with the solid nitrate salt. This advantage has been overtaken by the ready availability of 'anhydrous' nitric acid from modern plants so is now little used.

10.2.3 Nitration with Nitric Acid or Nitrate Salts in Other Acid Media

Sulphur dioxide, perchloric acid and certain fluorine compounds have all been cited as suitable materials to afford nitration using either nitric acid or one of its salts. The use of sulphur dioxide is discouraged due to its toxicity. Lewis acids (electron acceptors e.g., $AlCl_3$ and BF_3) in the presence of nitrate salts have also been cited as affording successful nitrating media.

10.2.4 Nitration with Nitric Acid

In the manufacture of RDX, the nitrating systems employed must not contain sulphuric acid. Traditionally, the nitration process was between hexamethylenetetramine (hexamine) and nitric acid on its own. The overall reaction known as the Woolwich Process is shown in Equation (10-2).

$$(CH_2)_6N_4 + 4HNO_3 \rightarrow (CH_2\text{-}N\text{-}NO_2)_3 + 3CH_2O + NH_4NO_3 \quad \textbf{(10-2)}$$

This reaction is said to proceed via a complicated sequence of reactions on the hexamine molecule. The poor utilisation of hexamine and consequent low yield of RDX, with the need for a large excess of nitric acid, 4 to 8 times of the theoretical quantity, results in an expensive process. Alternative systems have been tried, the inclusion of ammonium nitrate in the nitric acid is said to make the overall process more efficient in the use of hexamine. This gives an overall equation of:

$$(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 \rightarrow 2(CH_2\text{-}N\text{-}NO_2)_3 + 6H_2O \quad \textbf{(10-3)}$$

10.2.5 Nitration in Ethanoic Acid

The sulphuric acid in a nitrating mixture can be replaced with ethanoic acid or mixtures of ethanoic acid and its anhydride (*Bachman Process*). It has been suggested that the mixture of nitric and ethanoic acids gives an addition compound of the formula $HN0_3.CH_3COOH$ which has a weaker $HO\text{-}NO_2$ bond. There is also some evidence of the presence of nitronium ions from spectroscopic measurements. Nitration of hexamine in the presence of ethanoic (acetic) acid and its anhydride, yields precursors to RDX and HMX which produce these materials on further treatment with nitric acid and ammonium nitrate. The result is a mixture of RDX and HMX. Equation (10-4) shows the formation of RDX.

$$(CH_2)_6N_4{\cdot}2HNO_3 + 2(NH_4NO_3{\cdot}HNO_3) + 6(CH_3CO)_2O \rightarrow 2(CH_2\text{-}N\text{-}NO_2)_3 + 12CH_3COOH \quad \textbf{(10-4)}$$

10.2.6 Other Nitrating Systems

The use of oxides of nitrogen has been investigated as a method of nitrating organic materials. Of these, probably the most interest has been shown in the use of dinitrogen pentoxide, N_2O_5, which is the anhydride of nitric acid:

$$2\ HNO_3 \rightarrow N_2O_5 + H_2O \quad \textbf{(10-5)}$$

Dinitrogen pentoxide was first used in the nitration of cellulose. It has been suggested that the oxide undergoes heterolysis to form ionic materials in solution:

$$N_2O_5 \rightarrow NO_2^{+} + NO_3^{+} \quad \textbf{(10-6)}$$

This is demonstrated in Figure 10-6 below:

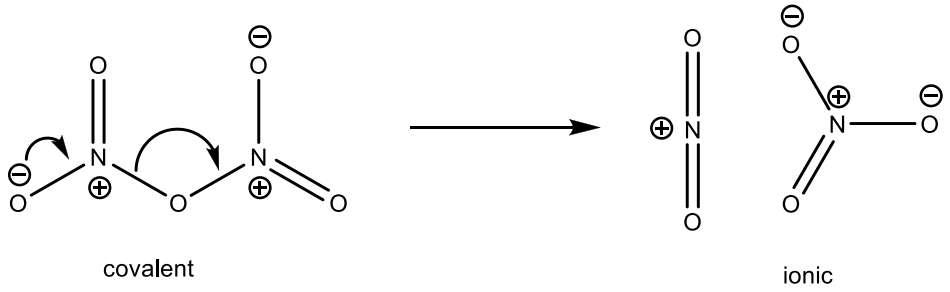


Figure 10-6 Heterolysis of dinitrogen pentoxide

The formation of the nitronium ion (NO_2^+) is the key to the nitrating properties of the material. Dinitrogen pentoxide can be produced by electrogeneration in a polar solvent. This method affords a non-aqueous reaction system which provides interesting alternative reaction pathways. An alternative method of generating dinitrogen pentoxide employs the use of a gas flow system. Recent advances in the ozonolysis of N_2O_4 to prepare dinitrogen pentoxide suggest that it may soon be readily available for the production of explosives and other nitrated materials.

Dinitrogen pentoxide is thermally unstable and it must be stored at <-20 °C or used as generated. Its decomposition produces highly toxic nitrogen dioxide gas:

$$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2 \qquad \textbf{(10-7)}$$

Dinitrogen pentoxide in HNO_3 may be used for the synthesis of nitramines while in dichloromethane (or chloroform) is used in the manufacture of PolyNIMMO and PolyGLYN, two common energetic binders. This nitrating medium allows the acid-sensitive substrates to be nitrated selectively. The resulting mono-nitrate esters, NIMMO and GLYN, are then polymerised.

There are a wide variety of other methods which will afford the introduction of a nitro-group into an organic molecule. Many of these are of little practical value due to the high relative cost of the materials. In practice, the utilization of mixed acids is currently the major method of nitration due to the relatively low cost of the readily available starting materials. As the use of HMX and RDX increases relative to that of TNT the mixed acids method of nitration is likely to diminish, and alternative clean and environmentally friendly nitrating systems based on dinitrogen pentoxide are likely to come to the fore.

10.3 MANUFACTURE OF COMMONLY ENCOUNTERED SECONDARY EXPLOSIVES

10.3.1 Nitration Process - General Considerations

There are two different methods of operation for a chemical plant. These are ‘continuous’ operation and ‘batch’ operation. A continuous operation is one where materials are fed in to the plant throughout the production sequence and the product is continually run off. Batch operation requires all the starting material to be loaded into the plant sequentially and the product is then recovered at the end of

the production run. The daily throughput of a continuous operation plant tends to be larger than that of a batch operation plant of the same size. The main difference in the two operations is the unit explosives risk: in a batch operation plant is the whole materials charge, while in a continuous operation plant the amount of explosive products in the reactor at any instant is relatively small, consequently the unit risk is considerably less. Both safety and economics are considered in deciding the relative merits of one method of operation against another. The more hazardous the process the greater the emphasis on ‘unit risk’ and hence the continuous operation method finds favour. With less hazardous materials the choice of batch operation or continuous operation could well be determined by economic factors. The production of primary explosives involves very hazardous operations; they are therefore generally manufactured in small batches. The high probability of damage to the plant makes the continuous operation method impossible.

For a process to be economically and environmental satisfactory, the spent nitrating acids must be recovered and recycled. The nitric and sulphuric acids must be re-concentrated. All organic waste must be destroyed and the water used for washing must be decontaminated before discharge. Any solvents used in the purification of the explosives must be collected and recycled.

The purification of explosives is done by re-crystallisation of the reaction product. The crude product needs to be separated from the reaction mixture (spent acids, by-products, etc.) and all traces of the reagents must be removed by washing and drying. The purification for the specific explosives is reported later in this Chapter.

Small batches (gram scale) of explosives can be made in the laboratory using batch or flow reactors. Pilot plant scale, batch or flow, is used for multi-Kg scale production and for the demonstration of a new technology or process.

All nitration reactions are exothermic and the temperature must be controlled during the manufacturing process. The heat release must be monitored to avoid “thermal runaway” or “fume off” due to the violent decomposition reactions even for small (<5 g) laboratory scale operations. Larger scale preparations require more efficient cooling in the reactor. External cooling jackets or cold baths are replaced by internal heat-exchange coils/pipes. On industrial scale processes, efficient stirring is vital for effective heat dissipation and avoid runaway. Dump-valves are still used in medium-to-large batch synthesis of nitrate esters.

Safe systems of work are indispensable to avoid any accidents during the manufacturing of all explosives. All the documents related to the process as manufacturing description, storage facilities availability, transportation and waste collection procedures must be clearly reported and authorised. Process assessments (i.e. General risk assessment, COSHH, DSEAR) need to be in place and REACH regulations (see 1.3.2.4.6) to be considered before starting the nitration process. Permission to work and continuous training of personnel guarantee the safest way to manufacture the explosives.

10.3.2 The Production of C-Nitro Explosives

10.3.2.1 Trinitrotoluene (TNT) production

Trinitrotoluene is generally manufactured by continuous production plants. The TNT is formed by the successive replacement of three hydrogen atoms from the benzene ring with nitro-groups using a mixture of concentrated nitric and sulphuric acids.

Toluene → Mononitrotoluene (MNT) → Dinitroluene (DNT) → Trinitrotoluene (TNT)

Figure 10-7 Conversion of toluene to trinitrotoluene

The introduction of nitro groups requires increasingly more vigorous conditions as the number of nitro groups increase. This is achieved in a modern continuous process by having many reactors, arranged in series, with the organic feed flowing in one direction and the mixed acid flowing in the opposite direction.

A typical TNT manufacturing plant operates as follows: the fresh nitrating mixture is introduced at one end of the plant and becomes less potent due to the production of H_2O as it flows towards the next reactor. DNT encounters fresh mixed acid, whilst toluene or MNT, which is more easily nitrated, encounter depleted mixed acid. Crude trinitrotoluene exits from the last reactor. In this way the acid concentration is lowest where the toluene is introduced, lowering the heat liberation and reducing the risk of fire.

In each nitrator the acids and organic materials are mixed together and partial nitration takes place. In the separators, the acids and organic material are immiscible and separate because of their density difference to facilitate their movement in opposite direction through the plant. Each nitrator is temperature controlled by either cooling to remove the heat liberated due to the mixing of the materials, or heating to accelerate the reaction. Typically some 8 to 15 nitrators and separators are placed in series in a TNT production plant. As the feed material passes along through a series of nitrators, the proportion of nitro-groups in the material increases.

In practice the production of TNT is in two stages: the formation of mononitrotoluene (MNT) and the subsequent conversion of MNT to trinitrotoluene (TNT). This method of production has been adopted due to the large amounts of heat liberated in the mixing of toluene with the mixed acids. Sufficient heat can be liberated by this process to ignite the toluene. By separating the two processes, any ignition is confined to the materials of the first reaction and is prevented from propagating through to the TNT, thus eliminating the risk of explosion.

Acids flow through the plant and are diluted by the production of water from the nitration reaction. Most of the nitric acid will have been used up by the time it has percolated to the end of the plant. The sulphuric acid, on the other hand, does not react; it is merely diluted and will be separated from the organic materials, purified and reused.

During the manufacturing process a small percentage of unwanted products are formed. These are materials nitrated in the 3-position or 5-position. These are not desired in the final product and must be removed. All of the nitration products are shown in Figure 10-8.

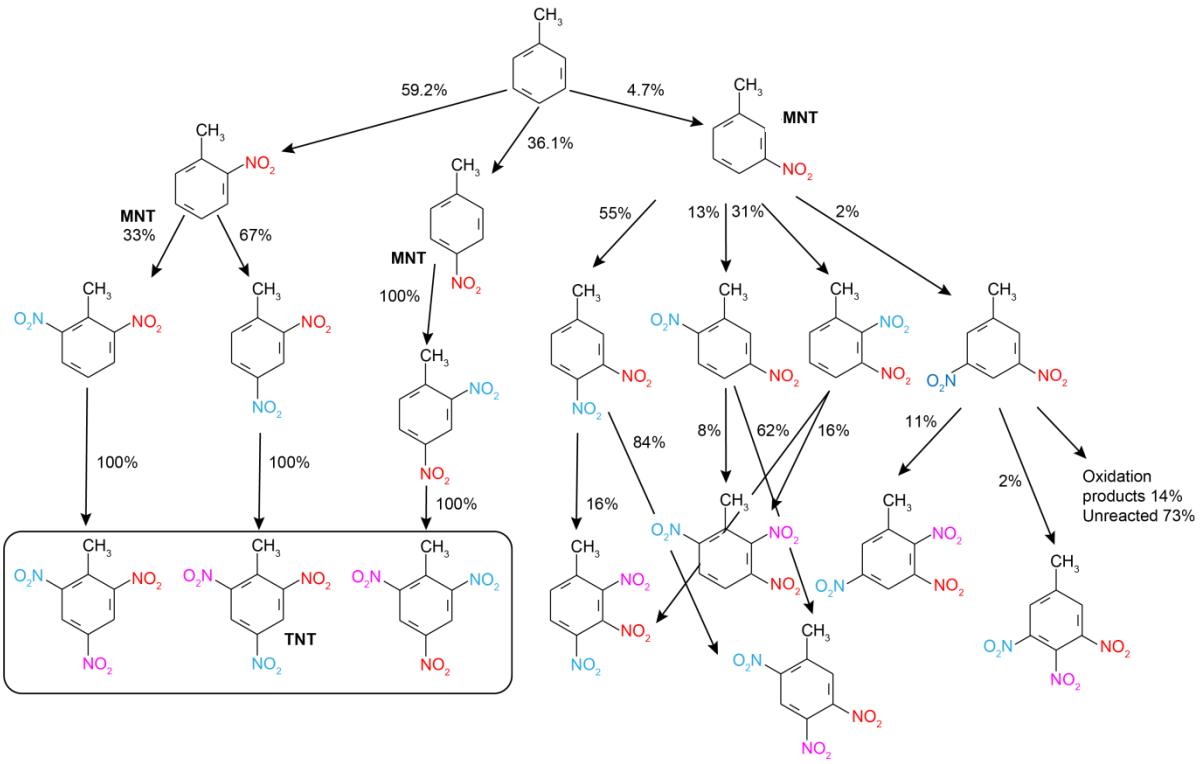
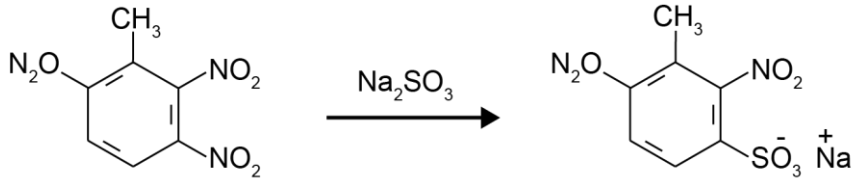


Figure 10-8 Nitration products of toluene during the three steps nitration reaction

The presence of oxidation products will generally afford increased sensitiveness (see 20.2.1), and the incorrectly nitrated materials lower the melting point of the TNT produced. The formation of oxidation products can be reduced by the careful control of the reaction temperature. In any production plant there will always be a small percentage of unwanted nitrated material formed, typically this is between 4-5 % w/w, which is removed by sulphite washing. The crude product from the plant is passed through a series of mixers and separators in counter current flow with a hot sodium sulphite solution which only reacts with NO_2 groups in the 3-position. The products form a water soluble sulphonate salt, which is then washed into the aqueous phase and removed from the TNT.



(10-8)

Final washing with water removes any salts or acid present and the TNT can be cooled to solidify and is then collected, often in the form of TNT flake when cooled on the surface of a rotating drum, then scraped off.

The washings from the TNT purification called “red water” have always been considered as a hazardous waste as they contain very toxic products of incomplete nitrate compounds as well as other complex by-products formed during nitration and purification stages in addition to DNT sulfonated compounds. They created concern related to environmental pollution and public health since most of them are toxic and mutagenic to humans and other animals even at low concentrations. Ground contamination may still exist in very old plants while common treatment methods for TNT waste water currently include activated carbon adsorption, evaporation to dryness (as the toxic components are not volatile), followed by incineration, biodegradation and other disposal methods.

The whole process is shown in Figure 10-9 below.

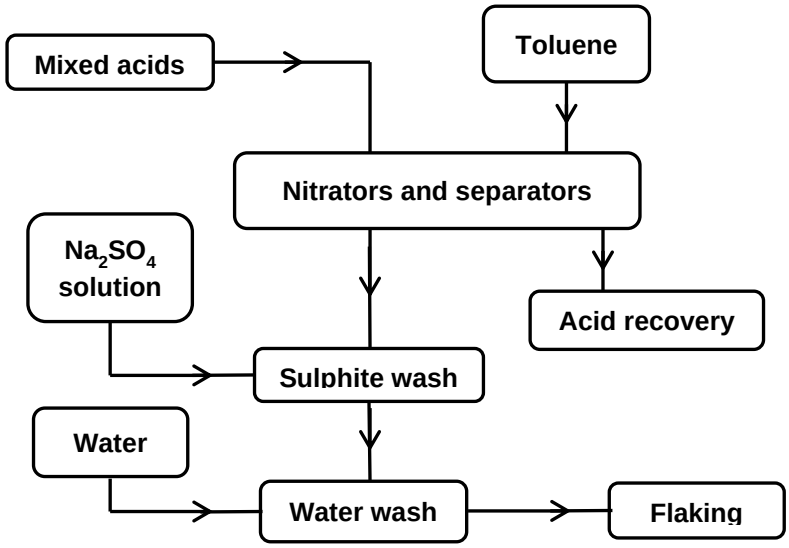


Figure 10-9 A flow diagram for the manufacture of TNT

10.3.2.2 Triaminotrinitrobenzene (TATB) production

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is an explosive with high temperature stability and low sensitiveness (see 20.2.1). It is manufactured, in a two-step process (Benziger process) in which 1,3,5-trichlorobenzene (TCB) is first nitrated to produce an intermediate compound, 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) as shown in Figure 10-10, which is then subsequently aminated to produce the final product.

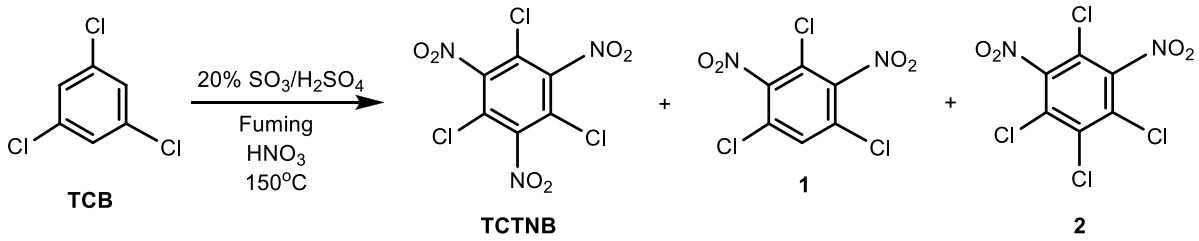
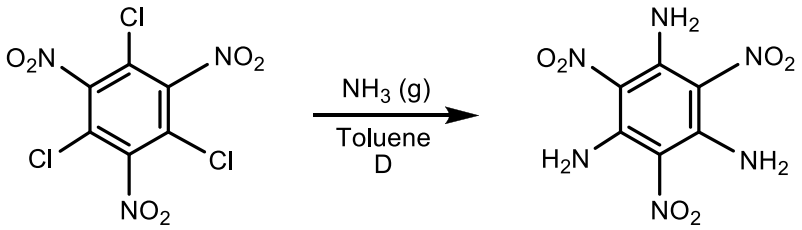


Figure 10-10 Conversion of trichlorobenzene to trichloro-trinitrobenzene

A mixture of 30 % v/v oleum and fuming nitric acid is used for the nitration of TCB at 90 ºC. TCB reacts with the mixed acid exothermically to produce first the mono-nitrate and then the di-nitrate intermediate. This reaction proceeds adiabatically and the temperature within the nitration vessel increases to about 140 ºC. However, this is not sufficient to drive the trinitration reaction; so towards the end of the reaction period, steam is passed into the jacket surrounding the vessel to raise the temperature to the required value. The trinitration reaction is kinetically slow and the whole nitration process takes about four hours to complete. At the end of this period, the contents are cooled and diluted and the intermediate product filtered off. The spent acid is returned to the acids section of the plant for re-concentration. The intermediate compound TCTNB is completely insensitive when wet, and even in the dry state has a very high Figure of Insensitiveness (169) (see 20.10.2.1). The unwanted by-products 1 and 2 are also insensitive.

At the beginning of the second stage of the process, the intermediate TCTNB is first washed and then dissolved in toluene before being charged into the amination vessel. Additional quantities of toluene and water are added, and the vessel is then sealed and heated. Gaseous ammonia is introduced and the amination reaction proceeds at 152 °C and 5 bar pressure for 4 to 6 hours.



TCTNB **TATB**

Figure 10-11 Conversion of trichloro-trinitrobenzene to triamino-trinitrobenzene

When the reaction as shown in Figure 10-11 is complete the contents are cooled and then diluted with water before being discharged to the filter press. The TATB cake is steamed in the press, washed, partly dried with compressed air, and then blended and packaged. The toluene in the filtrate is recovered by distillation.

An alternative, halogen free, synthetic route to TATB has been reported[1,2] as shown below in Figure 10-12. The synthesis of TATB is carried out in three steps:

1. Nitration of 1,3,5-trihydroxybenzene to 1,3,5-trihydroxy -2,4,6-trinitrobenzene
2. Alkylation of the trihydroxytrinitrobenzene product to give the trialkoxy intermediate
3. Amination of the trialkoxy intermediate with NH_3 (gas or liq.) to yield TATB in an overall yield of 87 %.

The trialkoxy intermediate also can be synthesised by alkylation followed by nitration.

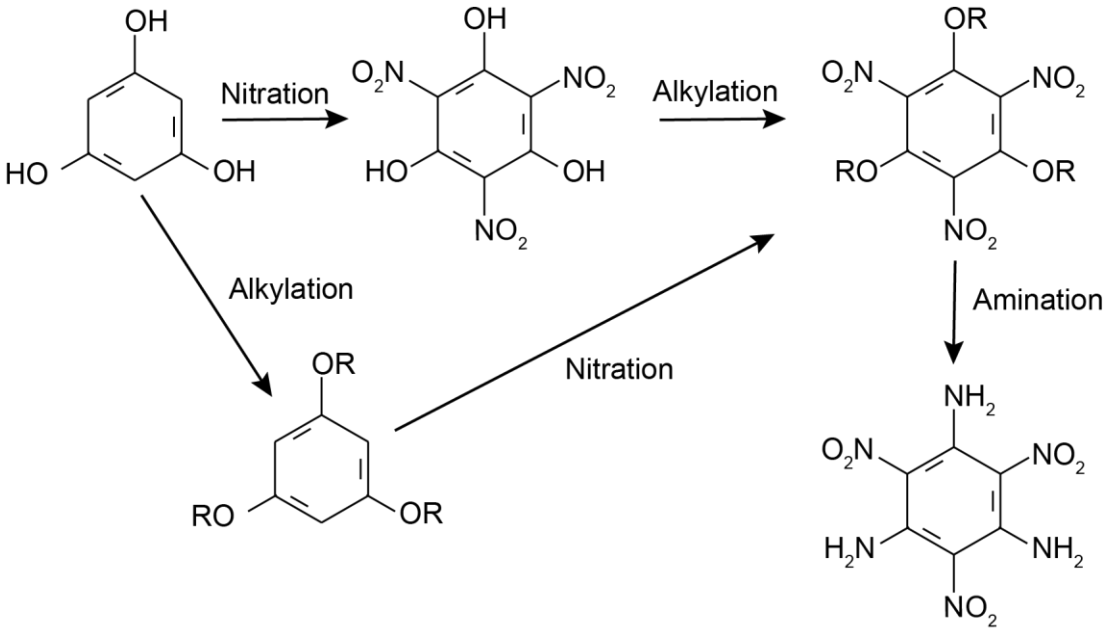


Figure 10-12 Halogen free synthetic route to triamino-trinitrobenzene

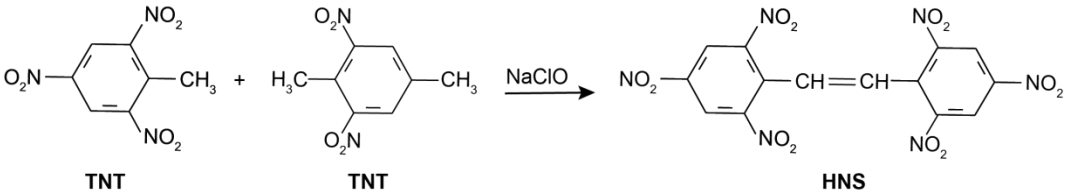
The nitration step is typically carried out with $NaNO_2$ in HNO_3 or with N_2O_5 in H_2SO_4. The alkylation step is carried out with K_2CO_3-dimethyl sulphate, or with a trialkylorthoformate alkylating agent, typically tri-methyl orthoformate or tri-ethyl orthoformate.

Finally, the amination is performed by NH_3 in a solvent. On a small scale, it is convenient to pass ammonia gas into a solution in an organic solvent at low temperature, but on a larger scale the use of liquid ammonia is preferred. The amination may be performed at the boiling point of liquid ammonia (-33 °C), or at ambient temperature under pressure (0.8 - 0.9 MPa). The substrate may be added directly as a solid to the liquid ammonia, or it may be introduced as a solution in an organic solvent.

The type of TATB, i.e. particle size, crystalline surface characteristics, etc., produced depends on conditions used during the amination step[3] and whether or not water and/or emulsifier is present during the reaction.

10.3.2.3 Hexanitrostilbene (HNS) production

HNS is relatively insensitive to impact and friction. It also is heat resistant with a melting point in the range 316-320 °C. It is manufactured by oxidative coupling of TNT using the Schipp process[4] shown in Equation (10-9). This employs a solution of sodium hypochlorite as the oxidizing agent acting on a solution of TNT in methanol to produce HNS as shown below. The process does not produce pure HNS but contains up to 6 % w/w hexanitrobibenzyl and other traces of impurity.



(10-9)

Attempts to remove this impurity by multiple washing have resulted in recrystallized material of a new geometry and consequently larger particle size. The larger particle size is undesirable in many applications. The recrystallization process of HNS-I to produce HNS-II improves the bulk density of the material and could be performed using a single or binary system of solvents. Current manufactures produce all four types of HNS from type I to type IV:

- HNS Type I - for initiation (WS 5003F specification): more stable than stipulated in the MIL specification thanks to a special purification process.
- HNS Type II - for oil and gas drilling: a special quality of HNS, coated with a high temperature resistant polymer, is produced according to WS 5003F specification.
- HNS Type III - for nucleation of TNT, produced under German and US specifications.
- HNS type IV - for Exploding Foil Initiator (EFI) detonators, it is characterized by a higher sensitivity and thereby good reliability of initiation[5].

10.3.3 The Production of N-Nitro Explosives

Nitramines, also known as nitroamines, are organic compounds containing a nitro group bonded to an amine group:

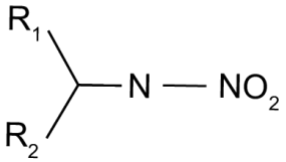


Figure 10-13 Nitramine structure

Nitration on a nitrogen atom, in general, gives a material with greater sensitiveness (see 20.2.1) than the C-nitro materials. N-nitro materials are, generally, more nearly oxygen balanced and have higher densities than C-nitro materials which gives an

increase in the performance of the explosive. Thus the introduction of the N-nitro explosives RDX and HMX during and after the Second World War, respectively, produced a range of higher performance military explosives for both power (see 9.2.2) and shock pressure (see 11.2). However, N-nitration is a more expensive process than C-nitration.

The most prominent members of this class are RDX; hexahydro-1,3,5-trinitro-1,3,5-triazine, (also known as trinitrotriazacyclohexane, hexogen and cyclonite); HMX; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (also known as tetranitrotetrazacyclo-octane and octogen), nitroguanidine also known as Picrite and NQ), and tetryl; 2,4,6-trinitrophenylmethylnitramine (also known as tetranitroaniline and CE – Composition Exploding).

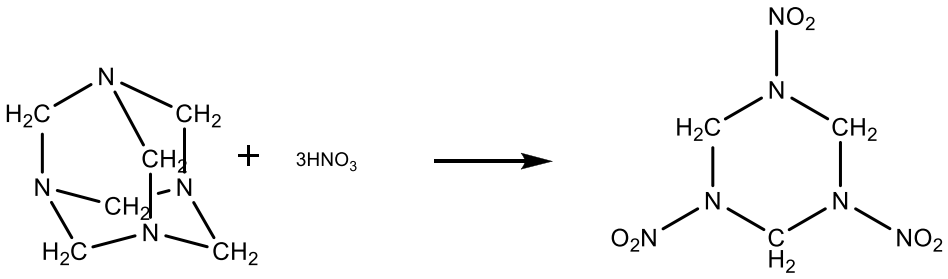
10.3.3.1 Trinitrotriazacyclohexane (RDX) production

RDX is the most commonly used member of the nitramines family. It is produced in large industrial quantities and used in military and civilian applications. There are several types of RDX depending on the method of manufacture, purity and crystal size (Table 10-1)[6,7].

RDX has been produced from hexamethylenetetramine (hexamine) in several ways; using fuming nitric acid (Woolwich method, (10-10)), nitric acid and ammonium nitrate or nitric acid, ammonium nitrate, glacial acetic acid, and acetic anhydride (Bachmann process).

Table 10-1 Types of RDX

Manufacture method		Purity (w/w)		Particle morphology
Type A	**Type B**	**Type I**	**Type II**	**RS (reduced sensitivity) or I (Insensitive)**
Direct HNO_3 nitrolysis process	Bachmann process	<5 % HMX content	4-17 % HMX content	RDX based on mean particle size, shape and impurity content that result in PBX formulations less sensitive to shock.



(10-10)

A continuous production plant will typically feed hexamine and nitric acid into a series of nitrators using co-current flow. The complex reaction taking place produces both ammonia and formaldehyde as by-products. These are both toxic gases and their removal is required on health and safety grounds. These by-products can be recycled as the hexamine is itself manufactured from them. Some

of the ammonia reacts with additional nitric acid to form ammonium nitrate. The process is inefficient in the utilization of the hexamine which adds to the costs of manufacture. In the manufacture, if there is evolution of excess oxides of nitrogen or a thermal run away, drowning of the reaction mixture may become necessary. The drowning is achieved by use of a release valve dumping the reaction mixture into a solution of urea.

After nitration, the RDX and other products of the reaction are passed into further tanks where the acid concentration is reduced by dilution with less concentrated nitric acid. At this stage the materials are heated to about 75 °C to decompose the more unstable impurities as the RDX precipitates as a white solid.

Filtration and washing with water complete the production process. Occluded acidity in the crystals is removed by grinding the damp RDX to a fine powder and boiling in water or by recrystallisation from cyclohexanone solution. The process is illustrated in Figure 10-14.

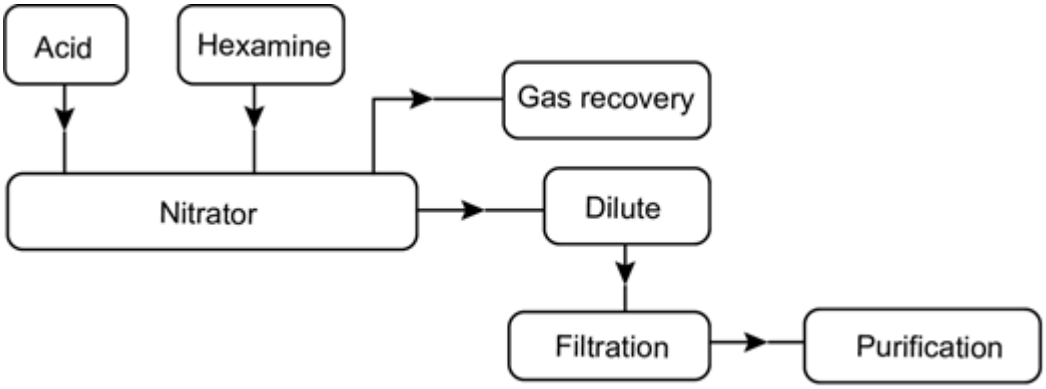


Figure 10-14 A flow diagram for the production of RDX

Alternative methods of production include the treatment of hexamine with ammonium nitrate and nitric acid, the reaction of sulphamic acid with methanal (formaldehyde) and nitric acid, and the treatment of hexamethylenediamine dinitrate with ammonium dinitrate in the anhydride of ethanoic acid (acetic anhydride). This is basically the manufacturing process widely used today as the reaction shown in Equation (10-11), although there are still manufacturers that use the Woolwich process.

$$(CH_2)_6N_4 2HNO_3 + 2(NH_4NO_3) + 6(CH_3CO)_2O \longrightarrow 2(CH_2)_3(NNO_2)_3 + 12CH_3COOH \quad \textbf{(10-11)}$$

10.3.3.2 Tetranitrotetrazacyclo-octane (HMX) production

HMX, also called octogen, is the highest performance explosive produced in industrial quantities. There are several types of HMX depending on the method of manufacture, purity and crystal size (Table 10-2).

Table 10-2 Types of HMX

Purity (w/w)		Particle morphology
Grade B	**High purity**	**RS (reduced sensitivity)**
<2 % RDX content	<0.2 % RDX content	Recrystallisation techniques provide particle shapes that reduce sensitivity for Insensitive Munitions (IM) purposes.

HMX is formed as a by-product of RDX manufacture using the Bachmann Process. By adjusting the reaction conditions it is possible to improve the HMX yield, although not normally higher than 65 % and reduce the amount of RDX produced. The nitrolysis of hexamine using a nitric acid/ammonium nitrate system containing paraformaldehyde with ethanoic acid/ethanoic acid anhydride (acetic acid/acetic anhydride) as solvent will give an HMX-rich product. RDX can be removed from the product by dissolution in hot water. The product can be purified to Military Grade of the correct crystal form (β - least sensitive to impact, Table 10-3) by re-crystallisation from cyclohexanone.

Table 10-3 Types of HMX and Their Relative Stability

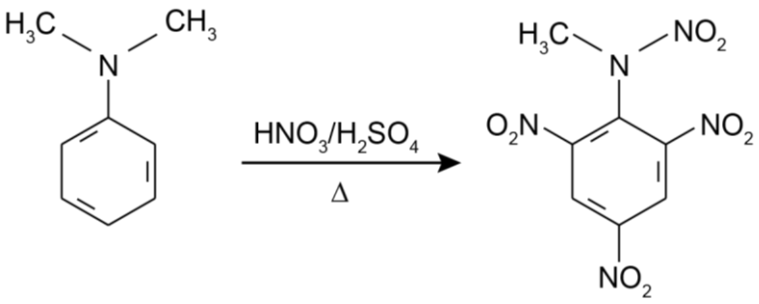
Properties	Form			
	α	β	γ	δ
Specific gravity[8]	1.87	1.96	1.82	1.78
Stability of crystalline form	Metastable	Stable	Metastable	Labile

Due to the larger quantities of acetic anhydride used to obtain HMX, and the need to free the product of RDX as the latter would reduce the performance of the HMX, the cost of HMX is considerably higher (~3×) than that of RDX.

Nitration with dinitrogen pentoxide is currently being investigated as a possibly cheaper and more efficient method of producing HMX. Hexamine is first converted to a non-energetic intermediate, 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (TAT), which is cleanly nitrolysed by N_2O_5 to give HMX. High yields (>80 % w/w) and high purity HMX can be obtained. This is an ideal laboratory process but not exploited industrially in practice.

10.3.3.3 Tetranitroaniline (Tetryl, CE) production

The basic process of nitration to manufacture tetryl starts from N,N-dimethylaniline which is readily nitrated with conventional nitrating mixtures. The replacement of three hydrogen atoms on the ring and the displacement of a methyl group by nitro-groups produces tetryl. The overall reaction is shown in Equation (10-12) below.



Dimethylaniline **Tetryl** **(10-12)**

A typical continuous nitrating plant would contain two heated nitrating vessels and a cooled diluter to precipitate the product. A block diagram for the process is shown in Figure 10-5. The crude product is washed to remove acid and recrystallized either from benzene or propanone to produce the final product.

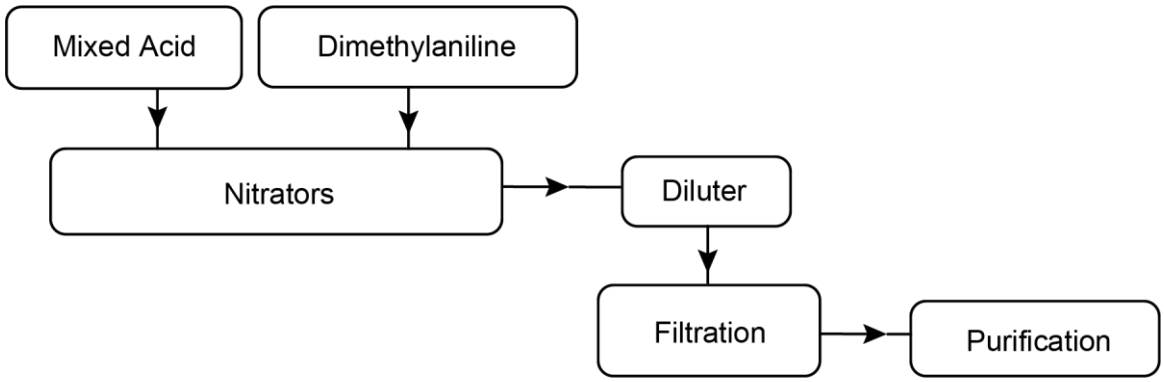


Figure 10-15 Flow diagram for the production of Tetryl

10.3.3.4 Nitroguanidine (Picrite, NQ) production

Nitroguanidine is mainly used in the preparation of triple-base propellants. The material is readily prepared by treatment of guanidine nitrate with sulphuric acid. Guanidine nitrate is a readily available starting material, it can be manufactured by heating calcium carbide in a stream of nitrogen, acidifying the product and then fusing with ammonium nitrate. The guanidine nitrate is added to a nitrator containing sulphuric acid with the temperature maintained at about 45 °C by cooling. The reaction is rapid and nitroguanidine is recovered in high yield (>90 %) by passing the nitration mixture into water to precipitate the product. The crude product, after washing to remove acid, is recrystallized from water. The reaction sequence is shown in Figure 10-16.

Another route to synthesise nitroguanidine starts with the fusing of ammonium nitrate with dicyandiamide to form guanidine nitrate. Concentrated sulphuric acid then converts this to nitroguanidine.

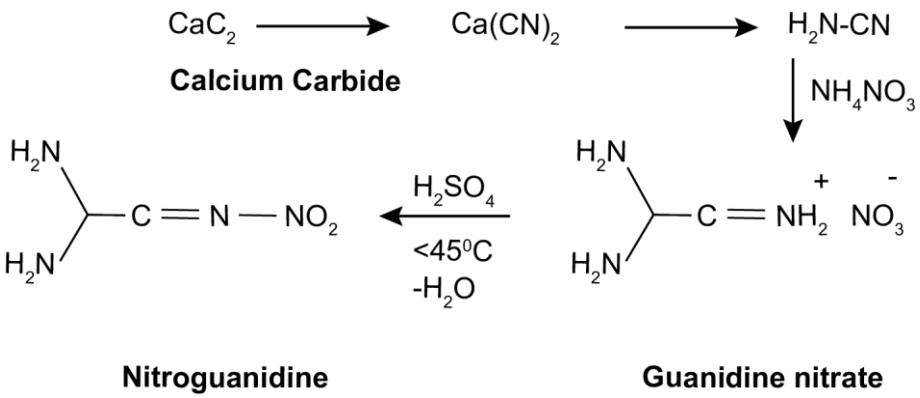


Figure 10-16 Synthesis route to manufacture nitroguanidine

10.3.3.5 Hexanitrohexaazaisowurtzitane (CL-20) production

CL-20 can be synthesised on a laboratory scale accordingly to the reaction scheme shown in Figure 10-17.

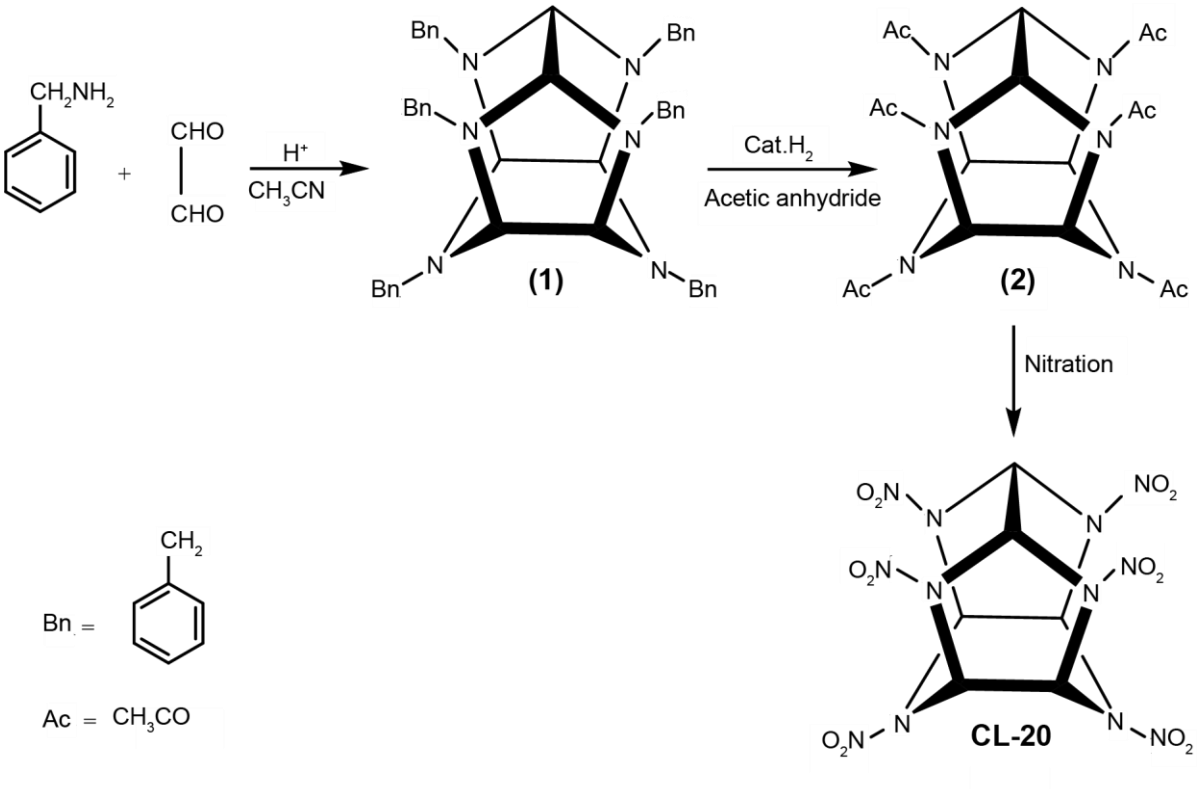


Figure 10-17 Synthesis route to manufacture hexanitro-hexa-azaisowurtzitane (CL-20)

2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (Compound 1) can be synthesised by reaction of benzylamine with aqueous glyoxal (40 % v/v) in aqueous acetonitrile in the presence of a catalytic amount of formic acid. Reductive acetylation of compound 1 with palladium hydroxide on carbon in acetic anhydride in the presence of catalytic amount of bromobenzene yields the tetra-acetate compound 2. Treatment of 2 with 3 mole equivalents of nitrosonium tetrafluoroborate in sulfolane followed by 12 mole equivalents of nitronium

tetrafluoroborate in the same vessel, produces CL-20 in 90 % yield[9]. CL-20 exists in four crystalline forms, stable at different temperatures. Only the ε and the β form are used currently.

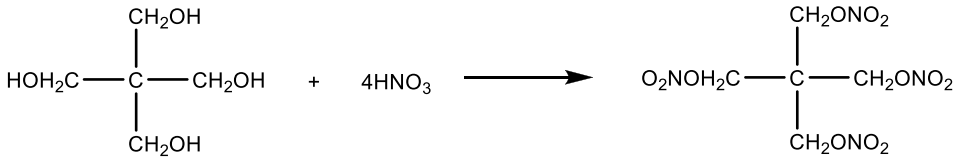
10.3.4 The Production of O-Nitro Explosives

Nitration on an oxygen atom produces more nearly oxygen balanced explosives (see 4.3.1) than the C-nitro or N-nitro explosives. Due to the higher oxygen balance of these materials they tend to have high heats of explosion (see 4.4.2), however, they tend to be less stable and to have a higher sensitiveness (see 20.2.1) than other explosives. The chemical stability of O-nitro compounds, or nitrate esters as they are also known, is relatively low, due to the ease of hydrolysis of the O-NO_2 bond. Further, the hydrolysis is catalysed by the presence of acid or alkali. In this context it is the presence of acid from the manufacturing process or as a degradation product that is generally of concern.

O-nitration readily takes place using conventional nitric acid/sulphuric acid mixtures. The production of nitroglycerine (a member of the O-NO_2 family) is probably the most dangerous explosive preparation performed on large scale.

10.3.4.1 Pentaerythritol tetranitrate (PETN) production

The nitration of pentaerythritol is achieved by the use of 98-99 % v/v nitric acid and is the only nitrate ester to be produced using only nitric acid. A typical continuous nitrator would require cooled nitrators for the mixing of nitric acid with pentaerythritol due to the exothermic reaction of the materials on mixing. After nitration the reaction mixture is diluted to ease separation of the precipitated pentaerythritol tetranitrate and recovery of the spent acid, which contains about 80 % v/v HNO_3. The acid is diluted to 30 % v/v HNO_3 with water, not only to reduce the PETN solubility but also to stabilise the mixture. Spent acid containing 75-80 % v/v HNO_3 is dangerously unstable due to the hydrolysis of PETN to its lower nitrates. The overall reaction is shown below in Equation (10-13).



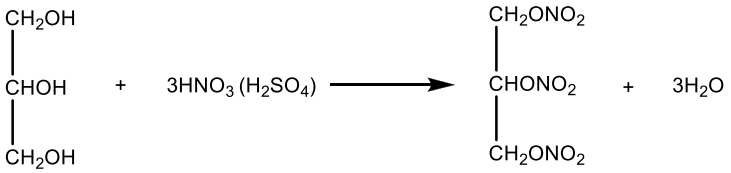
(10-13)

The product requires washing to remove acid residues and crystallization from aqueous acetone, with ammonia added to neutralise traces of acids, producing the required material. A second recrystallisation and precipitation is often carried out as a particle size adjustment process to produce a powder with the desired specific surface area. Resulting crystals have irregular faces in the size range 5-16 microns. The preferred shape for use in detonators is a tetragonal rod. Crystal morphology can be controlled by recrystallization using acetone/water mixtures where solvent addition, stirring rate and temperature are all critical conditions.

10.3.4.2 1,2,3-Trinitroxypropane (nitroglycerine, glyceryl trinitrate or NG) production

The explosive commonly known as nitroglycerine (NG) is probably the most sensitive explosive manufactured on a large scale. It has a low Figure of insensitiveness (see 20.10.2.1) and is susceptible to accidental initiation. Production methods take account of the dangers of NG production and traditional methods utilize gravity feed to move the material rather than any form of pumping. Due to this, the plant is normally raised on small, natural or man-made, hills. Modern plants may pressurize the starting materials to achieve movement through the plant.

There are three main types of continuous nitration plant in operation, these are based on: the Biazzi Process, the Nilssen and Brunnberg (NAB) Injector Process and, less common, the Hercules Tubular Process. In all the production processes, nitration takes place with ‘mixed acids’ in the reaction shown in Equation (10-14). The main differences occur in the method used to mix the acids and glycerine, and the size and geometry of the nitrator.



(10-14)

In a Biazzi Process, mixed acids and glycerine are metered and introduced into a nitrating vessel where they are stirred at high speed (Figure 10-18**).** The vessel is cooled to maintain a temperature in the range of 10 °C to 15 °C. The nitrated product overflows into the separator which is a larger vessel where the NG/acid emulsion slowly rotates affording time for separation. Nitroglycerine is removed from near the top of the separator and spent acid from the bottom. A large Biazzi plant can produce over 2000 kg h^{-1} but only 80 kg is at risk at any specific time. The overall process is shown in Figure 10-19.

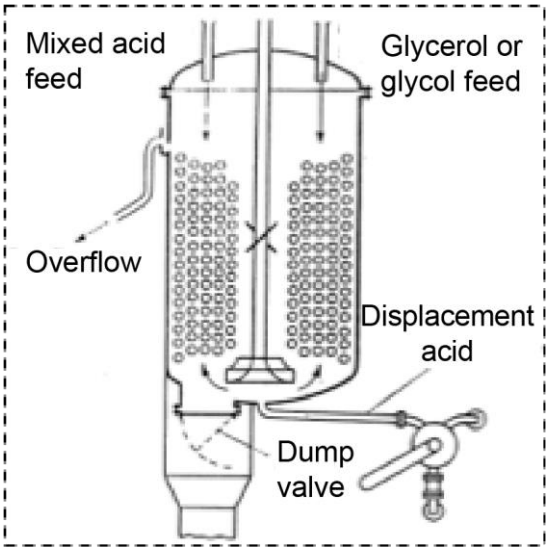


Figure 10-18 The Biazzi process reactor

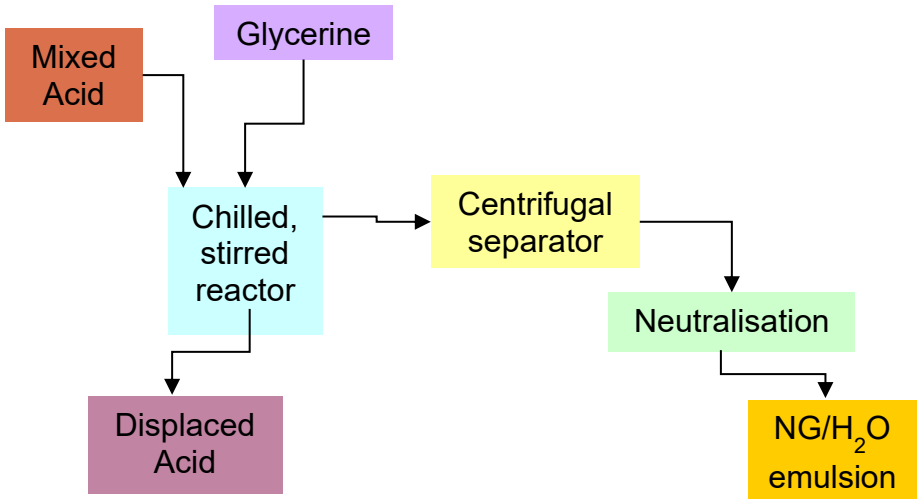


Figure 10-19 Schematic of the Biazzi process for NG production

The Nilssen and Brunnberg (NAB) Injector Process utilizes the flow of mixed acid through a small nozzle to 'suck' glycerine into the nitrator. The process allows the reaction mixture to achieve about 45 °C for half a second. This is followed by rapid cooling. Separation is achieved by a similar process to that carried out in the Biazzi Process. The unit explosion risk is reduced to 3.5 kg of NG. Mixed acids and glycerine, under pressure, are mixed at a T-piece before entering a tubular nitrator in the Hercules Process. After flowing through an uncooled portion of tube the reaction mixture enters a cooled portion of tube before separation. Again similar methods are used for the separation process.

Both processes will work with a range of acid compositions and nitration mixture to glycerine ratios. As the processes are hazardous, methods of quenching the system are required in case the reaction becomes uncontrolled. The Biazzi Process has built in dump facilities, the materials being deposited in water to dilute the acids in the event of excess temperature in the nitrator or separator. Automatic shut-down of the feed is also incorporated. The NAB Injector Process has a fail-safe shut-down operated by the closing off or reduction in the pressure of the mixed acids at the injector, which stops or greatly reduces the amount of glycerine 'sucked' in to the nitrator. Table 10-4 summarises the reaction conditions for the manufacture of nitroglycerine in Biazzi and NAB processes. Both procedures give very similar high yields.

Table 10-4 Reaction Conditions for Glycerine Nitration

Process	HNO_3	H_2SO_4	H_2O	$(HNO_3 + H_2SO_4)$/glycerine	Yield (%)
Biazzi	51	49	0	4.85	96
N.A.B.	27	63	10	12.1	94

In all production plants, washing of the product is required to remove acid from the nitroglycerine. This is commonly achieved by washing with sodium carbonate solution which neutralizes the residual acid. Storage of the final product can cause

problems and many manufacturing processes use the NG to manufacture propellant or commercial explosives directly without intermediate storage. Figure 10-20 gives a general flow diagram for the production of nitroglycerine.

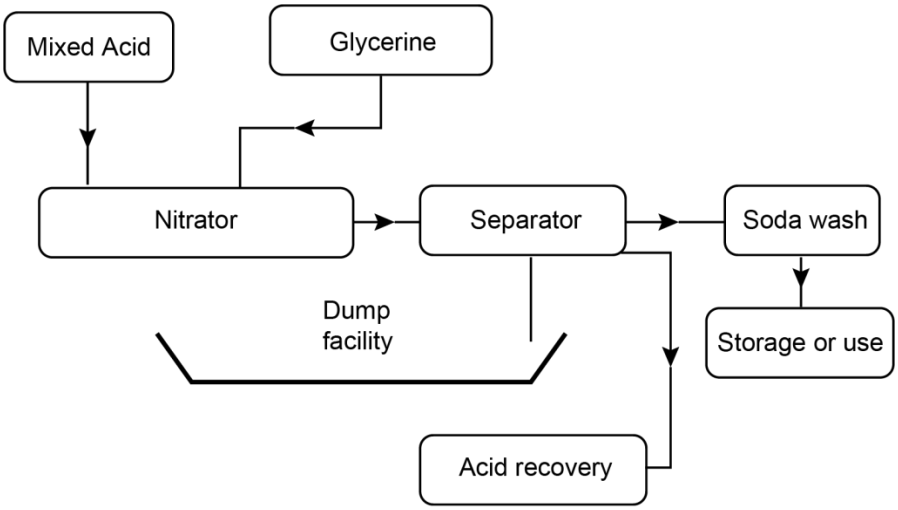
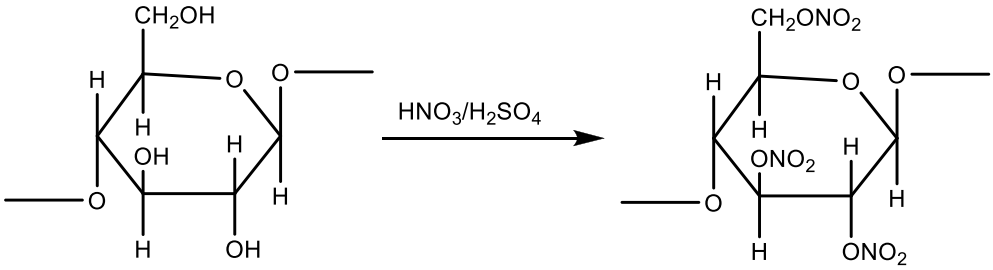


Figure 10-20 Flow diagram for nitroglycerine manufacture

10.3.4.3 Nitrocellulose (cellulose nitrate or NC) production

Cellulose is a polymeric material containing large numbers of glucose molecules joined together through an ether (-O-) link. The cellulose contains many thousands of glucose molecules. Nitrocellulose (NC) is readily formed by the treatment of cellulose with a variety of nitrating materials. However, the production of evenly and efficiently nitrated cellulose limits the practical nitration methods. Complete nitration of all hydroxyl groups (3 per glucose unit) gives a weight percentage for nitrogen content of 14.15 %. The percentage nitration (% N) determines many of the properties of the nitrocellulose including solubility, explosives properties and stability. In practice, nitration with HNO_3/H_2SO_4 gives at most 13.5 % N while products with higher levels of N are unstable; HNO_3/H_3PO_4 gives 14.04 % N and gaseous N_2O_5 gives 14.12 % N. The % N from an HNO_3/H_2SO_4 nitration is determined by the composition of the mixed acid and the contact time. The nitration reaction is shown below in Equation (10-15).



(10-15)

All methods of forming nitrocellulose require purified cellulose. This is available from natural or naturally based materials such as wood, cotton fibre or paper. The purification of the starting materials is essential to obtain a consistent product. Probably the richest source of cellulose is cotton fibre. This plant produces two types of fibre, a long fibre used in the manufacture of threads and hence fabric and

a shorter fibre, called linters, which is used in the manufacture of nitrocellulose. This fibre is collected and shipped to the manufacturer where it requires much pre-treatment before nitration.

The initial step in purification is the removal of unwanted ‘foreign bodies’, which will consist of parts of the cotton seed, stalks and even insects. The cotton linters are combed with mechanical combs to remove these unwanted materials. Autoclaving in dilute sodium hydroxide solutions is employed to chemically treat the cotton and remove some of the non-cellulose matter present with the cellulose. The final chemical treatment is that of bleaching with a chlorine bleach or chlorine itself. After this treatment the material requires thorough washing and some drying before nitration can take place.

The nitration of cellulose is carried out on a large-scale batch process. Nitrators capable of holding about 1 tonne of material (acids and cellulose together) are often grouped together to feed separators within a single large plant. Batches of material progress through the plant giving a semi-continuous operation. The degree of nitration, as measured by the percentage nitrogen in the product, will vary depending on the reaction conditions. The concentrations of nitric acid and sulphuric acid, the temperature and duration of nitration all play a part in the degree of nitration and quality of the product. In a typical production plant a ratio of between 1:40 to 1:60 of cellulose to mixed acids is employed. The composition of the acid varies but typical values of 20 % v/v nitric acid and 60 % v/v sulphuric acid are used.

Once the nitrator is loaded with acid, the cellulose is added and submerged. After nitrating for approximately 20 minutes, the acid and nitrocellulose are separated centrifugally to remove the bulk of the acid. Due to the absorbent nature of the cellulose fibre there will be a large amount of residual acid present within the fibre. This residual acid requires removal if the final product is not to spontaneously ignite. A process of washing and boiling is employed to remove this acid. Typically the product of a number of nitrators is boiled several times with fresh loads of water at elevated temperatures in an autoclave.

After stabilization the material is dried before it can be used in the manufacture of propellants. Dry NC is susceptible to initiation by friction and impact and in general the NC is handled with a controlled water content to reduce the risk. The overall process is illustrated in the flow diagram (Figure 10-21).

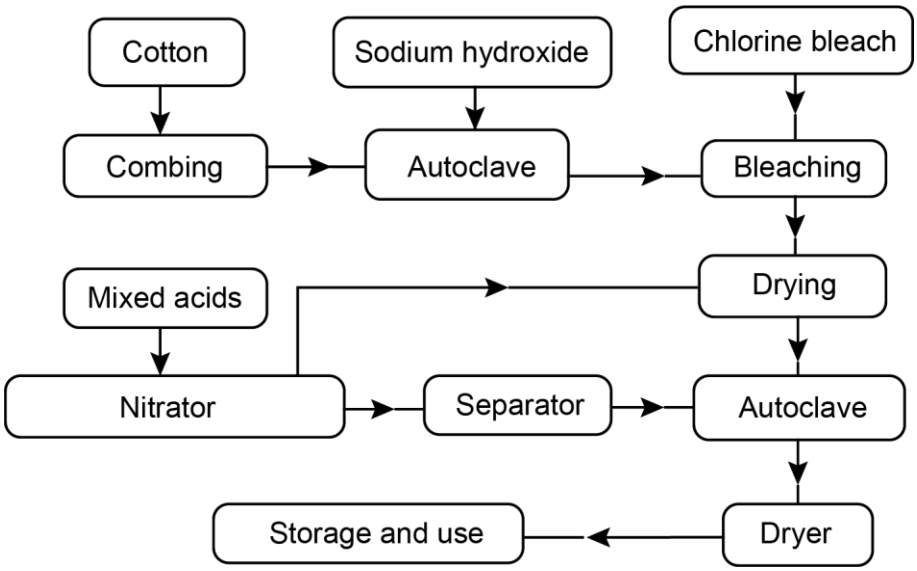


Figure 10-21 A flow diagram for nitrocellulose manufacture

10.3.5 Recent Developments

10.3.5.1 3-Nitro-1,2,4-triazol-5-one (NTO) production

The synthesis pathway for NTO shown in

Figure 10-22 involves two simple reactions, the reaction of semicarbazide hydrochloride with formic acid followed by a nitration with 99 % v/v nitric acid. Formic acid is added to solid semicarbazide hydrochloride at ambient temperature and the resulting solution is then heated to 65 °C and stirred to give the intermediate 1,2,4-triazol-5-one. The reaction mixture is cooled to ambient temperature and HNO_3 added. After 3 hours the mixture is filtered and the resulting solid is washed with cold water. Recrystallisation from hot water gives NTO as a white crystalline solid. The current manufacturing technique prevents full recovery of NTO.

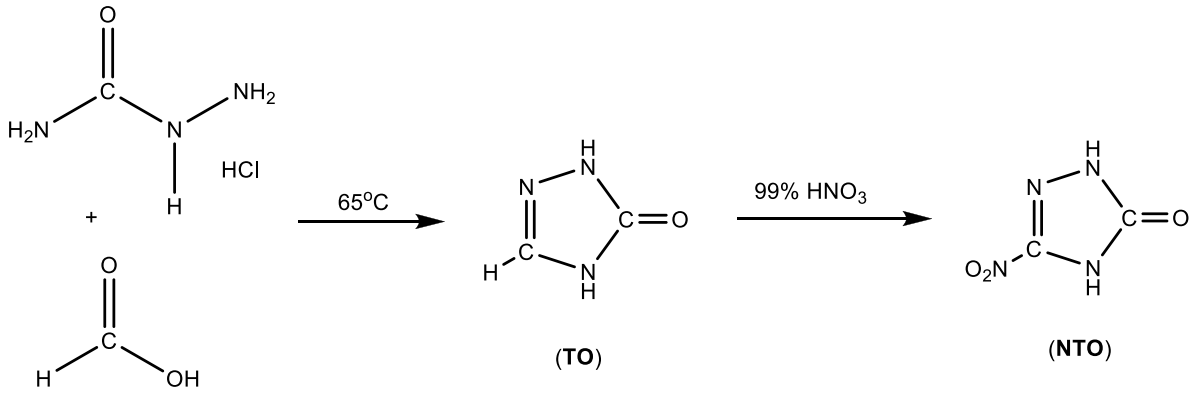


Figure 10-22 The synthesis pathway for NTO manufacture

10.3.5.2 1,1-Diamino-2,2-dinitroethene (FOX-7) production

The synthesis of FOX-7 is relatively easy and it can be synthesised in a single-step process[10]. The nitration using a mixture of concentrated nitric and sulphuric acid of the 2-methyl-4,6-dihydroxypyrimidine gives an intermediate, 2-dinitromethylene-5,5-dinitropyrimidine-4,6(1H,5H)-dione (Figure 10-23) which then is hydrolysed in water to produce FOX-7 after several hours at ambient temperature.

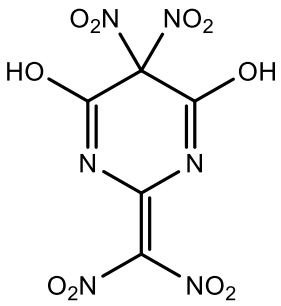
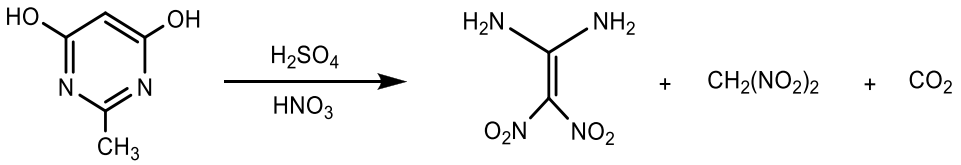


Figure 10-23 Structure of 2-dinitromethylene-5,5-dinitropyrimidine-4,6(1H,5H)-dione

The product separates out as it is formed and is finally filtered off and washed with water. Two by-products also are formed during the hydrolysis, dinitromethane and carbon dioxide, as shown in Equation (10-16) below.



(10-16)

2-Methyl-4,6-dihydroxypyrimidine **FOX-7**

FOX-7 exists as a canary-yellow solid and may be recrystallized from a variety of solvents, dimethylsulphoxide-water, *N*-methylpyrrolidin-2-one-water and dilute HCl being commonly employed. Figure 10-24 shows a schematic representation of a FOX-7 plant.

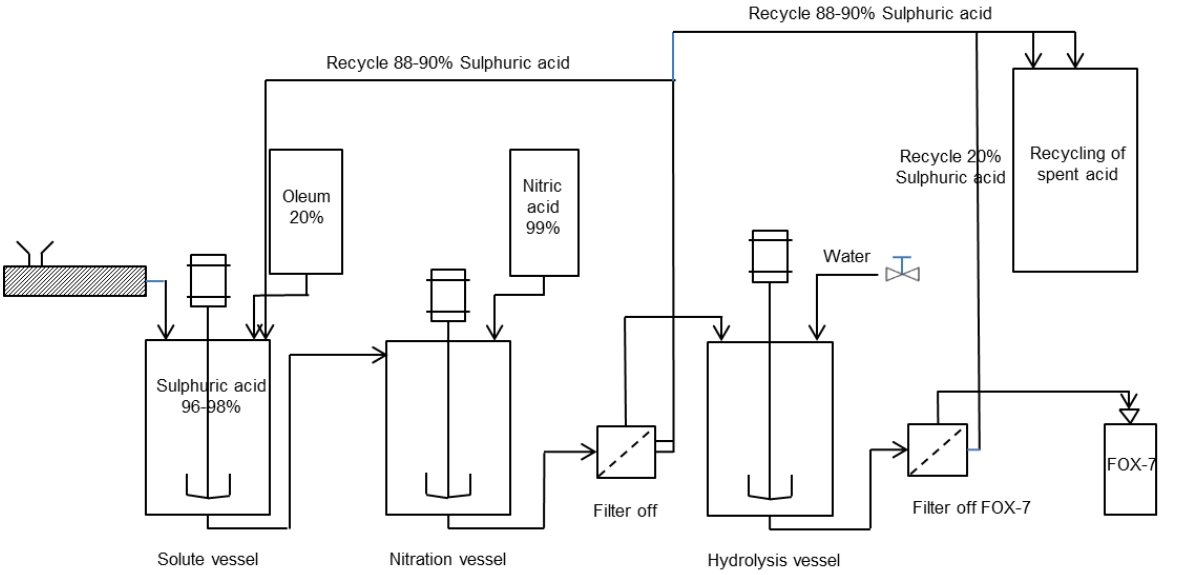
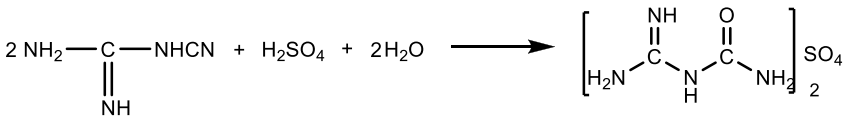


Figure 10-24 FOX-7 plant schematic

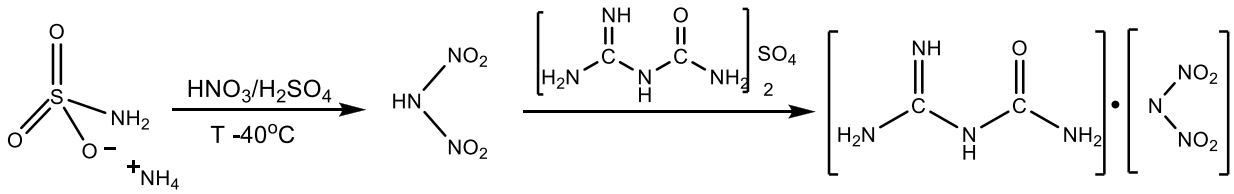
10.3.5.3 N-Guanylurea dinitramide (GUDN, FOX-12) production

GUDN is a low sensitiveness (see 20.2.1) explosive with good thermal stability and potential candidate for Insensitive Munition filling. It is also an important precursor for the synthesis of the solid oxidiser ammonium dinitramide (ADN) via potassium dinitramide[11].

GUDN is synthesised in a two steps process as shown in Figure 10-25; 1) synthesis of guanylurea sulphate from dicyandiamide and 2) nitration of ammonium sulphamate which reacts with guanylurea sulfate to give GUDN as a white crystalline solid.



STEP 1



STEP 2

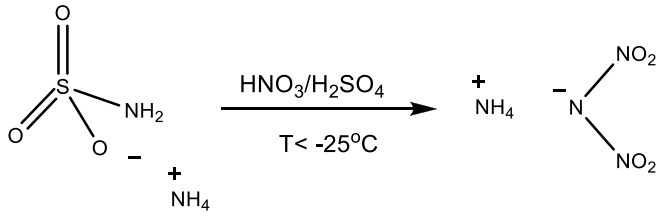
Figure 10-25 Schematic for synthesis of FOX-12

GUDN is more thermally stable compared to ADN. It exhibits a layered packing with intermolecular hydrogen bonds within the layers and van der Waals interactions

between the layers[12]. Low impact and friction sensitiveness, absence of melting point and low water solubility are attributed to the special molecular packing.

10.3.5.4 Ammonium dinitramide (ADN) production

ADN can be synthesized from standard industrial chemicals by direct nitration of salts of sulfamic acid by mixed nitric and sulphuric acids (Equation (10-17), followed by neutralization and separation of the ADN formed. Sulphamic acid is, for instance, used to produce sweeteners and as an ingredient in cleaning agents.



(10-17)

10.4 MANUFACTURE OF COMMONLY ENCOUNTERED PRIMARY EXPLOSIVES

10.4.1 General

Primary explosives are very much more readily initiated than the majority of high explosives. Their manufacture must take suitable precautions to account for this added danger. In general, the manufacture of primary explosives is carried out on a small scale, often in a very similar way to an ordinary laboratory scale preparation. The manufacture of several commonly encountered primary explosives is detailed in the following sections.

10.4.2 Lead Styphnate

Lead styphnate (lead 2,4,6-trinitroresorcinate) is particularly sensitive to initiation by electric spark. It is also a very weak explosive and as such is not normally used on its own.

10.4.2.1 General Manufacture of Lead Styphnate[13]

Styphnic acid (2,4,6-trinitroresorcinol) and magnesium oxide (or carbonate) are mixed in water to give a solution of magnesium styphnate. Lead styphnate is precipitated from solution by the addition of an aqueous lead nitrate or lead acetate solution. Filtering and drying are required and stringent safety precautions are employed during the manufacture, handling and storage of lead styphnate. The manufacture of RD1303, RD1346, RD1349 and RD1367, the various forms of lead styphnate, are detailed below.

10.4.2.2 RD1303

The RD1303 manufacturing processes[14] involve the preparation of stock solutions of magnesium styphnate prepared from styphnic acid and magnesium carbonate,

lead acetate and dilute nitric acid. For the precipitation, lead acetate solution is added to magnesium styphnate solution which is maintained at a suitable temperature and controlled rate of stirring. Basic lead styphnate is precipitated and then converted to the normal salt by the controlled addition of nitric acid. The reaction sequence is shown in:

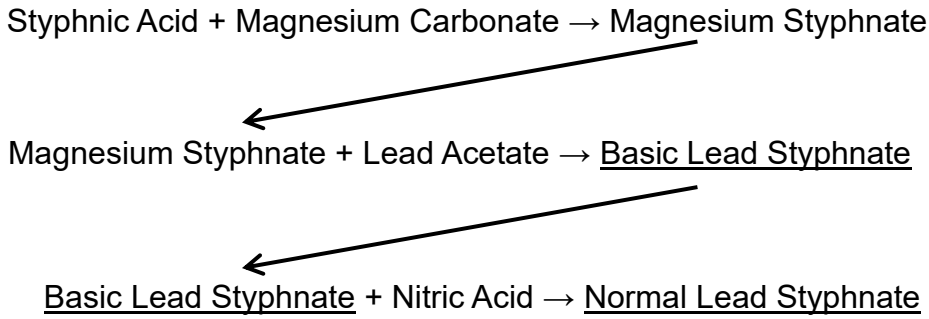


Figure 10-26 Reaction sequence to manufacture normal lead styphnate

The process gives rise to single crystals of lead styphnate that are rhombic varying from granular to prism form with a tendency to widely varying aggregation according to the conditions of its formation. Broadly the conditions tending towards aggregation are:

- Too rapid addition of acid
- Insufficient acidity and direct precipitation of the normal salt.
- Incomplete conversion of the basic salt due to inefficient stirring or reduced time gives rise to a powdery product.

Figure 10-27 shows normal lead styphnate (single rhombic crystals) and for comparative purposes basic lead styphnate (needle like crystals) are shown in Figure 10-28[15]. RD1303, Figure 10-29[15], is a free flowing powder consisting of bright yellow predominantly tabular crystals having an average particle size of approximately 0.03 mm.

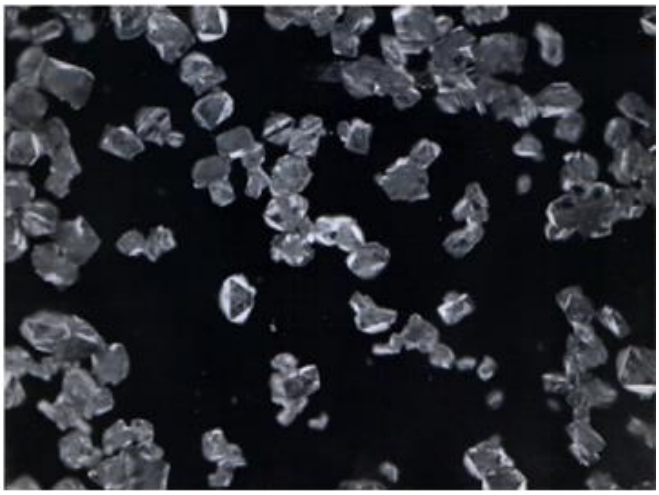


Figure 10-27 Normal lead styphnate (×80 magnification)



Figure 10-28 Basic lead styphnate (×80 magnification)

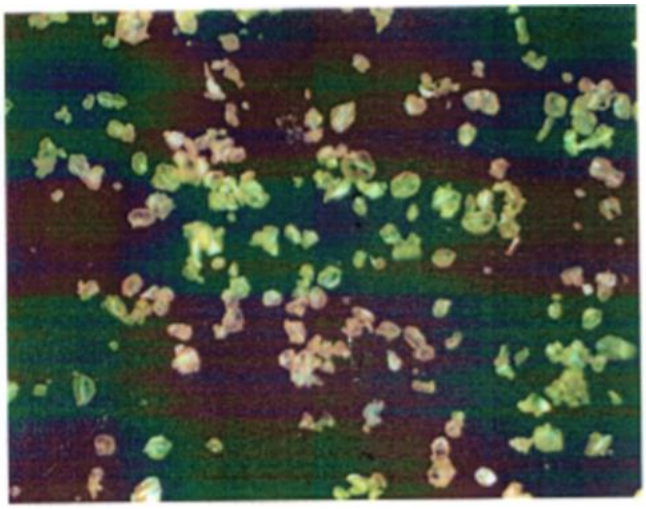


Figure 10-29 Lead styphnate, RD1303 (×100 magnification)

10.4.2.3 Manufacture of RD1346 and RD1349

Because of its water of recrystallisation normal lead styphnate monohydrate is not suitable for use in munitions which may be subjected to high temperatures (>130 °C) in use. For this purpose, mono basic lead styphnates have been found to be suitable. Two compositions based upon the β-form (obtained by careful precipitation) namely RD1346 and RD1349 are used in UK service. Both are granular in form and free flowing. The RD1346 has a higher bulk density than the RD1349 and is recommended for use in dry loading applications such as an ingredient for priming and bridgewire compositions. RD1349 is especially suitable for making fuseheads without cavitations.

10.4.2.3.1 RD1346

RD1346 is prepared[16] by reacting an aqueous solution of lead nitrate with an aqueous solution containing sodium styphnate, sodium hydroxide and 2-nitroresorcinol at a suitable temperature and rate of stirring. The product, Figure 10-30[15], is a free flowing powder consisting of orange, rounded granules, approximately 0.07 mm^2.

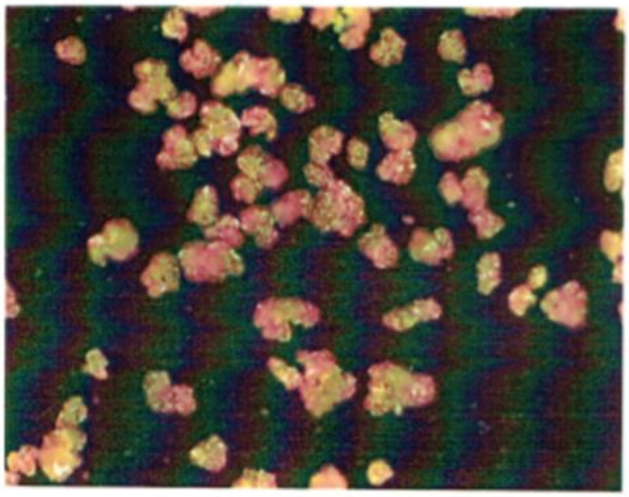


Figure 10-30 Lead styphnate, RD1346 (×100 magnification)

10.4.2.3.2 RD1349

RD1349 is prepared[16] by reacting an aqueous solution of styphnic acid and ammonium hydroxide with ammonium 2-nitroresorcinol solution with a mixed solution of lead acetate/ammonium hydroxide at a suitable temperature and rate of stirring. The product, Figure 10-31[15], is a free flowing powder consisting of small, brown single crystals with a distinctive ‘cigar-shape’. The approximate size of individual crystals is 0.06 mm × 0.01 mm.

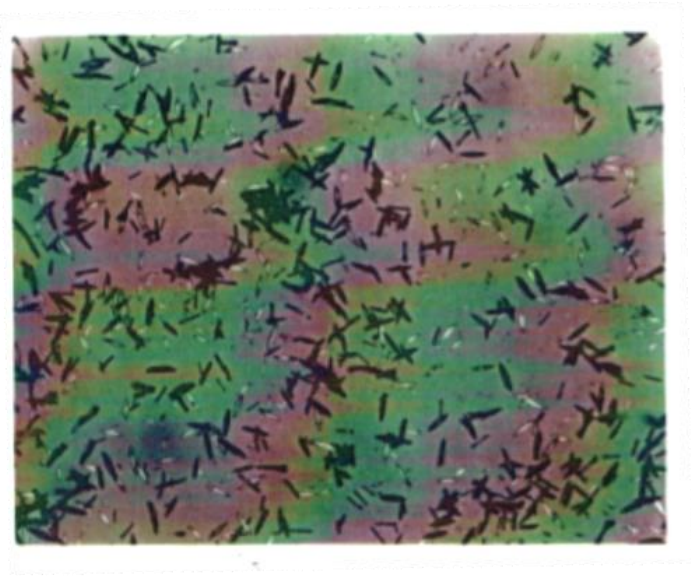


Figure 10-31 Lead styphnate, RD1349 (×100 magnification)

10.4.2.4 Manufacture of RD1367

The RD1367 process was introduced to provide a more economic method for the manufacture of lead styphnate. Although the RD1303 process is efficient with respect to the quality of the products it had fairly stringent requirements on the quality of the styphnic acid employed and yields were not high. The common process for preparing normal lead styphnate (commercial and RD1367) consists of the addition of lead nitrate solution to heated and stirred magnesium styphnate solution, prepared from styphnic acid and magnesium carbonate, at a set pH and concentration. The use of lead nitrate to make RD1367 rather than lead acetate which is used to manufacture RD1303 yields a more uniform crystalline product. The product, Figure 10-32[(15)], consists of a free flowing powder consisting of yellow/orange, single, equant crystals. The approximate size of individual crystals is 0.10 mm × 0.08 mm.

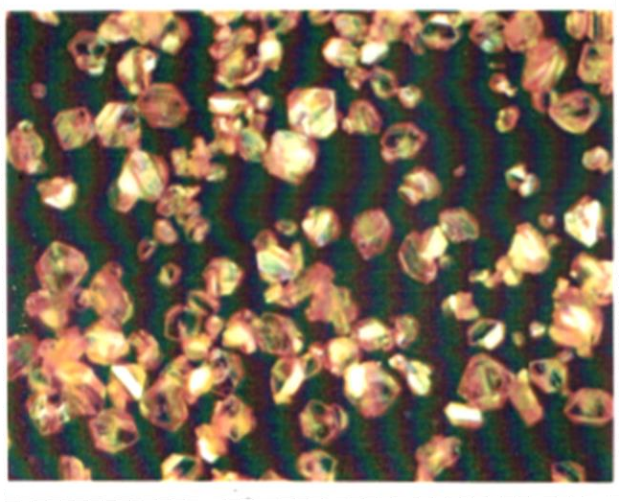


Figure 10-32 Lead styphnate, RD1367 (×100 magnification)

10.4.2.5 Eleyprime process

The Eleyprime process is based on the fact that the main explosive ingredient of VH2 and VH4 compositions, lead styphnate, can be formed after filling into the percussion cap by reaction between styphnic acid (2,4,6-trinitroresorcinol), which is not highly explosive or very sensitive, and lead dioxide. This reaction takes place only in the presence of water, which is not added until the insensitive reactants are filled into the percussion cap. Those ingredients of the mixture which are insoluble in water, namely the lead dioxide and antimony sulphide, are first mixed with wet tetrazene and dried (Mix A). The soluble or abrasive ingredients, comprising styphnic acid, barium nitrate and calcium silicide, are then added to Mix A and mixed in the dry state to produce a 'premix'. The resulting 'premix' at this stage behaves as a pyrotechnic and is relatively safe to handle and store. A measured quantity of the 'premix' is lightly pressed into the percussion cap and a drop of water added. The water causes the reaction to take place and after about 15 minutes the formation of lead styphnate is complete after which drying and final pressing takes place.

10.4.3 Barium Styphnate

Barium styphnate is a relatively insensitive primary explosive which is difficult to ignite by electric spark. When ignition is achieved, propagation is poor. It is less sensitive to impact and friction than lead azide or lead styphnate.

10.4.3.1 RD1320

RD1320 is prepared[17] by reacting an aqueous solution of barium acetate and an aqueous solution of magnesium styphnate at a suitable temperature and rate of stirring. A trihydrate salt is formed which is converted to the monohydrate by the addition of nitric acid. The product, Figure 10-33[15], is a free flowing yellow powder consisting of individual equant crystals approximately 0.15 mm × 0.10 mm with slight aggregation due to the small crystals.

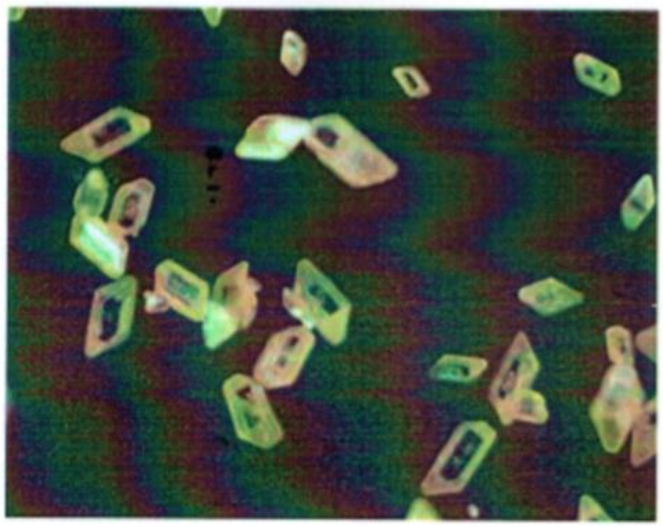


Figure 10-33 Barium styphnate, RD1320 (×100 magnification)

10.4.3.2 RD1320A

RD1320A is prepared[17] by reacting an aqueous solution of barium chloride and an aqueous solution of magnesium styphnate at a suitable temperature and rate of stirring. The product, Figure 10-34[15] consists of yellow free flowing columnar crystals approximately 0.15 mm × 0.10 mm with slight aggregation due to the small crystals.

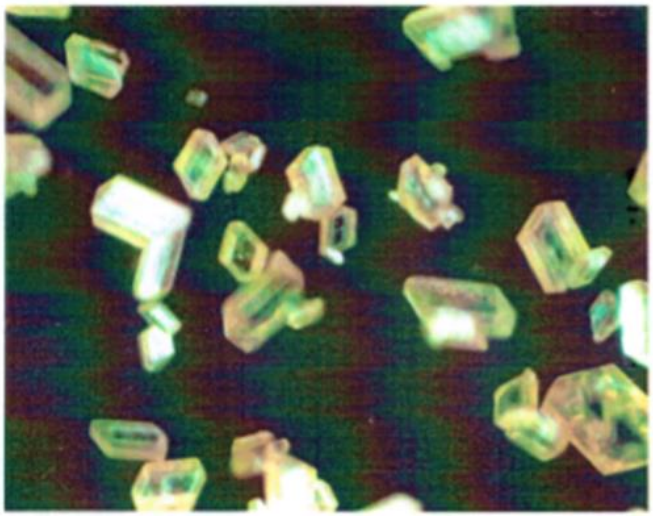


Figure 10-34 Barium styphnate, RD1320A (×100 magnification)

10.4.3.3 RD1320B

RD1320B is prepared[18] by reacting an aqueous solution of barium chloride and an aqueous solution of magnesium styphnate solution containing sodium carboxymethyl cellulose at a suitable temperature and rate of stirring. The product, Figure 10-35[15], consists of granular opaque rounded free flowing granules. Granules are approximately 0.3 mm × 0.15 mm.

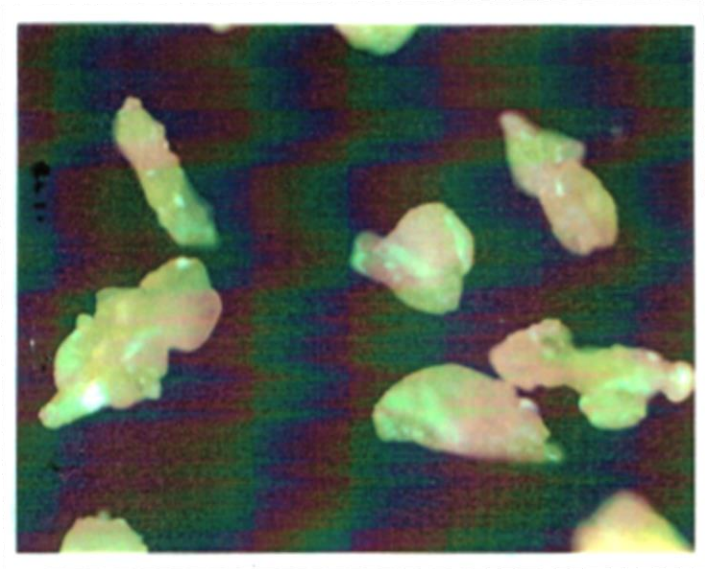


Figure 10-35 Barium styphnate, RD1320B (×100 magnification)

10.4.3.4 RD1340

RD1340 is prepared[19] by reacting an aqueous solution of barium acetate containing a non-ionic surfactant with an aqueous solution of magnesium styphnate at a suitable temperature and rate of stirring. Following this, nitric acid solution is added over a pre-determined time. The product shown in Figure 10-36[15], consists of a free flowing powder composed of yellow, plate-like crystals approximately 0.25 mm × 0.08 mm together with a number of smaller crystals approximately 0.07 mm × 0.04 mm. The small plates form a non-segregating mixture with potassium chlorate and antimony sulphide. This is due to the smaller particle size and low bulk density as compared with RD1320. The particle size of the product is controlled by the rate of addition of the nitric acid with slower addition producing larger crystals.

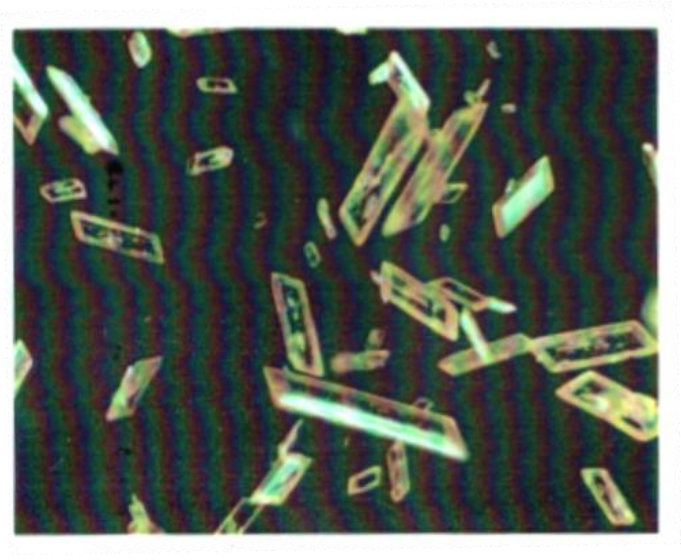


Figure 10-36 Barium styphnate, RD1340 (×100 magnification)

10.4.4 Lead Dinitroresorcinate

Lead dinitroresorcinate is an igniferous primary explosive which is sensitive to flash, impact or stab but is less violent than lead styphnate.

10.4.4.1 RD1308

RD1308 (4,6-lead dinitroresorcinate) is prepared[20] by reacting an aqueous solution of lead hydroxide, prepared by reacting an aqueous solution of sodium hydroxide, with an aqueous solution of lead acetate, an aqueous solution of sodium carboxymethyl cellulose and a suspension of 4,6-dinitroresorcinol at a suitable temperature and rate of stirring. The product, Figure 10-37[15], is a free flowing powder, consisting of orange, irregular, granules approximately 0.03 mm^2.

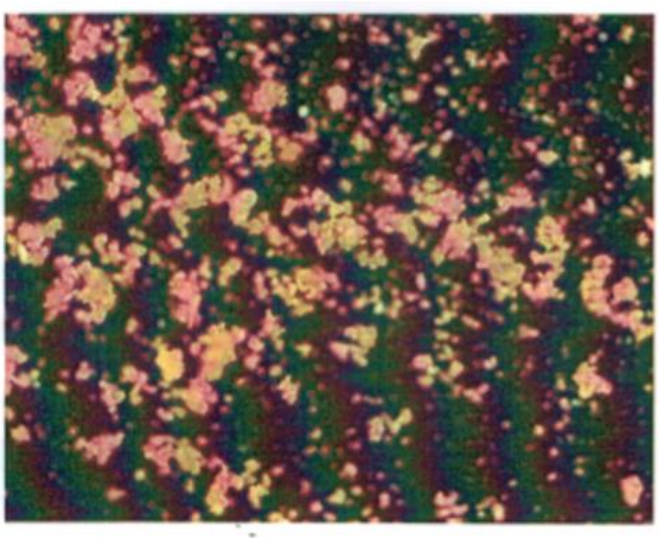


Figure 10-37 Lead dinitroresorcinate, RD1308 (×100 magnification)

10.4.4.2 RD1337

RD1337 (2,4-lead dinitroresorcinate) is prepared[21] by reacting an aqueous solution of sodium 2,4-dinitroresorcinate and an aqueous solution of lead acetate at a suitable temperature and rate of stirring. The product, Figure 10-38[15], consists of a free flowing powder consisting of individual orange/red granules approximately 0.10 mm^2 and some granular aggregates

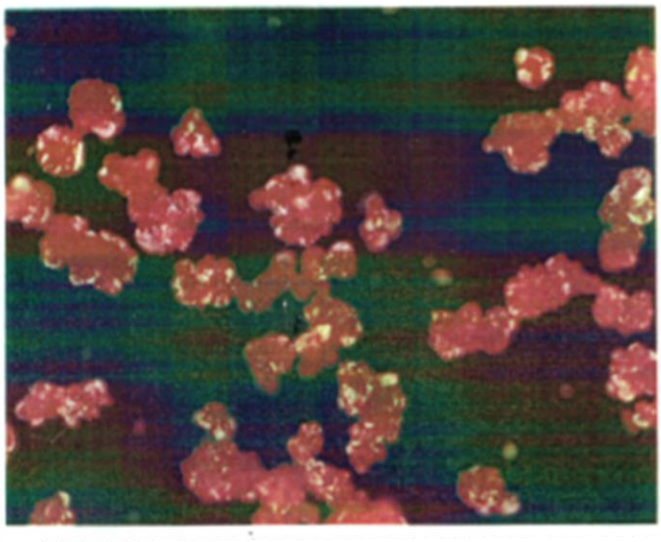


Figure 10-38 Lead dinitroresorcinate, RD1337 (×100 magnification)

10.4.5 Lead Azide

In the manufacture of lead azides and silver azide, safety is of primary importance to all concerned. The risks associated with the sensitiveness (see 20.2.1) of the azides cannot be overstressed. Lead azide is sensitive to shock, friction and low energy electrical discharge and it should be emphasised that wetting of the explosive does not appreciably reduce its sensitivity to shock and friction and in fact may increase the sensitiveness due to the formation of large crystals. As a result, precautions required to overcome dangers from electrostatic charges during the drying, sieving, weighing and pressing of the material are stringent and care must be taken to ensure that all apparatus is at earth electrical potential and that operatives do not build up an electrostatic charge whilst working with the material.

10.4.5.1 General manufacture of lead azide

The chemistry involved in the preparation of lead azide is relatively straightforward, however control of the reaction is critical as secondary growth of the lead azide crystals can occur and dangerous products can be formed. Lead azide is a white crystalline substance that is almost insoluble in water and can be prepared by mixing two solutions of a soluble and a relatively inert salt, lead acetate and sodium azide as shown below.

Sodium azide solution + lead acetate solution $\longrightarrow$ lead azide + sodium acetate

The insoluble lead azide is precipitated out and washed with distilled water to remove the excess ingredients and the other water soluble product, sodium acetate. If this mixing is done incorrectly or in a haphazard manner, the correct α-form of crystal will not always be obtained and one of the other crystal forms (β or γ) may result. This could cause the material to spontaneously detonate even though the material is suspended in a large volume of water. In order that the correct α-form

crystals are produced, the lead azide crystals are grown on a seed of lead carbonate crystal that has been formed by the addition of lead acetate and sodium carbonate to the distilled water in the precipitating pan.

10.4.5.2 Service lead azide (SLA)

The essential feature of British military detonator design was established in the early 1930s by the decision to use pure lead azide of a high output with its advantage of output/volume ratio compared with mercury fulminate. This decision led to the development of the Service lead azide process in which compact free flowing crystals were built up on nuclei of basic lead carbonate.

Service lead azide (SLA) is prepared by initially reacting an aqueous solution of lead acetate and an aqueous solution of lead carbonate. Small crystal of lead carbonate are formed which seed the lead azide as it is formed and ensure the preferred crystal type (α-form) is produced. Aqueous solutions of sodium azide and lead acetate are added at a controlled rate to the lead acetate/lead carbonate solution, maintained at a suitable temperature and rate of stirring. The lead azide is precipitated in the form of fine white crystals. A small amount of acetic acid is added to destroy any excess carbonate. The product, Figure 10-39[15], consists of free flowing white, short, thick rhombic crystals of high bulk density. The size of individual crystals is approximately 0.10 mm × 0.03 mm.



Figure 10-39 Service lead azide (×50 magnification)

10.4.5.3 Pure lead azide, RD1339

RD1339 is prepared[22] by reacting an aqueous solution of sodium azide containing a non-ionic surfactant with aqueous solutions of lead acetate and sodium azide at a suitable temperature and rate of stirring. The product, Figure 10-40[15], consists of a

free flowing powder consisting of aggregates of small, white crystals approximately 0.03 mm^2.

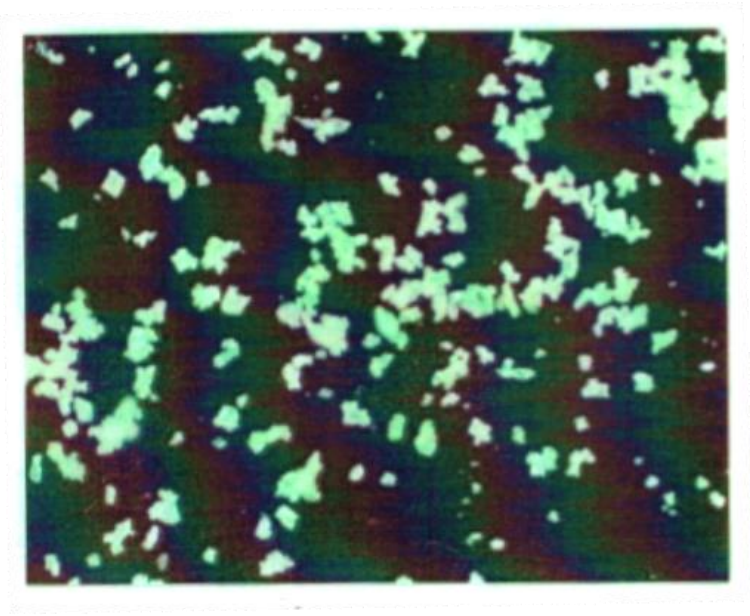


Figure 10-40 Pure lead azide, RD1339 (×100 magnification)

10.4.5.4 Colloidal co-precipitated lead azide, RD1343

RD1343 is prepared[23] by reacting an aqueous solution of sodium carboxymethyl-cellulose containing a non-ionic surfactant with an aqueous solution of lead acetate and a mixed aqueous solution of sodium azide and sodium hydroxide at a suitable temperature and rate of stirring. The product, Figure 10-41[15], consists of free flowing white irregular granules with no aggregation of individual granules. The size of the granules is approximately 0.15 mm × 0.08 mm.

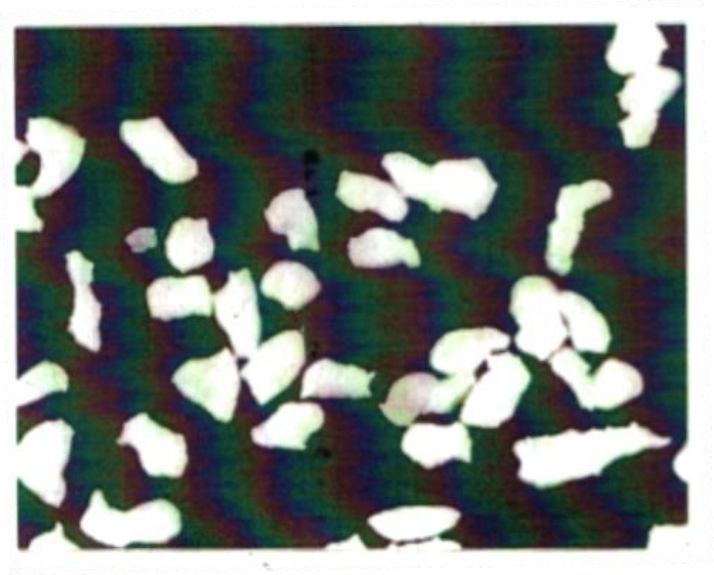


Figure 10-41 Colloidal co-precipitated lead azide, RD1343 (×100 magnification)

10.4.5.5 Dextrinated lead azide, RD1352

RD1352 is prepared[24] by reacting an aqueous solution of a non-ionic surfactant and an aqueous solution of dextrin with a mixed aqueous solution containing sodium azide, sodium hydroxide and Rochelle salt (potassium sodium tartrate) and aqueous solutions of sodium acetate and lead nitrate at a suitable temperature and rate of stirring. The product (lead azide coated and interspersed with dextrin granules), Figure 10-42[15], consists of free flowing white rounded granules which are less irregular than those of RD1333 giving a composition of increased bulk density. Some ‘dumb-bell’ formation is evident. The approximate size of individual crystals is 0.09 mm × 0.07 mm.

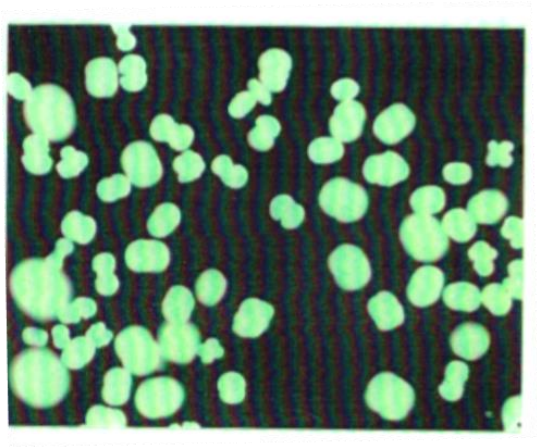


Figure 10-42 Dextrinated lead azide, RD1352 (×100 magnification)

10.4.5.6 Lead azide GAM

Gelatin, azide, molybdenum disulphide (GAM) form of lead azide was developed and introduced during 1967. It is manufactured by the precipitation of lead azide from a solution containing gelatin and a suspension of molybdenum disulphide which is incorporated in the crystal agglomerate to obtain the desired combination of cohesion and electrical properties. The electrical properties of the modified product are excellent, however, in comparison to dextrinated lead azide (bulk density 2.2 g cm^{-3} the bulk density of GAM (1.3 - 1.5 g cm^{-3}) is lower. The power of lead azide GAM is also lower than that of dextrinated lead azide. The product, Figure 10-43[15], consists of a free flowing powder consisting of grey/black rounded granules forming aggregates of approximately 0.08 mm^2.

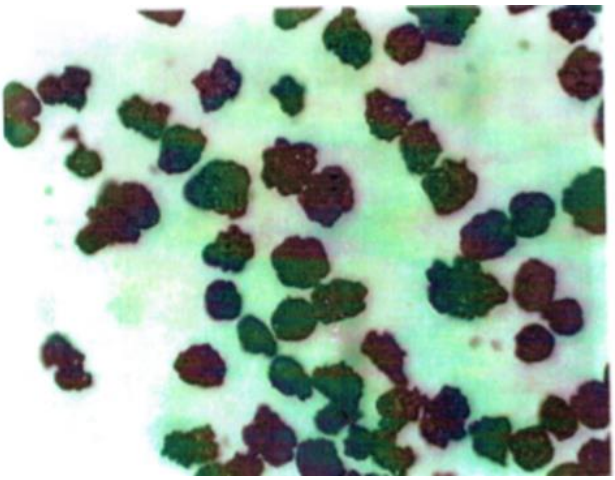


Figure 10-43 Lead azide, GAM (×100 magnification)

10.4.5.7 Basic Lead Azide

Basic lead azide is prepared by reacting aqueous solution of lead acetate containing Cepol DV and glycerine with a mixed aqueous solution of sodium

hydroxide and sodium azide containing trinitrophloroglucinol (TNPG) at a suitable temperature and rate of stirring. The process for the preparation of basic lead azide has been reported in the literature[25] and has been successfully established on a pilot plant scale (2.5 kg/batch). Basic lead azide is a crystalline, free flowing, non-hygroscopic material. It has a bulk density of 2.0 ± 0.2 g cm^{-3} and detonates high explosives efficiently. It also has a better thermal and hydrolytic stability and its compatibility with copper is better than Service lead azide (SLA)

10.4.6 Silver Azide

10.4.6.1 General manufacture of silver azide

The chemistry involved in the preparation of silver azide is relatively straightforward and it can be prepared by the mixing two solutions of a soluble and a relatively inert salt, silver nitrate and sodium azide as shown below.

Sodium azide solution + silver nitrate solution $\longrightarrow$ silver azide + sodium nitrate

The insoluble silver azide is precipitated out and washed with distilled water to remove excess ingredients and the other product, sodium nitrate. There are two manufactured forms of silver azide RD1336 and a modified form of this salt, designated RD1374.

10.4.6.2 RD1336

RD1336 is prepared[26] by reacting ammonium hydroxide solution with aqueous solutions of sodium azide, silver nitrate and nitric acid at a suitable temperature and rate of stirring. The product, Figure 10-44[15], consists of a free flowing powder comprising ~~of~~ irregular aggregates of small white crystals with the crystals having a uniform aggregate size of approximately 0.05 mm^2. The difficulties in applying this material to automated detonator filling, “fortress filling” resulted in the development of a modified silver azide, designated RD1374.

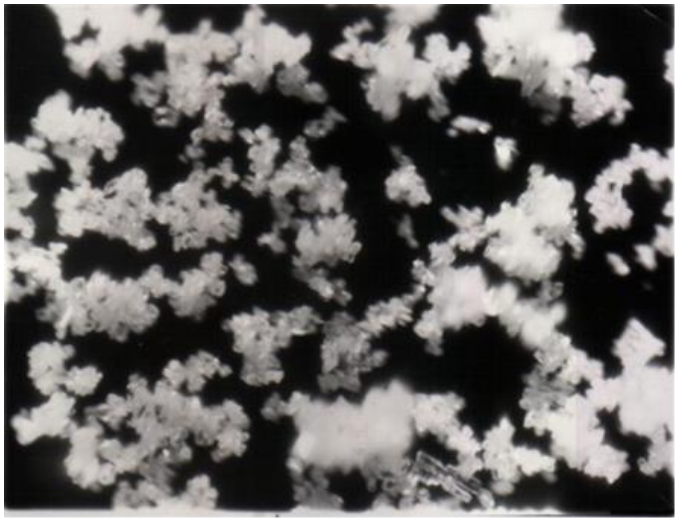


Figure 10-44 Silver azide, RD1336 (×100 magnification)

10.4.6.3 RD1374

RD1374 is prepared[27] by reacting aqueous solutions of sodium azide, potassium bromide, ammonia and silver nitrate at a suitable temperature and rate of stirring. The product, Figure 10-45[15], consists of a free flowing powder which unlike RD1336 consists of small single crystals approximately 0.20 mm × 0.15 mm in size.

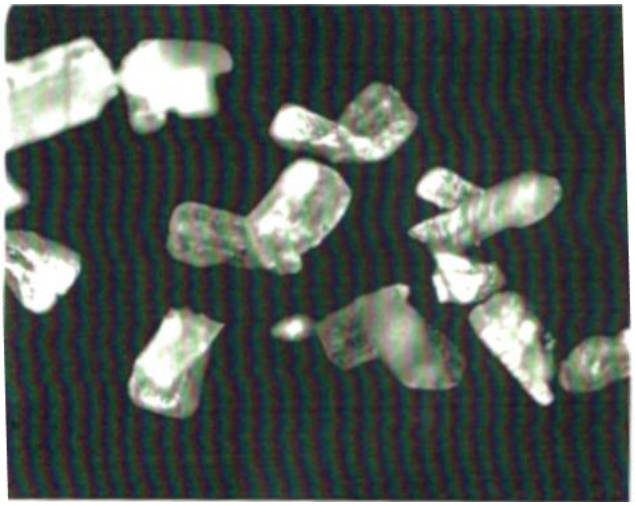


Figure 10-45 Silver azide, RD1374 (×100 magnification)

10.4.7 Tetrazene, RD1357A

RD1357A[28] is manufactured by the action of sodium nitrite on a heated solution of aminoguanidine sulphate in dilute ethanoic (acetic) acid. The reaction involves the formation of two diazonium links, one to form a ring structure, the other to increase the molecular mass. The basic process is carried out in a similar manner to the manufacture of lead azide and lead styphnate, i.e. small scale. The product, Figure 10-46[15], consists of a fine crystalline powder of rosette like aggregates with an approximate size of 0.07 mm^2, which when dried are free from agglomerates and are free flowing.

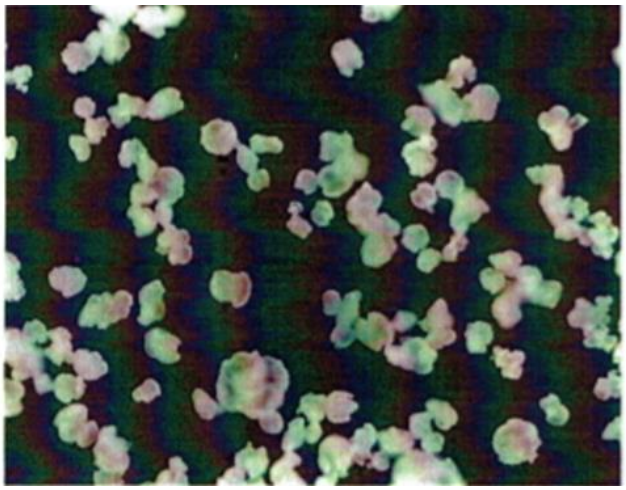


Figure 10-46 Tetrazene, RD1357A (×100 magnification)

10.4.8 Lead Free Primary Explosives

In recent years there has been a move to reduce the toxicity of primary explosives as mostly they contain lead. The term 'green explosives' is now often used to describe this development[29].

10.4.8.1 2-diazo-4,6-dinitrophenol (DDNP)

2-diazo-4,6-dinitrophenol (DDNP) was first prepared in the early 1800s by reaction of nitric oxide with 2-amino-4,6-dinitrophenol (picramic acid). More recent methods involve diazotisation of 2-amino-4,6-dinitrophenol or its sodium salt with sodium nitrite/hydrochloric acid. Depending on reaction conditions and the addition of crystal modifying substances, a free flowing form of DDNP can be obtained.

10.4.8.2 Potassium 4,6-dinitrobenzofuroxan (KDNBF), RD1372

The manufacture of KDNBF firstly involves the preparation of the precursor starting material 4,6-dinitrobenzofuroxan (DNBF). The method used involves the oxidation of ortho-nitroaniline in alkaline solution to benzofuroxan. The benzofuroxan is isolated and nitrated in a mixture of nitric acid and sulphuric acid to give 4,6-dinitrobenzofuroxan (DNBF), which is then recrystallised from nitric acid to give the compound in a pure form.

The KDNBF is prepared[30] by conversion of the DNBF to the soluble sodium salt by the addition of sodium bicarbonate to an aqueous suspension of DNBF at 70-75 °C and then slowly adding a solution of potassium nitrate. The formation of the KDNBF is carried out in the presence of a flocculant, which acts as a crystal habit modifier. Slow cooling of the solution results in the precipitation of the KDNBF. The product, Figure 10-47[15], consists of a free flowing powder consisting of rounded orange/red granules with an approximate size of 0.10 mm^2 with some aggregation of granules.

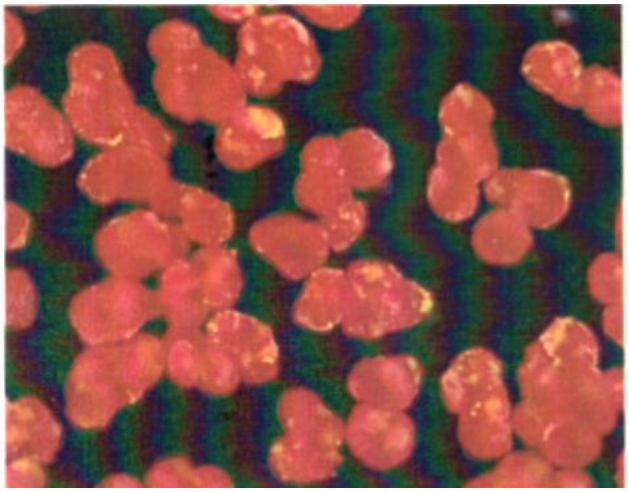


Figure 10-47 KDNBF, RD 1372 (×100 magnification)

10.4.8.3 Copper (I) salt of 5-nitrotetrazole, DBX-1

The traditional synthetic procedure for making DBX-1 is exposure of 5-aminotetrazole to a modified Sandmeyer reaction resulting in the formation of a copper acid salt, which is converted to the sodium salt of 5-nitrotetrazole (NaNT) upon exposure to sodium hydroxide (NaOH). Subsequently, copper (II) chloride ($CuCl_2$) is treated with sodium ascorbate ($C_6H_7NaO_6$) to generate the copper (I) species in situ, which reacts with NaNT to yield DBX-1. However, it should be noted that there were several safety issues associated with this procedure which were a major drawback and limited practical application for the material. However, there have been a number of modifications made to the procedure to increase process safety and interest in DBX-1 continues[31].

10.4.8.4 Potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (KDNP)

The potassium salt of 7-hydroxy-4, 6-dinitrobenzofuroxan (KDNP) was originally produced from the nitration and rearrangement of commercially available 5-chlorobenzofuroxan, however this process produced a very friction sensitive material due to occluded water from the recrystallisation process. Although other solvents could be used, this process was deemed unsuitable for larger scale production. An alternative 2 step process starting from commercially available 3-bromo-anisole has been reported[32]. Nitration, azidation and ring closure gave a crude product which could be crystallised to give control of particle size and tailoring for specific use (e.g. bridgewire vs primer). The main advantage of this process is that 3-bromo-2,4,6-trinitroanisole is an intermediate in the synthesis of dipicramide (DIPAM), a well-known insensitive high explosive. Dipicramide was produced on a large scale in the 1960s and therefore the nitration chemistry is well understood. The KDNP produced by this route is in the anhydrous form unlike the monohydrate produced by the original method.

Performance studies[33,34] carried out on a range of applications demonstrated the advantages of this material and it was qualified by US Naval Sea Systems Command as a primary explosive in accordance with the requirements of US NAVSEAINST 8020.5C and identified it as safe and suitable for service use for weapons development.

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CHAPTER 11
HIGH EXPLOSIVES

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11 HIGH EXPLOSIVES

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11.1 AWARENESS SUMMARY

11.1.1 Application of High Explosives

High explosives are those, which detonate in their designed use and find defence application in warheads and demolition charges. In the commercial sector high explosives are employed in building demolition, quarrying and mining.

A detonating explosive has two outputs that can be used to create damage, the detonation shock pressure of the detonation shockwave as it passes through the explosive charge and the expanding hot gas products from the detonation. These outputs can be manipulated mainly though the choice of explosive formulation, that is, which explosive molecular type or types are present together with other reactive ingredients such as metal powders and binders.

Where metal driving applications are required as for fragmentation, shaped charge and explosively formed projectile (EFP) warheads the significant output is the detonation shock pressure. For warheads that have their effectiveness through airblast, underwater bubble pulse or cratering ability the significant output is the gas expansion or power effectiveness. Examples are given in Table 11-1. An artillery shell is effective mainly though fragment lethality with blast a useful secondary effect. Shaped charge and EFPs require optimum metal driving through a very high shock pressure and the gas expansion from these warheads is of little consequence. Both the air dropped 1000 lb bomb and the torpedo warhead require maximum gas expansion effects to create airblast/cratering and underwater bubble pulse respectively.

Table 11-1 Energy Optimisation for Some Warhead Types

Warhead	Shock pressure	Power
Artillery shell	High	High
Shaped charge/EFP	Very high	High
1000 lb bomb	High	Very high
Spearfish blast warhead	High	Very high

Commercial explosives normally will be breaking concrete or rock and as such do not need the performance of military explosives that fragment or drive metal. In general their shock pressure is very modest although gas expansion effects are quite reasonable as lift and heave are often the main requirement.

11.1.2 Choice of Explosive Type

There are a number of different explosives available to produce high explosive formulations as shown in Table 11-2. The choice for a particular application, however, may not be as simple as its detonation pressure or power values.

Table 11-2 Performance of Some Established Explosives

Explosive	TMD* ρ (g cm^{-3})	m.p (°C)	Ignition temp (°C)	Detonation Pressure (GPa) at ρ	Power (TNT equiv.)	Rotter test (F of I)
NG	1.60	13	188	24 (1.60)	1.52	30
PETN	1.76	141	205	26.9 (1.56)	1.50	50
TNT	1.64	80	240	17 (1.57)	1.00	150
RDX	1.81	204	213	35 (1.81)	1.52	80
HMX	1.91	278	300	39.2 (1.89)	1.50	60
TATB	1.94	340	359	28.3 (1.88)	0.90	>200
HNS	1.74	318	325	20.8 (1.70)	0.98	>150

* Theoretical Maximum Density

Nitroglycerine (NG) would not be suitable for a military high explosive on several counts even though it is a very powerful explosive although with modest detonation shock pressure. Above 13 °C it is a liquid, it has a very low ignition temperature and has very high impact sensitiveness (see 20.2.1). PETN is little better from a safety perspective and is not employed in main high explosive charges. However, due to its ability to detonate in very small diameter charges it is used in detonating cord and the base charge of detonators.

To provide explosive charges with good detonation shock pressure RDX and HMX are good candidates and as such either one or the other will be found in most warhead formulations. The impact sensitiveness for both is not ideal and so they are desensitised by mixing with either TNT or an inert binder. TNT was a main filling of choice between the 1st and 2nd World Wars before RDX and HMX became available as it can be readily melt cast having a melting point well below its ignition temperature. This makes it suitable to desensitise RDX and HMX as it allows them to be slurried in crystalline form in molten TNT well below their ignition temperatures and melt cast in to warheads.

11.1.3 Formulation Requirements

Modern high explosive formulations are chosen to be suitable for the following performance requirements:

1. Metal driving/shattering for fragmentation warheads and demolitions
2. Metal driving for Shaped Charge and Explosively Formed Projectile warheads
3. Gas expansion effects for airblast and underwater weapons

Other factors also are important:

1. Acceptable levels of safety
2. Acceptable service life
3. Suitable for filling methods
4. Cost effective

With the exception of TNT, most high performance explosives have high melting points which are too close to their ignition temperatures to allow warhead filling by melt-cast techniques. Other solid additives may be required by the formulation, such as ammonium perchlorate or aluminium. A binder is therefore required to enable solid charges with favourable mechanical and safety properties to be made and be suitable for a filling process.

Initially, the binder that allowed explosive formulations to be manufactured with RDX and HMX during and following the 2nd World War was TNT. It provided safe explosives and a ready melt-cast filling method. Inert binders such as waxes followed and then in the 1960s the use of polymers. All of these are still to be found in UK defence explosives. Across all natures of ammunition containing high explosives in UK service around 40 % w/w contain TNT.

11.1.4 TNT Formulations – General Aspects

TNT has a melting point when pure of 80.65 °C. For UK military use, a melting point of at least 80.2 °C is required to ensure a sufficiently low contamination with its isomers and dinitrotoluenes to prevent exudation which, apart from constituting a fire-risk and explosion hazard, might penetrate into exploder systems and safety and arming units, thus preventing their proper functioning. An example of exudation is shown in Figure 11-1 where the TNT filling has exuded in to the threading of the fuze pocket. With a tetryl exploder, which may still be found in obsolete ammunition, a liquid eutectic of very high sensitiveness is formed with the exudate.

There are additional safety hazards associated with TNT filled munitions particularly for those that will experience high g-force accelerations such as artillery shells. The melt-cast filling process is complicated by the shrinkage by about 10 % as the liquid TNT sets and becomes solid. Steps must be taken to control the cooling to avoid the development of cavities or low density areas and cracks in the solid charge. If cracks or cavities are present they can collapse

under the extreme g-forces on launch causing adiabatic compression of the air leading to ignition of the explosive and subsequent run to detonation within the shell. This can occur within the gun barrel. To avoid this the molten TNT is filled in to a pre-heated shell body with controlled cooling and a liquid TNT header maintained above the setting filling to fill any cracks or voids, a method known as the Meissner process.

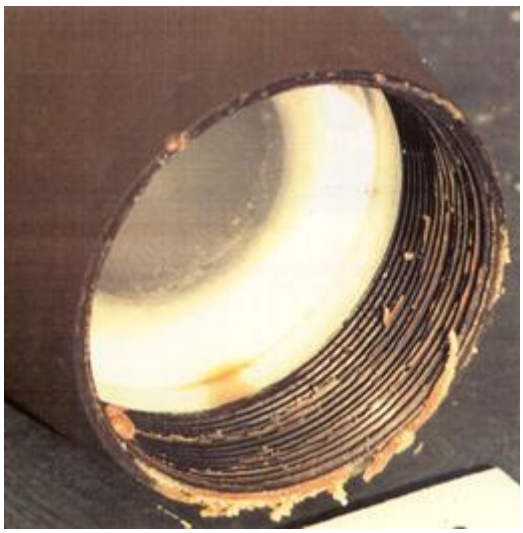
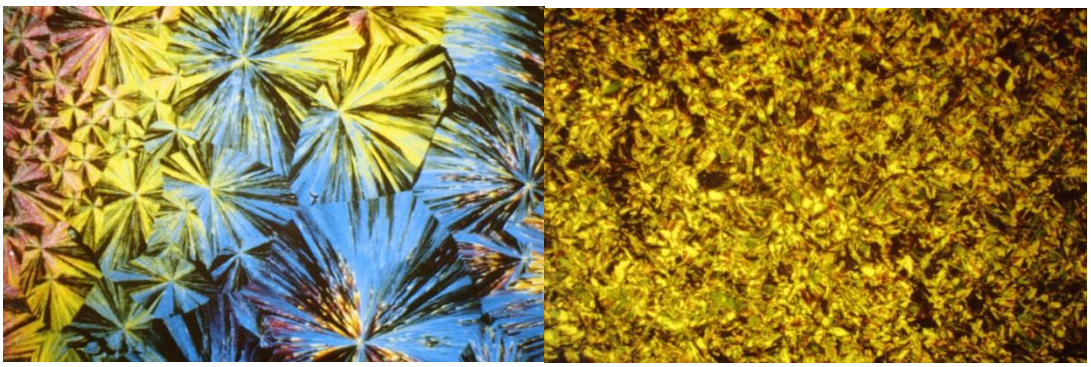


Figure 11-1 TNT exudation in a fuze pocket thread

The potential for cracks or voids to form is exacerbated by the propensity for TNT to crystallise in large crystals (Figure 11-2(a)) orientated in the direction of heat flow which forms planes of weakness in the explosive. To minimise this problem the crystal habit may be modified by adding a small quantity of hexanitrostilbene (HNS) to the melt giving smaller grains as can be seen in Figure 11-2(b). When added to compositions at the 0.3-0.5 % w/w it ensures that the TNT crystallises out as very small randomly orientated interlocking crystals. The strength of the cast charge may be increased as much as fivefold and its cracking resistance considerably enhanced.



(a) **(b)**

Figure 11-2 (a) Unmodified TNT, (b) TNT with 0.2 % w/w HNS

A similar effect can be obtained using ‘creamed’ TNT. Here the material is allowed to cool to its setting temperature with continuous agitation. When a slurry has formed, about 10 % w/w of finely powdered TNT is added to the slurry and the mix poured for immediate casting. These fine crystalline forms of TNT are more sensitive to detonation shock initiation than the coarser material although they are not unduly sensitive.

Another disadvantage in the use of TNT in warheads is the tendency for TNT formulations to have high explosiveness (see 20.2.1) making them unsuitable for Insensitive Munition (see 2.12) fills. This has been the main driving force for a move to polymer desensitised explosives. Formulations that use wax as a desensitiser in general also exhibit high explosiveness.

11.1.5 TNT Explosives in Service Use

TNT is of modest performance as a military high explosive as so is mixed with nitramines such as RDX and HMX to provide improved performance munition fillings. A common composition is RDX/TNT (60/40 % w/w) with a detonation pressure of around 25 GPa and an F of I of 120 (see 20.10.2.1). If greater detonation pressure is required then HMX is included in place of RDX with high solids content such as HMX/TNT (75/25 % w/w). If greater power is required then aluminium powder is added as in the Torpex type explosive such as RDX/TNT/Al (40/40/20 % w/w).

11.1.6 Other RDX and HMX Explosives in Service Use

Desensitisers other than TNT are used to produce formulations of suitable performance and safety. These include waxes and polymers where the non-explosive component is usually between 5 and 12 % w/w of the composition. Again, if high detonation pressure is required the explosive used will be HMX together with small amounts of the inert component such as HMX/polymer (95/5 % w/w).

A standard formulation with RDX would be RDX/binder (88/12 % w/w). Again, as for the TNT compositions, if high power is required then aluminium powder is added to produce the RDX/Wax/Aluminium (RWA) series of explosives.

11.1.7 Next Generation Explosives

New explosive molecules are now being considered as replacements of RDX and HMX to either improve performance or safety. A US explosive, CL-20 has greater detonation shock pressure than HMX, the previous best performer in this regard. NTO is considered a safer explosive component than RDX, which has very similar performance.

As replacement for TNT the explosive DNAN is now being considered as it can also be melt-cast for filling and provides compositions that have improved safety.

11.2 HIGH EXPLOSIVE FORMULATIONS FOR SHOCK PRESSURE

As noted earlier high explosives are chosen to be effective through either:

1. The shock pressure output that is used to create fragmentation, accelerate metal in shaped charges or EFPs or shatter structural materials in demolitions,
2. Gas expansion to produce airblast or underwater bubble pulse.

The pressure of the shockwave in a detonating explosive (p) depends on two variables, Velocity of Detonation (D) and density (ρ) of the explosive in a relationship shown in Equation (11-1).

$$\text{Detonation pressure } (p) \alpha \rho \times D^2 \qquad \textbf{(11-1)}$$

To formulate explosive charges with high detonation shock pressure explosive types are chosen that will maximise these characteristics. RDX ($D = 8750$ m s^{-1}, $\rho = 1800$ kg m^{-3}) and in particular HMX ($D = 9110$ m s^{-1}, $\rho = 1890$ kg m^{-3}) are ideally suited compared to TNT ($D = 6950$ m s^{-1}, $\rho = 1640$ kg m^{-3})[(1)]. Table 11-3 shows how this markedly affects the shock pressure.

11.2.1 RDX/TNT and HMX/TNT Formulations

The use of TNT as an energetic binder and desensitiser with the nitramines RDX and HMX produces formulations that have improved safety compared to the pure nitramines by reducing sensitiveness (see 20.2.1) values but still maintaining useful performance as shown in Table 11-3.

Table 11-3 Sensitiveness and Performance Data for RDX/HMX/TNT Explosives

Explosive	F of I	Mallet Friction Test	Shock pressure (GPa)
RDX	80	100/50/50	35 (1.80 g cm^{-3})
HMX	60	100/100/100	39.2 (1.89 g cm^{-3})
TNT	150	0/0/0	17 (1.57 g cm^{-3})
Composition B RDX/TNT (60/40 % w/w)	120	0/0/0	29.2 (1.71 g cm^{-3})
Octol HMX/TNT (75/25 % w/w)	90	0/0/0	32.5 (1.81 g cm^{-3})

In manufacture the nitramines as powdered solids are held in a liquid slurry in the molten TNT prior to casting. The UK uses air castable RDX/TNT Type A as a standard filling in artillery shell, large scale demolition charges and cratering munitions. A Type G variant is used in artillery shell and these compositions are shown in Table 11-4. UK service TNT compositions contain beeswax as an

extra desensitiser for the nitramines to that conferred by the TNT alone. The US equivalent to RDX /TNT Type A is Composition B which incorporates RDX manufactured by the Bachmann rather than the Woolwich process (see 10.3.3.1) and contains up to 10 % w/w HMX. The filling for Shell 155mm HE L15 is a modified RDX/TNT Type G with X28M plasticiser added comprising polyvinyl nitrate/mononitrotoluene (22/78 % w/w).

To increase the performance of TNT melt cast explosives, the solids loading can be increase or HMX substituted for RDX as shown in Table 11-5. This development has been seen with:

1. RDX/TNT compositions with higher RDX content e.g. RDX/TNT 75/25 % w/w developed in Germany
2. The development in the UK of EDC1 series of compositions, in which HMX replaces all but 4 % w/w of the RDX.
3. The development of HMX/TNT (Octol) compositions with high loadings of up to 85 % w/w HMX.

The viscosity of these compositions necessitates the use of vacuum casting, and in addition, for the highly loaded RDX and HMX compositions, pressure sedimentation as well.

Table 11-4 RDX/TNT Formulations

Formulation	TNT (% w/w)	RDX (% w/w)	HMX (% w/w)	HNS (% w/w)	Beeswax (% w/w)
RDX/TNT Type A	39.5	59.5	-	-	1
RDX/TNT Type G	39.3	55.5	4	0.2	1
CW 3	RDX/TNT Type G	99.7	-	X28M plasticiser	0.3

Table 11-5 EDC Formulations

Formulation	Composition
EDC1	TNT/RDX/HMX (25/4/70 % w/w)
EDC1A	EDC1/TNT (95/5 % w/w)
EDC1G	EDC1/HNS (99.8/0.2 % w/w)
EDC1S	EDC1G/X28M plasticiser (99.7/0.3 % w/w)

11.2.2 RDX and HMX Formulations with Inert Desensitisers

Another route to the production of formulations containing RDX and HMX that have acceptable sensitiveness (see 20.2.1) values and still maintain the required performance is to include waxes, greases or polymers in the formulation. Although these are non-explosive components the performance is not unduly lessened as a much smaller amount is required than the large percentages used for TNT desensitisation. These materials are often called phlegmatisers as a phlegmatic person is not easily excited, a good analogy to reduced sensitiveness.

11.2.2.1 Wax desensitised

The only formulation designed as a main charge utilising shock output that is wax desensitised in the filling of the High Explosive Squash Head (HESH) round (see 7.3.2.3). The filling is a mixture of RDX and Wax Special No. 8 88/12 (% w/w).

Formulations with significantly less desensitiser are employed as booster charges. RDX and Wax Special No. 8 are mixed in a 93/7 ratio. Other formulations including US compositions A3, A5 and CH6 are employed in UK munitions with details given in Table 11-6. The Debrix compositions are manufactured using a special process that gives a thin coating of Wax No.10 such that they have acceptable sensitiveness values for boosters but maximise the shock output to initiate a main charge.

Table 11-6 RDX/Wax Booster Compositions

Composition	RDX (% w/w)	Wax (% w/w)	Other (% w/w)	F of I(1)
RDX/Wax	93	7		
Composition A3	91	9		140
Composition A5	98.75 – 99.0	0	Stearic acid 1.25 – 1.0	110
CH6	97.5		Calcium stearate 1.5 Graphite 0.5 Polyisobutylene 0.5	100
Debrix 11	99	1		110
Debrix 12	95.8	4.2		120
Debrix 18 AS	95.3	2.7	Zinc stearate 1.5 Aerosil 0.5	120

11.2.2.2 Polymer desensitised

The title ‘Polymer Bonded Explosive’ (PBX) is applied to a variety of explosive mixtures which contain a large percentage of explosive powder in an intimate mixture with a polymeric binder. In some instances, a plasticiser is included in the composition to further modify the physical properties of the explosive charge. The polymer forms a matrix in which the solid components of the formulation are embedded.

Choice of polymer and plasticiser provides the possibility of achieving explosive charges with much higher melting temperatures than those employing TNT or wax as desensitiser. Their physical properties can be controlled, such as reduced brittleness, which reduces explosiveness (see 20.2.1). Good chemical stability, required explosive output and insensitiveness to handling, shock and thermal input, are all achievable with PBXs.

11.2.2.2.1 Polymeric binders

Properties required for a polymeric binder are:

1. Elasticity with a low modulus
2. Strain-rate and temperature insensitive
3. Low glass transition temperature
4. Good heat-sink
5. Good adhesion to particulate system
6. Easy to process

There is a wide range of commercially available polymers and they can be divided into three groups:

1. Thermoplastics
2. Thermosetting materials
3. Elastomers

Thermoplastics are stable polymers which soften and melt on heating, and can be moulded in the plastic state to yield products of varying degrees of hardness and toughness. Examples of thermoplastics are listed in

Table 11-7. All materials have reasonable mechanical strength at ordinary temperatures, but only Nylon, Terylene and PTFE remain hard and strong above 150 °C.

Table 11-7 Examples of Thermoplastic Polymers

Material	Softening point (°C)
Polyvinyl chloride (PVC)	82
Polyethylene (low density) (LDPE)	82 - 87
Polystyrene (PS)	82 - 103
Polymethyl methacrylate (PMMA)	85 - 115
Nylon (type 6)	220 (m.pt.)
Terylene	230
Polytetrofluoroethylene (PTFE)	above 250

Thermosetting plastics are processed from monomers or partial polymers, in the form of liquid resins or moulding powders. These are polymerised by heat, pressure and catalysts to yield hard plastic materials which cannot be melted or softened by heat. Examples of the thermoset materials are phenolics, polyesters, epoxy resins and polyurethanes. These materials provide varying degrees of hardness and toughness over a wide range of temperatures. They are stable at 200 °C. PBX compositions are conveniently prepared from thermosetting resins or moulding powders, by intimate mixing of the ingredients followed by polymerization under the influence of gentle heat, pressure and catalysts. Such preparations may be filled and polymerised directly in a weapon case. Alternatively, a charge may be machined from the plastic bonded product. The requirements of such castable binders are:

1. Compatibility with high explosives
2. Thermal stability
3. Low toxicity (isocyanates are therefore a problem)
4. Ready availability
5. Good processability (e.g. a low number of reagents)
6. Low viscosity - for room temperature and easy casting
7. Long pot life
8. Good curing at low (<60 °C) temperatures, no exothermic reactions, short cure period, low glassy temperature.
9. Predictable and controllable polymerisation

Elastomers are polymers containing crosslinks and undergo elastic deformation. The degree of hardness of an elastomer depends upon the number of cross links present. Elastomers include polyurethanes, polybutadienes, natural and synthetic rubbers. PBX compositions are prepared from elastomers by mixing the elastomeric resins with the particulate system. Crosslinking of the elastomer during curing will impart rigidity to the PBX.

Some polymer binders used in UK service explosives are given in

Table 11-8.

There is interest in using polymers that incorporate explosophores such as nitro groups in their structure. Such polymers can contribute to the explosive performance of a PBX formulation in their own right and are called ‘energetic binders’. These materials are presently the subject of research a promising material being poly-NMMO (poly 3-nitratomethyl-3-methyloxetane).

Table 11-8 Some Polymer Binders in UK Munition Formulations

Binder	Type
Viton	Fluoroelastomer
HyTemp	Polyacrylate
Polyisobutylene	Elastomer
HTPB-IPDI *	Polyurethane
Estane	Polyurethane
Poly(dimethylsiloxane)	Silicone

*Hydroxyl-terminated polybutadiene/Isophorone Di-isocyanate cross linking agent

11.2.2.2.2 Plasticisers

The mechanical properties of a PBX e.g. glass temperature, hardness, may be modified by incorporating a liquid plasticiser into the polymer. Typical plasticisers are dioctyladipate (DOA), dioctylsebacate and di-2-ethylhexylsebacate with DOA being the most common.

11.2.2.2.3 PBXs in UK munitions

Table 11-9 gives examples of PBX explosives in UK service use. The US composition PBXN-5 is used in a number of munitions as a booster pellet. With a high percentage of HMX it will be sensitive to pick up from a detonator and have a high shock output to detonate the main charge. A similar composition PBXW-11 also is used as a booster charge.

Polymer binders have allowed a number of explosives with very high detonation shock pressure, through having HMX content of over 90 % w/w, to be accepted in to service. As shown in

Table 11-9 they find use in either shaped charge or high performance fragmentation warheads. Currently, PBX explosives are found only in warheads that do not experience high g-force loading.

Table 11-9 PBX Formulations in UK Munitions

Name	Composition (w/w)	Use
PBXN-3	HMX/Nylon (86/14 %)	Missile fragmentation warhead
PBXN-5	HMX/Viton (95/5 %)	Booster pellets and small shaped charges
PBXN-9	HMX/HyTemp/DOA (92/2/6 %)	Anti-armour shaped charge warhead
PBXW-11	HMX/HyTemp/DOA (96/1/3 %)	Booster pellets and anti-armour shaped charge warhead
PBXN-107	RDX/Polyacrylate (86/14 %)	Large unitary land attack warhead
LX-14	HMX/Estane (95.5/4.5 %)	Anti-armour shaped charge warhead
KS32	HMX/HTPB Polyurethane/DOA (85/14/1 %)	Missile fragmentation warhead

11.2.2.3 Mouldable and flexible formulations

Demolition and bomb disposal activities rely on the availability of hand mouldable and flexible sheet explosives known universally as plastic explosive. For a considerable time the cartridged and bulk PE4 and sheet SX2 have been the inventory explosives for these purposes. PE4 consists of 88.0 % w/w RDX, 1.0 % w/w pentaerythrite dioleate and 11.0 % w/w DG-29 lithium grease (2.2 % w/w lithium stearate and 8.8 % w/w paraffin oil BP). There is a legal requirement to add a chemical detectable by vapour detector to all plastic explosives. The taggant added is (2,3-dinitro-2,3-dimethylbutane, DMNB) at 1.0 % w/w. On very long term storage in paper wrapped cartridge form there is a tendency for the mineral oil to evaporate and the formulation becomes slightly crumbly. Sheet explosive SX2 is a mixture of 88.2 % w/w RDX, 8.2 % w/w polyisobutene, 2.2 % w/w di(2-ethylhexyl)sebacate and 1.4 % w/w PTFE hot rolled to a thickness of 3 mm.

Both PE4 and SX2 have been replaced with the explosives PE8 and SX4 both using the formulations containing nominally 87 % w/w RDX, which is desensitised using polyisobutenes with dioctylsebacate plasticiser.

11.3 HIGH EXPLOSIVE FORMULATIONS FOR GAS EXPANSION

Since the 1st World War aluminium powder has been employed in explosive mixtures to provide heat for gas expansion as the combustion of aluminium is highly exothermic. Initially the compositions used an oxidiser such as ammonium nitrate to provide the oxygen such as in ammonal, which also included small quantities of TNT as the war progressed. The explosive was a powder and not suitable for munition fillings but perfectly suited to the large

mines placed in tunnels under enemy lines. During the 2nd World War this type of composition was used mainly to supplement the meagre stocks of TNT although its main use was in sea mines and had very good underwater explosion effects. Developments to specifically increase the gas expansion effects of high explosives began in this period and have relied on RDX as a major component of these formulations desensitised either with TNT or using PBX technology.

In modern formulations the aluminium does not need a specific oxidant such as ammonium nitrate to be added as it is capable of reacting with the initial products of explosion formed from the carbon, hydrogen and nitro groups. As the explosive molecules react they form carbon dioxide, carbon monoxide and water. The following reactions of these gases with aluminium can then occur:

$$3H_2O + 2Al = Al_2O_3 + 3H_2 \quad \Delta H_r = -844 \text{ kJ} \qquad \textbf{(11-2)}$$

$$3CO_2 + 2Al = Al_2O_3 + 3CO \quad \Delta H_r = -820 \text{ kJ} \qquad \textbf{(11-3)}$$

$$3CO + 2Al = Al_2O_3 + 3C \quad \Delta H_r = -1340 \text{ kJ} \qquad \textbf{(11-4)}$$

As explosive power is proportional to Heat of Explosion × Gas Volume Equations (11-2) and (11-3) will increase the amount of heat produced but maintain the gas volume as one mole of any gas occupies the same volume (22.4 litres $mole^{-1}$). However, if reaction shown in Equation (11-4) occurs then heat energy is produced but as the product carbon is a solid the gas volume will decrease. This limits the amount of aluminium that can be added to a formulation if no other source of oxygen is present to between 18 % and 25 % by weight.

Other developments turned to the addition of large amounts of oxidants such as ammonium perchlorate with either TNT as binder, or an energetic binder such as PBX mixed with energetic plasticiser or wax and energetic binder/plasticiser. Although these have excellent gas expansion performance their sensitiveness (see 20.2.1) and explosiveness (see 20.2.1) preclude them from modern formulation requirements.

Table 11-10 Enhanced Performance Formulations Containing Large Oxidant Percentages with Aluminium

Formulation	Ingredients w/w				
	TNT %	Binder/plasticiser	RDX %	Al %	Oxidant %
Minol-2	40	-	-	20	40(AN)*
CTX-1	14	-	15	24	41(AP)**
CPX-100	-	9 % HTPB***/21 % K10****	60	22	28(AP)
PBXN-105	-	4 % Wax/13 % BDNPA/F*****	7	26	50(AP)

* AN = Ammonium Nitrate

**AP = Ammonium Perchlorate

***HTPB = Hydroxyl Terminated Poly Butadiene

****K10 = Trinitroethylbenzene/dinitroethylbenzene (35/65 % w/w)

*****BDNPA/F = Bis(2,2-dinitropropyl)acetal/formal

11.3.1 Aluminised RDX Explosives

The Torpex series of explosives, where RDX and aluminium are bound with TNT, have been in use since the 2nd World War. Examples of Torpex compositions and the US equivalent (H-6) are given in Table 11-11. With such large solids loadings TNT is not a perfect binder. Therefore a series of formulations with wax as binder was developed as the RWA series (see

Table 11-12).

Initially aluminised explosives were developed for underwater weapons and several current torpedoes and depth charges have either Torpex or RWA fillings as do large air dropped bombs. Aluminised PBXs also have been developed and employed in large air dropped ordnance including PBXN-109, where the aluminium content is similar to the TNT and wax desensitised compositions (

Table 11-13).

Table 11-11 Formulations with RDX, TNT and Aluminium

Name	TNT (% w/w)	Additive	RDX (% w/w)	Aluminium (% w/w)	Beeswax (% w/w)
Torpex - 2	39.7	-	41.6	18	0.7
Torpex - 4A	53.2	2.9 % w/w	19	24.3	0.3
H-6 (USA)	29	5 % w/w Wax	45	21	-

Table 11-12 Formulations with RDX, Wax and Aluminium

Name	RDX (% w/w)	Wax (% w/w)	Aluminium (% w/w)	Other (% w/w)
RWA-2	70.5	9	20	0.5
RWA-3	73	10	15	2
RWA-4	71	7	20	2
Hexal	55	5	40	-
Hexal W30	66.5	3.5	30	-

Table 11-13 PBX Aluminised Explosives

Name	Nitramine (% w/w)	Polymer/ Plasticiser (% w/w)	Aluminium (% w/w)
PBXN-109	RDX 65	14	21
PBXIH-18	HMX 64.4	5.6	30
DPX-6	HMX 50	4	46

11.3.2 Enhanced Blast Explosives

It has been recognised that if an aluminised explosive detonates in air then further reaction of aluminium with atmospheric oxygen can enhance blast output. This has led to the development of formulations with aluminium content well in excess of the previous limitations for underwater explosions. The Hexal compositions shown in

Table 11-12 can be found in medium calibre cannon rounds and formulations such as PBXIH-18 and DPX-6 in

Table 11-13 are listed as anti-structure or enhanced blast explosives, which are highly effective in enclosed spaces.

11.4 NEW FORMULATIONS

11.4.1 Potential Explosives for Future Formulations

There are a number of explosive molecules that are of interest to develop new explosives (Table 11-14). Some are already in use by other nations and some being studied in the UK as potential replacements for current formulations.

Nitrotriazolone (NTO) has for some time been considered as a replacement for RDX, particularly in formulations designed to produce munitions that pass the Insensitive Munitions (IM) tests. When NTO replaces RDX even in TNT containing formulations the IM properties are improved. However, the most recent development of specific interest in the UK is the replacement of TNT in melt-cast compositions with 2,4-dinitroanisole (DNAN).

Table 11-14 Explosives in Potential Future Formulations

Substance	Velocity of Detonation ($m\ s^{-1}$)	Density ($g\ cm^{-3}$)	Impact sensitiveness	Temperature of Ignition (°C)
CL-20	9,380	2.04	20 (F of I)	220
TATB	7970	1.94	>200 (F of I)	320
DADNE (FOX-7)	8800	1.885	100 (F of I)	217
NTO	8430	1.91	80 - 90 (F of I)	>270
DNAN	5670	1.52	>100 (ERL Impact Test, RDX = 18)	244

The explosive hexanitrohexa-azaisowurtzitane (CL-20) has a detonation pressure of 44 GPa compared to a value of 39.2 GPa for HMX, the current explosive of choice in formulations that require very high shock pressure. There is international interest in developing formulation containing this explosive and it is commercially available.

11.4.1.1 New melt cast insensitive high explosives

In 2005, the US Army began a programme to replace TNT and Composition B in its artillery and mortar rounds to make them more IM compliant. An extensive down-selection process was undertaken, resulting ultimately in two formulations

being selected. The replacement for TNT was IMX-101, which comprises DNAN, NTO and nitroguanidine (NQ) and the replacement for Composition B was IMX-104, which comprises DNAN, NTO and RDX. The compositions of these formulations are given in Table 11-15 (for IMX-104 this is the range for Qualification).

Table 11-15 US Melt-Cast Explosives with Improved IM Suitability

	Ingredients (% w/w)			
	DNAN	**NTO**	**NQ**	**RDX**
IMX-101	43.5	19.7	36.8	-
IMX-104	29.7-33.7	51-55	-	13.3-17.3

The performance of IMX-101 and IMX-104 is very similar to TNT and Comp B respectively. The detonation performance of these explosives is given in Table 11-16.

Table 11-16 Performance of TNT and Composition B vs IMX Replacements

Composition	Density (g/cm^3)	VoD ($m\ sec^{-1}$)	Detonation pressure (GPa) - calculated
TNT	1.60	6,900	19
IMX-101	1.64	6,900	19.5
Comp B	1.71	7,980	27.2
IMX-104	1.75	7,400	24

IMX-101 and IMX-104 have been subjected to IM acceptance tests with the results shown in Table 11-17. IMX-101 meets all the IM acceptance criteria. Whilst IMX-104 does not meet the criterion for shaped charge jet attack, it performs markedly better than Composition B.

Table 11-17 IM test Results for IMX101 and IMX104

	IM TEST					
	Fast Cook Off	Slow Cook Off	Bullet Impact	Fragment Impact	Sympathetic Detonation	Shaped Charge Jet
IM Passing Criteria	V	V	V	V	III	III

	IM TEST					
	Fast Cook Off	Slow Cook Off	Bullet Impact	Fragment Impact	Sympathetic Detonation	Shaped Charge Jet
155mm TNT	III	III	IV	IV	I	I
155mm IMX-101	V	V	V	V	III	III
81mm Comp B	II	II	III	III	I	I
81mm IMX-104	V	V	IV (a) / V (b)	III (c) / IV (d)	III	I
120 mm Comp B	II	I	I	I	I	I
120 mm IMX-104		V	IV	V	III	

a - 0.50" Cal, b - 7.62 mm, c - 8300 ft s^{-1}, d - 6000 ft s^{-1}

11.5 COMMERCIAL EXPLOSIVES

Apart from military formulations which have commercial equivalents, for example plastic explosives, the common commercial explosives divide into 4 types:

1. Ammonium Nitrate/Fuel oil (ANFO) mixtures
2. Emulsions and emulsion blends
3. Nitroglycerine gelatines and dynamites
4. 'Permitted' explosives

Over the last 20 years emulsion explosives have become the dominant commercial explosive together with ANFO as they have developed in to a range of bulk delivered explosives for quarrying and mining and cartridged explosives that have largely replaced nitroglycerine equivalents.

The performance of commercial explosives, particularly the detonation pressure (see 11.2), is inferior to military explosives based on RDX, TNT and HMX as highly brisant (shattering) explosives would be unsuitable for commercial activities. Quarrying, for example, requires sufficient shattering capability to start the rock fracturing, which then is acted on by the expanding gasses with a heaving effect. The rock produced (the muck pile) must have rock pieces that can be handled by quarry plant including crushers. For rock such a limestone this does not need high detonation pressure.

Commercial explosives manufacturers express the performance of their products in terms of strength. This is measured by comparing the work done by an explosive with that done by either an equal weight (weight strength) or an equal volume (bulk strength) of a standard explosive. The standard chosen initially was blasting gelatine although it is common in recent times to use ANFO as the standard. Care must be taken when considering a quoted strength as blasting gelatine is around 25 % more powerful than ANFO. Table 11-18 provides data on the performance of commercial explosives compared to typical military explosives.

Table 11-18 Performance of Some Commercial and Military Explosives

Explosive	TNT equivalence	Detonation pressure (GPa)	Velocity of detonation (m s^{-1})
ANFO mixtures	0.8 – 0.9	2 - 3	2000-3500
Emulsion/emulsion blends	0.8 – 1.0	5 - 9	4000 - 6000
Gelatine dynamites	0.8 – 1.1	6 - 11	4500 - 6000
TNT	1.0	17	7000
RDX/TNT (60/40)	1.3	24	7800

Another difference between military and commercial explosives is that the cost of the explosive is of much less concern for the manufacture of ammunition than for commercial blasting operations. The vast majority of commercial explosives used worldwide are based on ammonium nitrate as the major component, which is a very cost effective ingredient. In comparison TNT, RDX and HMX are very expensive explosive ingredients.

11.5.1 ANFO Type Explosives

ANFO is a mixture of 94.5 % w/w pure (>98 % w/w) ammonium nitrate and 5.5 % w/w fuel oil (diesel oil), or closely similar percentages. The ammonium nitrate is used in the form of prills, which are smooth spheres about 2 mm to 3 mm in diameter, which are made by allowing the molten nitrate to fall inside a high tower. Porosity is achieved by driving out the last few percent of moisture from the material after it has been prilled, and this enables the prills to soak up the oil more efficiently. The crystal density of ammonium nitrate is 1.7 g cm^{-3}, but the bulk density of prills is only about 0.8 g cm^{-3} and the addition of the comparatively small percentage of oil makes little difference to this figure.

ANFO can be obtained ready-mixed from explosives manufacturers, or alternatively the prills and oil can be purchased separately and mixed on the blasting site. For large operations ANFO can be truck mixed and augered in to bore holes. ANFO is not resistant to water and must be kept dry. It cannot be initiated by a detonator alone or by standard detonating cord. A primer with

good shock pressure output is used to initiate ANFO. The detonation velocity of ANFO will be in the range of 2000-3000 m s^{-1} unless it is loaded pneumatically in to bore holes as this increases the filling density, which can increase the detonation velocity to nearly 4000 m s^{-1}. This can improve the shattering ability of the explosive.

11.5.2 Emulsion Explosives

The term 'emulsion explosive' is taken to mean a high internal phase, water-in-oil emulsion of a concentrated (often supersaturated) solution of nitrate salts in water emulsified into an oil base. Emulsion explosives have unusually high rates of detonation for such a heterogeneous explosive (Table 11-18).

The velocity of detonation depends on maintaining an intimately mixed liquid system. The emulsified droplets are of the order of 1 μm in diameter separated by an oil film of the order of 3 mm thick. The use of water is limited because it inhibits detonation. The production of an oxygen balanced explosive requires a large quantity of oxidising salt. The emulsion is a supersaturated meta-stable solution, typically containing 70 % w/w ammonium and sodium nitrates, 20 % w/w water emulsified in oil or oil/wax phase.

The emulsion is not in itself an explosive and can be stored and transported as a product known as emulsion matrix with a Hazard Classification Code of 5.1 (Oxidising substances). To convert it to a detonable material voids are introduced either in the form of hollow glass or plastic spheres, by air beaten in to the mixture or by a chemical reaction. These voids provide a mechanism for the conversion of energy in the shockwave from the detonation to heat energy necessary to produce chemical reaction and to sustain detonation. The sensitivity and velocity of detonation of the explosive are dependent on the quantity and size of the bubbles. Emulsion explosives can be made to be detonator sensitive in small critical diameters and with a velocity of detonation in the range 4000 m s^{-1} to 6000 m s^{-1}. The energy of the explosive, increasing power (strength), can be further enhanced by incorporating aluminium powder as in military explosives. The consistency of emulsion explosives ranges from that of thick cream to a stiff paste. Shelf life for cartridged, also known as packaged, emulsions is usually 1 year.

It is now common practice for large scale use of emulsion explosives such as in quarrying and mining to have a range of emulsions to match the local requirements that can be fine-tuned at point of use. The explosive company will provide bulk emulsion trucks known as 'Mobile Manufacturing Units' (MMUs) or 'Mobile Charging Units' (MCUs) that contain the emulsion matrix in a tank but also carry prilled ammonium nitrate and a gassing agent. The gassing agent is mixed with the emulsion matrix as it is pumped in to the borehole and reacts to form gas bubbles sensitising the matrix to shock detonation. This reaction can take some hours before sensitisation occurs but will remain usable for up to 2 weeks or more. This is called the 'sleep time', that is how long between borehole loading and detonation. The ammonium nitrate prills are mixed with

the emulsion matrix as the borehole is loaded a typical mixture being 70 % w/w matrix and 30 % w/w prills. The ratio is adjusted for the specific requirements of the blast.

11.5.3 Nitroglycerine Explosives

Nitroglycerine (NG) (see 4.2.2) based explosives dominated the commercial explosives scene until the mid C^{20th} when explosives based on ammonium nitrate became available. The ingredients for nitroglycerine explosives divide into two parts, the explosive molecular components NG, ethyleneglycol dinitrate (EGDN) and nitrocellulose (NC) and secondly an oxidant/fuel mixture (see 4.2.1) known traditionally as 'dope'. The oxidant is ammonium nitrate and the fuel woodmeal and this acts as a base material to absorb the liquid NG and EGDN. NC is present to further bind or gel with the liquid explosives and provides a rigid gelled solid if sufficient NG/EGDN is present. This led to the generic name being a gelatine dynamite or gelignite. As the liquid component is reduced the term semi-gelatine is used and finally at low amounts the mixture is not a rigid solid and is called NG powder

The EGDN originally was added to the mixtures to prevent the NG freezing in cold conditions. NG has a freezing point of 13 °C and so temperatures below this may be encountered when in use. Frozen NG is far more sensitive than when in the liquid state and so the EGDN mixed with the NG lowers the freezing point of the mixture. EGDN has a freezing point of -22 °C and the mixtures with NG values that are significantly lower. In modern gelatine explosives the EGDN is the major component compared with NG. With a zero oxygen balance (see 4.3.1) EGDN is actually more powerful than NG.

Table 11-19 Performance of Nitroglycerine Containing Explosives

Type	Weight Strength vs BG (%)	Density (g cm^{-3})	Velocity of Detonation (m s^{-1})
Blasting Gelatine (BG)	100	1.6	7000
Gelatine Dynamite	80 – 65	1.5 – 1 4	6600 - 5500
Semi-gelatine	65 – 50	1 3	6000 – 5000
NG Powder	<50	1.15	4000

The true gelatines are rubbery and are filled into cartridges by extrusion. Because of their physical homogeneity they have good water resistance and shelf life. Their sensitivity falls with storage time, however, due to the loss of occluded air. Blasting gelatine has little or no dope with some mixtures containing up to 93 % w/w NG mixed with NC and an antacid stabiliser. It is very sticky to handle and is rarely if ever used. The commonly used explosives are the gelatines, semi-gelatines and NG powders, the gelatine types as paper wrapped cartridges and the powder in cardboard or plastic tubes as it has no

water resistance. The NG content reduces from gelatines through to the powders, the latter containing around 20 % w/w NG and 80 % w/w dope. The performance of these explosives is shown in Table 11-19.

11.5.4 Permitted explosives

A Permitted Explosive is one that has passed the tests required for use in coal mines where there is a risk of explosion caused by ignition of flammable gases such as methane or of coal dust. The main requirement is that it produces a flame of lowest possible temperature for the minimum possible time. The explosive is tested in a gallery into which flammable gases can be introduced. In the UK these are known as the Buxton Tests. The explosive contains components that are flame suppressants and flame coolants such as sodium chloride and sodium bicarbonate (

Table 11-20). The first British list of permitted explosives was published in 1899. Typical detonation velocities range from 3800 m s^{-1} for a gelatine type to 1800 m s^{-1} for some NG powders.

Table 11-20 Some Formulations of Permitted Explosives

	Gelatine (% w/w)	Semi-gelatine (% w/w)	NG Powder (% w/w)
NG/EGDN	27.00	16.00	10.0
NC	0.75	0.25	-
AN	30.50	42.75	64.00
Sodium Chloride	28.50	26.00	16.50
Kaolin	3.00	2.00	-
Carbonaceous fuel	1.25	2.00	8.50
Barytes (barium sulphate)	5.00	5.00	-
Calcium sulphate	-	4.00	-
Other	4.00	2.00	1.00

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CHAPTER 12
GUN PROPELLANTS

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12 GUN PROPELLANTS

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12.1 AWARENESS SUMMARY

Gun propellants consist of a polymer (normally nitrocellulose (see 12.2.2.1)) plus additional explosives and additives, carefully formulated to burn smoothly without detonating to produce hot gases to propel a projectile. Gun propellants are sometimes called smokeless powders, a term which originated in the nineteenth century to distinguish the newly developed nitrocellulose (NC) propellants from the traditional corned gunpowder ones. They are indeed largely smokeless on firing, certainly so when compared with gunpowder, which gives more than 50 % of its weight as solid products.

They are not, however, 'powders' in the ordinary sense of the word. They are produced in characteristic shapes such as flakes, ribbons, spheres, cylinders or tubes. The charge in a gun consists of an aggregate of such shapes, which are called grains, or if greatly elongated, sticks, even in small arms cartridges the individual grains are large enough for their characteristic shape to be discernible to the naked eye.

In addition to the wide spectrum of size and shape, the many possible combinations of ingredients multiply the variety of gun propellants. All conventional propellants contain NC in the form of a gel, together with at least one non-explosive additive. NC, being a nitrated natural polymer, gives the mechanical strength and resilience necessary to prevent breaking up of the grains during handling and firing which would otherwise alter the ballistic performance of the charge. Furthermore, NC gives a degree of choice as to the amount of chemical energy available, since it can be of different degrees of nitration and hence of different energy content.

In addition to NC, there are two other major ingredients of conventional gun propellants, which are explosive in character, nitroglycerine (NG) and nitroguanidine (NQ). Most conventional gun propellants comprise three basic types of composition, called respectively single-, double- and triple-base depending on how many of the above ingredients they contain.

The Force constant of a propellant, F also known as Specific Energy or propellant impetus (in the USA), is one of the energy features of a propellant. It is an important ballistic character of the propellant that can be used to compare propellant performance. Its value is calculated as shown in Equation (12-1).

$$F = nRT_o = \frac{RT_o}{\overline{M}} \qquad \textbf{(12-1)}$$

Where n is the number of moles of gas produced by 1 g of propellant, $\overline{M}$ is the mean molar mass of the gas produced (g mol^{-1}), R is the gas constant (J K^{-1} mol^{-1}), and T_o is the adiabatic flame temperature (K).

A propellant in which NC is the only explosive ingredient is called a single-base type. These are employed in all kinds of guns from pistols to artillery weapons. Their Specific Energy (or F value) is generally in the range 920-1075 J g^{-1}.

Double-base propellants contain nitroglycerine (NG) or a similar liquid nitrate ester in addition to NC. They are more energetic than single base propellants, having F values 1075-1175 J g^{-1} depending on the proportion of NG present. The percentage of NG is much lower than when double base propellants were first introduced in the late nineteenth century, due to the erosive effect of 'hot' propellants.

Triple-base propellants contain, as well as NC and a limited amount of NG, a large proportion of nitroguanidine (NQ), up to about 55 % w/w. NQ, which has the pseudonym picrite, is a white crystalline solid, and it is finely ground before being mixed with the NC/NG gel to form a particulate suspension. The triple-base propellants have F values intermediate between those of the other two types, ranging from 1000-1100 J g^{-1}. Their use is restricted to the larger types of guns because of their difficult ignition characteristics and because their chief virtue, the production of minimal gun-flash, is of most value in that field.

Single- and double-base propellants have existed for a century or more. The triple-base ones date back only half that time, having been developed between the world wars with the object of reducing flash and making gun positions less easy for the enemy to locate during night firing.

Despite the large number of compositions that have been manufactured and tested over the years, no single formulation comes near to fulfilling all user requirements. This is not surprising when considering the list below, particularly bearing in mind that each separate requirement covers a range of problems and in some cases mutually exclusive solutions. Briefly an ideal propellant should possess the following properties:

1. An acceptably high energy/bulk ratio
2. A predictable burning rate over a wide range of pressures
3. An acceptably low flame temperature
4. Capability of being easily and rapidly ignited
5. An acceptably low sensitiveness (see 20.2.1) to all other possible causes of initiation
6. Capability of cheap, easy and rapid manufacture and blending
7. Long shelf life under all environmental conditions
8. Minimum tendency to produce flash or smoke
9. Minimum tendency to produce toxic fumes

Because the search for more efficient weaponry is never-ending, and because the propellant is an essential part of a gun system, research aimed at superior propellants goes on continuously in various parts of the world. One successful line is to incorporate a cyclic nitramine such as RDX (see Figure 4-4), into traditional propellant mixes, which increases performance without unduly compromising safety. Other compositions, which have superficial attractions, have to be disregarded for various reasons. For instance, the ‘composite’ type

of rocket propellants, which are based on ammonium perchlorate suspended in a fuel matrix, have high-energy values but give toxic and corrosive combustion products and much smoke making them unsuitable for use in guns. Attempts to develop completely revolutionary types of propellant are being made in several countries, but for the moment the conventional types of propellant continue to give good service and they provide a wide choice to the designers of gun systems.

Table 12-1 Some Conventional Gun Propellant Compositions

Type	Name (Country)	Nitrocellulose (NC)		NG (% w/w)	NQ (% w/w)	Other Ingredients (% w/w)
		(% w/w)	% N (w/w)			
SB	FNH (USA)	84.0	13.15	-	-	DNT 10.0, DBP 5.0, DPA 1.0 + Solvent
	AR2206 (Aus)	92.0	13.15	-	-	DNT 7.0, DPA 1.0 + K_2SO_4, Graphite, Solvent
	IMR (USA)	89.0	13.15	-	-	DNT 7.0, DPA 0.5, K_2SO_4 1.0 + Solvent
	Snia GM3 (Italy)	96.0	13.1	-	-	DPA 1.0, MC 1.0, DBP 2.0
	Neonite (UK)	95.0	13.1	-	-	DPA 1.0, MC 2.0, DBP 2.0
DB	Nitro Neonite (UK)	90.0	13.2	8.0	-	EC 2.0 + Graphite
	M9 (USA)	57.5	13.25	40.0	-	EC 1.0, KNO_3 1.5 + Solvent
	HSC (UK)	49.5	12.2	47.0	-	EC 3.0, Chalk, 0.5
	[Mark 1 Cordite (UK)	37.0	13.1	58.0	-	Mineral jelly 5.0
TB	M30 (USA)	22.0	13.15	21.5	54.7	EC 1.5, Cryolite 0.3 + Solvent
	NQ (UK)	20.8	13.1	20.6	54.7	EC 3.6, Cryolite 0.3 + Solvent
	Cordite-N (USA)	18.5	13.15	18.5	55.0	EC 7.0, K_2SO_4 1.0 + Solvent
	MNLF2P (UK)	16.25	12.30	16.25	54.0	EC 7.5, K_2SO_4 2.0, DBP 4.0 + Solvent

12.2 TYPES OF PROPELLANT CHARGES

12.2.1 Introduction

In this chapter the term gun propellants includes small arms propellants unless otherwise indicated, but where both types are included in the same table care has been taken to distinguish small arms propellants from artillery types. As far as the formulation and thermochemistry of the traditional propellants are concerned, there is little difference between the two types. The in-bore pressures and temperatures developed, and the associated muzzle velocities acquired by the projectiles, are of the same order of magnitude, although the rate of acceleration of small arms and cannon projectiles is generally much greater than that of a large calibre gun projectile and the whole ballistic cycle considerably shorter. In the future there may arise wide differences of composition and physical form between artillery, cannon and small arms propellants, because modern developments aimed at the final elimination of the traditional metallic cartridge case are proceeding in different directions, as will be seen later in this chapter. At the present time, however, British service ammunition for both guns and small arms contains the familiar solid, colloidal propellants in granular form, which in essence have changed little over the last fifty years.

In addition to NC, there are two other major ingredients of conventional gun propellants that are explosive in character, nitroglycerine (NG) and nitroguanidine (NQ). They are compared in the table shown below.

Table 12-2 Comparison of Key Ingredients in NC Propellants

Energetic compound	Q^* (w.g) J g^{-1}	V* at STP cm^3 g^{-1}	Flame temp. K
NC - Nitrocellulose $(C_6H_7N_3O_{11})_n$ (13.1 % N)	3745	880	3290
NG - Nitroglycerine $C_3H_5N_3O_9$	6275	740	4900
NQ - Nitroguanidine $CH_4N_4O_2$	2680	1077	2100

* Q = Heat of explosion (see 4.4.2), ** V = Gas volume (see 4.4.3)

In theory, many stable explosive compounds of low volatility that do not very readily burn to detonation are candidate ingredients of gun propellants. For instance, in World War II the Germans made extensive use of di-ethylene glycol dinitrate (DEGDN) as a replacement for NG, thus avoiding the diversion of raw material needed for the manufacture of foodstuffs. Meanwhile the Americans tried tetramethylolcyclopentanone tetranitrate (fivonite) and also di-(2-nitroxyethyl)-nitramine (DINA), similarly to replace NG, and from the latter they developed in 1945 the 'flashless' propellant ‘albanite’ for large naval guns.

In more recent times some countries have replaced NG in propellants by ethylene glycol dinitrate (EGDN), which is more energetic but more volatile

having a higher vapour pressure. In practice, conventional gun propellants comprise three basic types of composition, called respectively single-base, double base and triple-base depending on how many of the ingredients NC, NG and nitroguanidine they contain.

12.2.2 Conventional (Nitrocellulose) Propellants

The first part of this chapter is concerned with these 'conventional' propellants, this term being used to include the new high energy, colloidal propellants containing RDX. A note is included on the intended next step forward, the use of an insensitive synthetic binder to replace the traditional NC/NG gel for RDX propellants.

Table 12-3 Summary of the Different Types of NC Propellants

Designation	Energetic Compounds	Comments*
Single-base propellant	NC	Low F 900 - 1000 J g^{-1}
Double-base propellant	NC + NG	High F and T_o 1100 - 1200 J g^{-1}
Triple-base propellant	NC + NG + Nitroguanidine (NQ)	Intermediate F and T_o Lower flash 1000-1100 J g^{-1}
Multibase, High Energy or Nitramine propellant	NC + NG + NQ + RDX	Very high F and T_o 1100-1250 J g^{-1}

* F = Force constant and T_o = Flame temperature

12.2.2.1 Nitrocellulose (NC)

NC, being a nitrated natural polymer, gives the mechanical strength and resilience necessary to prevent breaking up of the grains during handling and firing, which would otherwise alter the ballistic performance of the charge. Furthermore, NC gives a degree of choice as to the amount of chemical energy required, by varying the degree of nitration.

NC is a vital ingredient not only of all conventional gun propellants and many rocket propellants but also of numerous commercial blasting explosives. The compound is correctly named cellulose nitrate, and not nitrocellulose, which is a misnomer, since it contains the characteristic nitrate ester grouping -C-O-NO_2. NC is no longer manufactured in the UK and is procured from overseas. It is manufactured by the action of mixed nitric and sulphuric acids on cellulose in the form of cotton linters and also from paper originating from wood. Cellulose is a natural polymer consisting of anhydroglucose repeating units.

The effect of nitration is to replace some of the –OH groups in the molecule by nitrate groups -ONO_2. Figure 12-1 shows fully nitrated cellulose, however,

complete nitration cannot be achieved in practice; the extent to which it occurs in a given sample depends on the reaction conditions selected, particularly the composition of the acid and the time and temperature of nitration. NC is therefore an ill-defined substance consisting of a random mixture of cellulose mono-, di- and trinitrates.

The customary way to define its composition is to express the nitrogen content as a percentage by weight. If the product were entirely dinitrate $[C_6H_7O_2.OH.(ONO_2)_2]_n$ the nitrogen content would be 11.1 % w/w, however, if it were entirely trinitrate $(C_6H_7O_2.(ONO_2)_3]_n$ it would be 14.14 % w/w. In practice NC types used in various propellant applications vary from 12.2 - 13.5 % N (w/w).

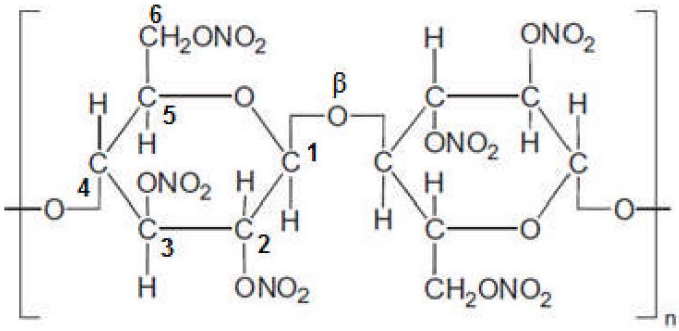


Figure 12-1 Structure of (tri)nitrocellulose

Because two additional oxygen atoms accompany each nitrogen atom, which is introduced on nitration, the percentage of oxygen is linked to that of nitrogen. In any explosive of the CHNO type, the relationship between the percentage of oxygen and that of the fuel elements, carbon and hydrogen, is known as the oxygen balance (see 4.3.1). The nearer the composition approaches to an oxygen balance of zero, the more heat is evolved per unit mass of explosive upon combustion. All grades of NC have a negative oxygen balance, but the higher their percentage of nitrogen and oxygen the higher is the Force constant (F) or (Specific Energy), their heat of explosion (Q) (see 4.4.2) and the temperature achieved by their combustion.

US MIL-DTL-244C amendment 1 (2014) defines the grades and nitrogen contents of NC and the test methods. STANAG 4178 (edn. 2) has recently been updated and the NC test methods are now aligned with the MIL-DTL.

All NC types originating from cotton and wood are pulped white solids, which do not melt but ignite in the region of 180 °C. When dry they are very sensitive to initiation by percussion, friction and flame, but these hazards can be avoided by keeping the sample wet as NC is insoluble in water. In all grades the chemical stability depends on the removal of all traces of acid in the manufacturing process amongst other things.

Whereas cellulose is insoluble in most organic solvents, NC dissolves in such solvents to some extent, forming a gel. Strictly solubility is not the correct term

to use since NC is a large molecule and is suspended in the liquids to give colloids. However, the term will continue to be used here as a shorthand. The gel retains the physical strength derived from the polymeric structure, and is an essential feature of conventional gun propellants, double-base rocket propellants and gelatine and semi-gelatine commercial blasting explosives. The important candidate solvents for the manufacture of these products are acetone, ethanol, ether/ethanol mixture and nitroglycerine. All grades of NC above 10 % N are soluble in acetone but the solubility in other solvents tends to vary with the nitrogen content. NC of up to 11.2 % N (approx.) is soluble in ethanol, but this grade of NC is not sufficiently energetic for use in explosives compositions. NC of up to 12.6 % N (approx.) is soluble in 2:1 ether/ethanol mixture, the solubility peaking at 11.5 % N. This solvent is used in the manufacture of single-base gun propellants. The solubility of NC in nitro-glycerine peaks between 12.0 and 12.2 % N. and NC of this grade known as 'blasting soluble nitro-cellulose' is used in the manufacture of commercial blasting explosives. For the higher proportion of NC required in double-base gun propellants either an acetone/water mixture is used as a solvent, or alternatively a 'solventless' process is used. In the latter process a water-wet mixture of NC and NG is gelatinised by passing it between heated rollers. Triple-base gun propellants are made by a combination of the 'solvent' and 'solventless' processes, called the 'semi-solventless' process. Table 12-4 shows the application of NC for differing levels on nitrogen content.

Table 12-4 Application of NC as Function of % Nitrogen

% Nitrogen in NC	Uses
10.2-11.0	Celluloid containers for mortar bomb augmenting charges. Celluloid is NC/camphor (75/25 % w/w)
11.2-12.2	Formerly used in photographic film and currently used in paints and lacquers
12.2 (known as "Type A")	Propellant SC. Extruded double-base rocket propellants
12.5	Neonites NRN*
12.6	Cast double-base (CDB) rocket propellants
12.65	Ballistite
12.9-13.1 (known as "Type B")	Propellant WM. Triple-base propellants N and NQ
13.15	Propellants NH, FNH
13.2	NNN
13.4	Neonites (NRN)*, NPP
14.14	Theoretical percentage for complete nitration

* Neonites contain mixtures of NCs having N = 12.5 % and N = 13.4 %

Some single and double-base propellants for small arms are manufactured by a technique known as the Ball-Powder process. The first steps in this process is the formation of a “lacquer” of partially gelatinised stabilised-NC (usually 13.1 % N) using a solvent, which is immiscible with water, for example, ethyl acetate. The lacquer is then tipped into water in a stirred pan and breaks up into globules. A solution of NG in the solvent may be added at this stage if a double – base propellant is required, the NG being absorbed by the globules. Raising the temperature drives off the solvent and the globules of lacquer harden to solid spheres, their consistent size and quality being maintained by careful control of conditions such as stirrer speed and heating rate.

12.2.2.2 Single-base propellants

A propellant in which NC is the only explosive ingredient is called a single-base type. These are employed in all kinds of guns from pistols to artillery weapons. Their heat of explosion (Q) (see 4.4.2) is generally between 3100 J g^{-1} and 3700 J g^{-1}. It should be noted that energy values of propellants are quoted on the conventional assumption that the water formed on combustion is in the liquid phase, unlike the case of high explosives. The water is in fact gaseous, and the difference in the calculated value of Q is of the order of 10 % higher for water gaseous (w.g) than for water liquid (w.l).

12.2.2.3 Double-base propellants

Double-base propellants contain NG or a similar liquid nitrate ester in addition to NC. They are more energetic than single-base propellants, having Q values between 4300 J g^{-1} and 5200 J g^{-1} depending on the proportion of NG present. The percentage of NG is much lower than when double-base propellants were first introduced in the late nineteenth century, due to the erosive effect of 'hot' propellants.

12.2.2.4 Triple-base propellants

Triple-base propellants were developed between the World Wars to render gun positions less easy to locate during night firing. These contain NC and NG, as well as, up to about 55 % w/w, NQ. NQ, which has the pseudonym Picrite, is a white, finely divided crystalline solid, and was mixed with the NC/NG gel to form a particulate suspension. The old triple-base propellants have Q values similar to single-base, ranging from 3200 J g^{-1} to 3700 J g^{-1}. The use of triple-base propellants has traditionally been restricted to the larger types of gun, where the production of minimal gun-flash, is of most value.

12.2.2.5 High energy gun propellants

The ideal properties required of a propellant have been enumerated previously in this chapter. Since World War II, when RDX was successfully used as a high explosive, much research has been conducted into the incorporation of this compound in gun propellants, to make them approximate more closely to the ideals. Like NQ, which had been incorporated in gun propellants before World War II, RDX is a nitramine explosive (see 4.2.2), but its thermochemical

properties are considerably different and, from certain points of view, better for propellant use. Table 12-5 shows these properties for the four main explosive constituents of solid gun propellants.

Table 12-5 Thermochemical Properties of Explosive Constituents Used in Conventional (Nitrocellulose) Propellants

	NC (13.1% N)	**NG**	**NQ**	**RDX**
Oxygen balance Ω (%)	-31.2	+3.5	-30.8	-21.6
Temperature of detonation T_d (K)	3278	4900	2418	4255
Gas production n (mol g^{-1})	0.394	0.32	0.048	0.04
Force constant F (J g^{-1})	1074	1568	965	1415

12.2.3 Low Vulnerability Ammunition (LOVA) Propellants

NC has remained the essential ingredient of virtually all gun propellants for over a hundred years despite numerous attempts to find a suitable alternative. Although this material has a number of advantages, one of its major disadvantages is that it is not elastomeric, and therefore a plasticiser is necessary to provide acceptable mechanical properties in NC based propellants. In double-base and triple-base propellants the plasticiser has traditionally been a liquid nitrate ester such as NG. However, experience has shown that propellants containing NC and NG are rather vulnerable to the effects of enemy attack, or to accidental stimuli.

In general, propellants containing NC have relatively low ignition temperatures of about 170 °C. If ignition is caused by an external stimulus (e.g. a high velocity fragment penetrating a cartridge case) the burning rate at atmospheric pressure is sufficiently high to ensure that the propellant charge is rapidly and completely consumed, with highly incendiary effect.

In recent years there have been moves to develop new types of propellant for large calibre guns, which contain no NC or NG. These would be less sensitive to initiation by fragment attack and would moreover have a lower burning rate at atmospheric pressure. Major programmes on these lines are now under way in the UK and the USA with the acronym LOVA (Low Vulnerability Ammunition) and in other countries. These programmes are part of a general policy towards Insensitive Munitions (IM) (see 2.12). In the United States LOVA programme the initial aim was to replace the traditional propellants by different compositions of similar force constant. This can be achieved by incorporating RDX, say 75 % (w/w), in an inert polymeric binder, such as cellulose acetate butyrates with a similarly inert plasticiser. To produce possible second generation LOVA propellants of higher force constant of around 1170 J g^{-1}, it will be necessary to use an energetic plasticiser, with examples given in Table 12-6.

These programmes were part of a general trend towards IM but this is now a basic requirement for all energetic materials and so terms such as LOVA tend not to be so widely used now. There are also other important drivers, in addition to IM, for the development of new propellants such as environmental and hazardous chemical legislation and raw material export limitations.

The ultimate high-energy, low-vulnerability advanced gun propellant, which may have a force constant of about 1300 J g^{-1}, will need to contain both an energetic plasticiser and an energetic binder to support the energetic filler. A number of candidate energetic binders have been considered; including nitrated hydroxyl-terminated polybutadiene (NHTPB) and nitro polyurethanes. The most promising binder materials appear to be polyoxetanes with nitrato-substituents, for example poly-3-nitratomethyl-3-methyloxetane (poly-NIMMO) and polymers such as glycidyl-azide-polymer (GAP), which contain energetic azido-groups. Some of the new propellants with improved performance and IM properties still retain NC as companies that manufacture NC will wish to have continuing use of this material as a major gun propellant component.

Table 12-6 Definition of LOVA Gun Propellant Generations (Comparison Between Eurenco and MSIAC)

Generation	EURENCO	MSIAC*
1st	RDX Inert binder (CAB) Inert or energetic plasticiser NC (small amount)	Nitramine (RDX) Inert binder (CAB) Inert plasticiser
2nd	FOX-12 or FOX-7 NC binder Energetic plasticiser	Nitramine (RDX) Inert binder (CAB) Energetic plasticiser
3rd	FOX-7 Energetic binder (e.g. GAP) Energetic plasticiser (e.g. NENA)	Nitramine (RDX) TPE or cellulose inert binder Energetic plasticiser
4th	–	Nitramine (RDX) ETPE (energetic) binder Energetic plasticiser

*Munitions Safety Information Analysis Centre (NATO)

Advanced gun propellant research in the UK has focused mainly on the investigation of RDX and HMX-based compositions containing an energetic binder (~15 % w/w of the composition) and an energetic plasticiser (~10 % w/w of composition). The most widely investigated binder has been poly-NIMMO but a wide range of plasticisers has been used, including GAP Azide (a GAP oligomer), Bis-dinitropropylacetal/formal (BDNPA/F), BTTN/TMETN (less shock sensitive nitrate esters) and various NENAs (nitratoethylnitramines) such as n-

butyl-NENA, methyl-NENA and ethyl-NENA. A plasticiser has a major effect on the glass transition temperature of the propellant: in a typical poly-NIMMO composition this can range from -15 °C when there is no plasticiser to -63 °C when the plasticiser is an ethyl-NENA/methyl-NENA mixture. This in turn affects the mechanical properties of the propellant, particularly at low temperatures, and can therefore influence the vulnerability characteristics. In general it has been found that poly-NIMMO-based LOVA compositions can be formulated with specific energies of around 1300 J g^{-1} and low responses to small scale shaped charge attack. The vulnerability is influenced by the web size of the grain, with lower responses being found at smaller web sizes. Interestingly HMX-filled compositions have been found to be less vulnerable than those containing RDX. One further advantage of these propellants is that they have lower flame temperatures than conventional nitrate ester propellants of comparable energy. This can be as much as 400 K and therefore leads to significantly lower barrel erosion in the gun. Figure 12-2 shows the expected performance and combustion temperature of future LOVA gun propellants compared with the existing single- double- and triple-base propellants.

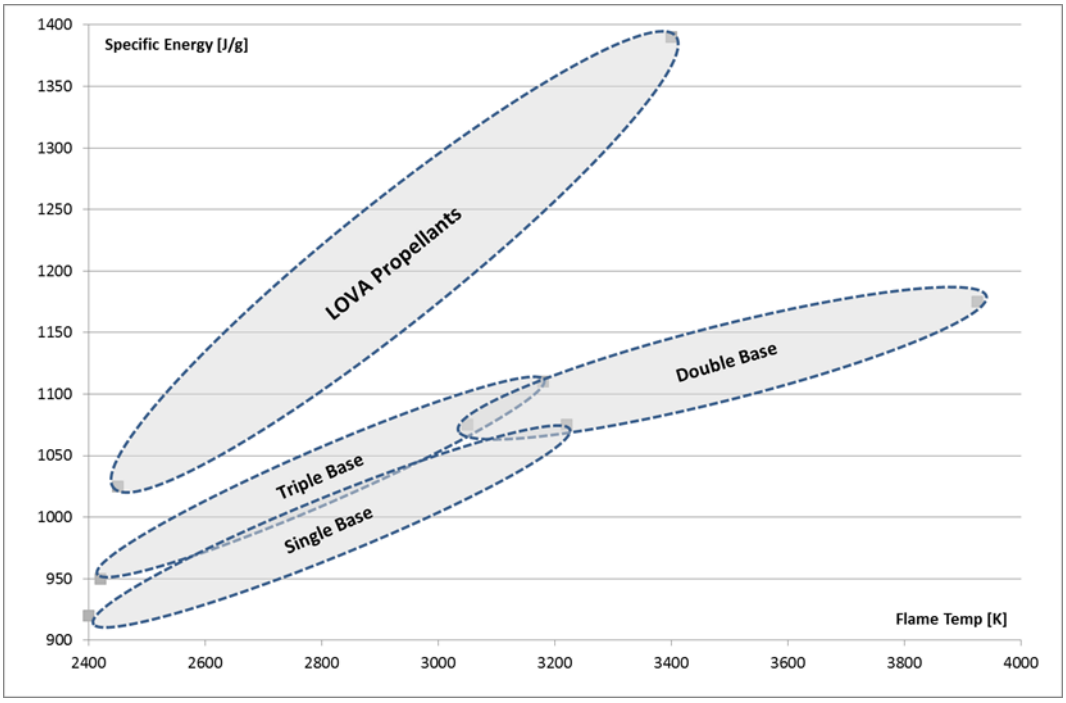


Figure 12-2 Comparative performance of existing gun propellant types and LOVA propellants

In recent years new fillers for gun propellants have been investigated that show superior properties to RDX and HMX. Two of particular note are N-guanylurea dinitramide (GUDN or FOX12) and 2-nitrimino-5-nitro-hexahydro-1,3,5-triazine (NNHT). One of the characteristics of these energetic fillers is their high nitrogen and low carbon contents, which means that on combustion the propellants produce more N_2 and H_2 (and less CO_2 and H_2O) than conventional propellants, leading to lower flame temperatures but higher specific energies.

The fillers are also less sensitive to impact than RDX. New fillers with similar features are likely to be developed in the future.

12.2.4 Propellant Additives

Each type of propellant contains one or more additives, which can be classified according to their function as follows:

1. Stabilisers
2. Plasticisers and coolants
3. Surface moderants
4. Surface lubricants
5. Flash inhibitors
6. Decoppering agents
7. Anti-wear additives

Some additives fulfil more than one of the functions listed above, and this is convenient means of simplifying the manufacture of propellants where possible.

There are three distinct ways in which an additive may be brought into contact with the parent composition:

- The additive can be incorporated in the propellant mix during manufacture and thus be evenly dispersed throughout the finished product. This is the sole method applicable in the case of stabilisers, plasticisers and coolants.
- The additive can be applied to the grains after they have been formed and can then exist either as an absorbed coating (surface moderants) or a surface glaze (lubricant).
- In cartridges for larger guns it is possible to insert the additive as a separate component in the cartridge, so that it decomposes or disintegrates under the influence of heat when the round is fired. This is an option in the case of flash inhibitors, decoppering agents and anti-wear additives.

12.2.4.1 Chemical stabilisers

NC in all types of conventional gun propellant undergoes slow degradation at normal propellant storage temperatures as a result of the loss of nitrate ester groups. Such reactions lead ultimately to stabiliser depletion (see below) and hence to autocatalytic decomposition and potential auto ignition of the propellant. The onset of autocatalysis therefore defines the "chemical safe life" of the propellant but before this is reached the NC will have degraded to a point where both the ballistic and the mechanical performance of the propellant are severely compromised. The shelf life is therefore more usually determined not by stabiliser depletion but by the deterioration of physico-mechanical properties or ballistic performance which can render the propellant unsafe to handle or unreliable in use. "Physico-mechanical life" is strongly influenced by the degradation of NC, the reduction in its average molecular weight causing increased grain brittleness. The "ballistic life" of a propellant is also affected by

the reduction in NC molecular weight with age but other factors such as surface moderant migration and changes in volatile content are often more important in this case.

The one additive common to all conventional gun propellants is the stabiliser. NC and NG are nitrate esters (see 4.2.2) and decompose slowly at normal temperatures to form oxides of nitrogen, mainly nitrogen dioxide, NO_2. If these oxides are not chemically removed from the system as they are formed they catalyse further decomposition, eventually leading to the shortening of storage life of the propellant and in extremis to auto ignition. The natural decomposition process is shown in Figure 12-3 as NO_2 and then the acidic HNO_2 are formed. If there was no stabiliser present the HNO_2 would react with NC causing further decomposition leading to more acid and a more rapid decomposition (autocatalytic process). The stabiliser reacts with the HNO_2 as it forms and prevents further reaction with the NC. Therefore during the life of the propellant the stabiliser content will decrease and finally to a level where autocatalytic reaction will occur

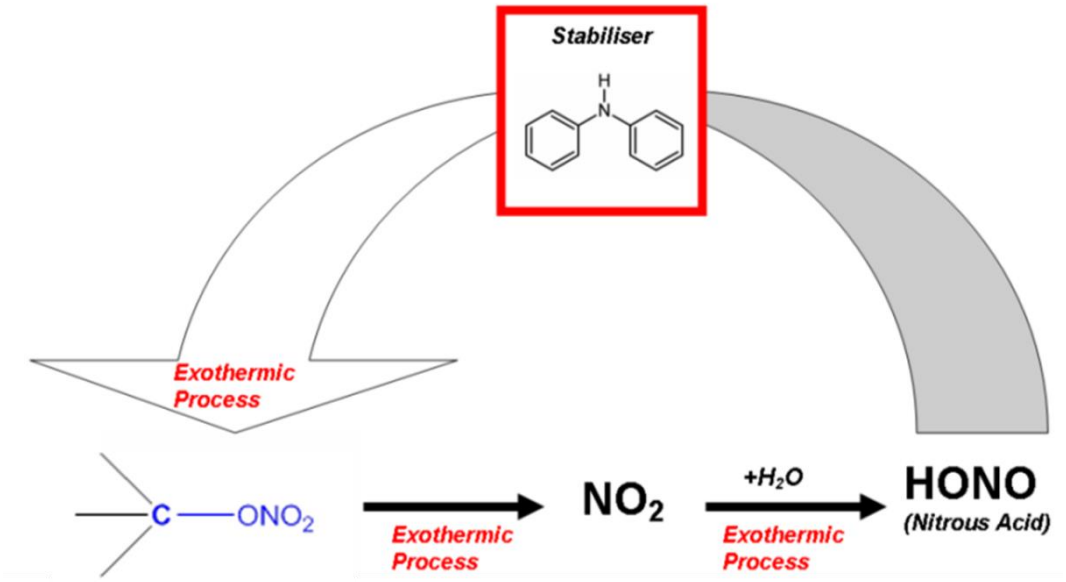


Figure 12-3 Schematic of NC decomposition – detailing the role of chemical stabilisers in preventing an autocatalytic decomposition reaction

All conventional gun propellants therefore contain an additive to react with the products of decomposition. The desirable properties of such a stabiliser are as follows:

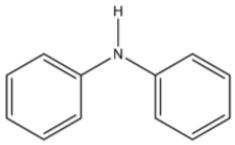
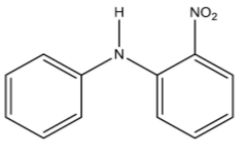
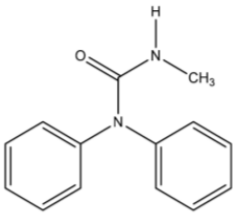
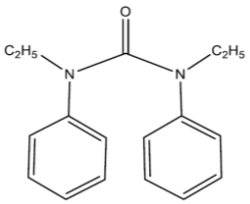
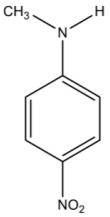
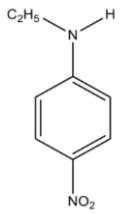
- Capacity to absorb oxides of nitrogen
- Ability to neutralise acids
- Ability to dissolve in the propellant matrix
- Inertness to NC or NG before and after reaction with the decomposition products

Recent investigations have suggested that an important additional role of some stabilisers (e.g. DPA) is to act as an anti-oxidant that blocks the oxidation

reactions of aldehydes (thereby reducing initial gas production) and terminates radical reactions within the propellant.

Stabilisers used in NC propellants are often aniline-urea compounds or their derivatives like alkyl-aryl amines, diaryl amines or aromatic urea derivatives, which are capable of reacting by chemically binding with the radical ·NOx (generic nitrogen oxides) produced from the degradation of the C-NOx bonds. Examples of aromatic urea derivatives (where N is substituted with a diaryl group is N-methyl-N',N'-diphenyl urea (Arkadite II). Other aromatic urea derivatives where N is substituted with alkyl aryl groups are N',N',-diethyl-N'-N'diphenylurea (ethyl centralite) and N',N'-dimethyl-N',N'diphenylurea (carbamate II). Table 12-7 is a list of common stabilisers used in nitrate ester propellants. The reaction of stabilisers with NOx is effectively a combination of nitration and nitrosation reactions, which can lead to the formation of stabiliser derivatives or daughter products.

Table 12-7 Common Stabilisers for Nitrate Ester Propellants

Stabiliser	Structure	Stabiliser	Structure
Diphenylamine (DPA)		2- nitro diphenylamine (2 NDPA)	
N-methyl-N',N'-diphenylurea (Arkadite II)		1,3-diethyl-1,3-diphenyl urea (ethyl centralite)	
N-methyl-4-nitroaniline (pNMA)		p-nitro-N-ethylaniline	

Mineral jelly (Vaseline) was one of the earliest stabilisers, and was employed in Mark I cordite (1893), originally in the hope that it would be deposited in the bore by each round fired and would thus provide lubrication for the next projectile. Had this idea been successful in the way intended, mineral jelly would have been classed as what we now call an anti-wear additive. In fact no lubricating effect was found, but it was discovered that mineral jelly, which is a mixture of the higher alkanes from petroleum, contained small amounts of alkenes, which absorbed nitrogen dioxide from the propellant and thus acted as

a stabiliser. Mineral jelly was therefore retained in this role for several decades and was included to the extent of 5-6 % (w/w) in the early cordites. Mineral jelly does not neutralise the acids, which are also products of propellant decomposition. In the early cordites this was done by calcium carbonate, which was deposited in the mass of NC by the process of boiling in hard water during its manufacture. In some UK propellants this uncertain amount of calcium carbonate was supplemented by a fixed proportion of chalk (< 1 % w/w) incorporated in the mix.

Diphenylamine (DPA) has been used in single-base propellants from their early years to the present time. It is a white, crystalline solid, which melts at 53 ^{o}C. Chemically it behaves as a base and reacts with the initial decomposition products of NC, initially to form N-nitrosodiphenylamine, which is then converted into various nitro-derivatives of diphenylamine. Diphenylamine is used in the single-base Neonite propellant for modern 7.62-mm ammunition and also in the artillery propellants NH and FNH. It is too basic for use with NG and is therefore not used in double- or triple-base propellants. One disadvantage of diphenylamine is the difficulty of dispersing it evenly through the mix. Its derivative 2-nitrodiphenylamine is less basic and is often used in double-base propellants. In recent years the production of toxic N-nitrosamines by stabilisers such as DPA has become an increasing concern. Indeed many of these stabilisers or their daughter products are toxic in nature, and new stabilisers are being investigated that do not produce such toxic daughter products. Derivatives of α-ionone for example have shown promising stabilisation potentials and a friendly toxicity profile.

The successor of mineral jelly in double-base propellants, later used in triple-base compositions, was carbamite. This name is a pseudonym originally coined for security reasons: the chemical name is diphenyl diethyl urea, known outside the UK as ethyl centralite (EC). It forms as white crystals which, when pure, melt at 72.5 °C.

Ethyl centralite chemically acts as a weak base and reacts with the NC decomposition products to form nitro- and nitroso-derivatives. In addition to its stabilising property it acts as a plasticiser and a coolant. It is used in double-base small arms propellants and also in the triple-base artillery propellant NQ (there may be some confusion in that NQ here is a triple-base composition (see 12.9) but as seen earlier NQ is also used to denote nitroguanidine, which is present in NQ propellant). Methyl centralite is the methyl analogue of carbamite, i.e., it is diphenyl dimethyl urea. It has a melting point of 121 °C. It is a good stabiliser and serves alternatively, but not simultaneously, as a surface moderant.

NQ (nitroguanidine) has a mild stabilising effect, accounting for the extraordinary service life of triple-base propellants.

12.2.4.2 Plasticisers and coolants

In order to convert NC from its natural fibrous state into a gel it must be treated with a solvent, which may be either a volatile one (later removed by evaporation) or the NG that is part of the propellant composition. In either case the process may require the assistance of a plasticiser. The versatile substance carbamite fulfils this role well. Other plasticisers are liquid esters of viscous nature and high boiling points. They have traditionally included dibutyl phthalate (DBP) that was used in the single-base artillery propellants NH and FNH. However the use of dibutyl phthalate was restricted in 2015 under REACH (see 1.3.2.4.6). Therefore dibutyl phthalate has been replaced with liquid plasticisers such as dioctyl adipate (DOA), dioctyl sebacate (DOS), or glycerol triacetate (Triacetin), which also act as coolants.

12.2.4.3 Surface Moderants and Lubricants

Some small arms propellants have their mass burning rates reduced during the early part of the combustion process in order to slow the rise of chamber pressure. This is done by coating the surface of the grain with a substance that absorbs heat when it decomposes. Surface moderation reduces the mechanical shock imparted to the gun on firing and also increases the muzzle velocity of a projectile by allowing it to move significantly before the maximum gas generation rate is reached. This latter property can be enhanced by compacting the propellant grains to give increased loading densities.

The ‘moderating’ substance is allowed to penetrate the outer layer to the required depth. The volume of the grain thus moderated (or ‘deterred’ in US terminology) can be up to 40 % of its total volume. Thus the distinction between ‘coolant’ additives and ‘surface moderants’ lies not in their chemical identity but in the way in which they are incorporated in the grain: a coolant is dispersed evenly through the grain whilst a surface moderant is present only in the outer layer. Surface moderants can be either solid or liquid. Solids such as dinitrotoluene or methyl centralite must be dissolved in a suitable solvent in order to penetrate the grain, whilst liquids such as dibutyl phthalate can be applied in their natural state. Modern British small arms propellants, e.g. NRN (for 7.62 mm ammunition) and NNN (for 5.56 mm ammunition) employ methyl centralite as the surface moderant. Carbamite can be used as a surface moderant but in practice it is more commonly employed in its stabiliser/plasticiser/coolant role.

A glaze of graphite on the grains has been traditionally used in the case of gunpowder and in recent times has been applied to more modern propellants, including ballistite and NRN. The purpose of this is three-fold: it lubricates the surface to allow easy filling into cartridges, it renders the surface more resistant to moisture and it forms an electrical conductor to dissipate electrostatic charges that may otherwise accumulate.

12.2.4.4 Decoppering Agents

In a large gun the driving band of the shell becomes partially molten during its passage along the bore and leaves a deposit of copper there. If this deposit is allowed to accumulate it eventually affects the ballistic performance of the gun. To counter this a decoppering agent is used with the propellant. This can be done in one of two ways. Firstly, the propellant composition can contain compounds of lead or tin, or secondly a piece of lead or tin foil can be juxtaposed to the propellant in the cartridge. In either case the metallic element combines with the copper deposit and forms a brittle alloy, which is removed by friction when the next projectile is fired.

Table 12-8 summarises some possible functions of the additives mentioned thus far. Notice that some can function in more than one role.

Table 12-8 Possible Function(s) of Some Propellant Additives

Function / *Additive*	Stabiliser	Plasticiser	Coolant	Surface Moderant	Typical % w/w
Chalk	✓	-	-	-	0.4
Diphenylamine	✓	-	-	-	1
Carbamite	✓	✓	✓	✓	1-9
Methyl Centralite	✓	✓	✓	✓	4
Dibutyl Phthalate	-	✓	✓	✓	2
Dinitrotoluene	-	-	✓	✓	10

12.3 CAUSES AND REDUCTION OF MUZZLE FLASH

The flash from a gun can be regarded as comprising two portions:

1. **Muzzle glow** - red in colour and probably due to incandescent particles in the hot gases from the propellant.
2. **Secondary flash** - a much larger flame, usually of considerable light intensity, occurring for some distance in front of the muzzle. This is due to the burning of the gases hydrogen and carbon monoxide after admixture with oxygen from the air.

$$CO + O_2 \rightarrow \tfrac{1}{2}\, CO_2 \qquad \Delta H = -281.7 \text{ kJ}$$

$$H_2 + O_2 \rightarrow \tfrac{1}{2}\, H_2O \qquad \Delta H = -241.8.7 \text{ kJ}$$

Secondary flash from large guns is undesirable because at night it can disclose the position of the gun to the enemy and it can also temporarily impair the vision

of the crew. Accordingly, for many decades attempts have been made to overcome the problem, via both gun design and propellant chemistry. What might seem to be the obvious remedy, i.e. increasing the oxygen content of the propellant so that complete combustion occurs within the gun, cannot be applied, because the extra heat liberated by the reactions will increase bore erosion and heat transfer to an unacceptable extent.

There are, however, some practical methods by which flash can be reduced, though not eliminated. Flash can be reduced by the addition of metallic salts, especially by those of potassium, such as potassium sulphate or nitrate, and potassium cryolite. Sodium cryolite can also be used. The predominant mechanism of the reaction is probably the breaking of one of the chain reactions that occur in the oxidation of hydrogen, by radical removal processes. This theory is supported by the fact that potassium hydroxide, which is formed from the original potassium salt additive under the influence of the high in bore temperature, has been found to be a more effective flash-inhibiting additive than any potassium salt. Another mechanism for the reduction of muzzle flash by potassium salts is the inhibition of the water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) that normally occurs as the propellant gases cool producing flammable hydrogen. However, the addition of such salts may increase the amount of smoke.

Another method is to decrease the calorimetric value of the propellant by the addition of coolants such as dinitrotoluene. Experiments have shown that the gases from the ‘cooler’ propellants contain more methane than those from the ‘hotter’ propellants, and methane is less easily flammable than hydrogen. This may explain why the comparatively ‘cool’ single-base propellants (NH and FNH) give relatively little flash although the calculated compositions of their muzzle gases show a greater proportion of $CO + H_2$ than for the ‘hotter’ double-base propellants.

The most effective method is to add to a double-base composition an additional constituent which liberates a large quantity of nitrogen in its combustion and which may also act as a coolant. The best candidate substance is nitroguanidine (NQ), which has the structural formula:

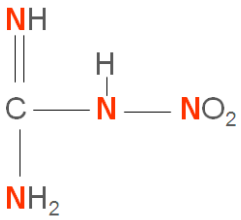


Figure 12-4 Structure of nitroguanidine

Nitroguanidine contains 53.9 % w/w of nitrogen and it is necessary for NQ to be present in a large proportion of the propellant to be effective producing the triple base class of propellants. Table 12-9 shows that the muzzle gases produced by triple-base propellants contain a much lower ratio of flammable gases to

nitrogen than do either single-base or double-base types. The three methods of flash reduction can be combined; propellants N and NQ contain not only nitroguanidine but also sodium cryolite and carbamite as additives.

An interesting property of certain flash inhibitors, particularly potassium bicarbonate and ammonium bicarbonate, is that these additives are also useful in reducing gun bore erosion. The mechanism of the latter affect is not known but it is thought that the decomposition products of the additives bring about changes in the processes of heat transfer to the bore. Ammonium bicarbonate has the further advantage, when incorporated in gun propellants, of not increasing the production of smoke.

Table 12-9 Composition of Muzzle Gases for Different Propellants

Propellant	Gas Volume at STP ($cm^3\ g^{-1}$)	Molar composition of muzzle gases	
		% CO + H_2,	Ratio %CO + H_2 to %N_2
Single-base			
NRN*	924	57.1	5.2
NH	980	67.6	6.4
FNH	1030	71.2	7.0
Double-base			
NPP*	870	44.7	3.5
NNN*	920	56.9	4.9
Triple-base			
N	1060	53.8	2.0
NQ	1000	44.5	1.5

* Small arms propellants

12.4 ELIMINATION OF THE CARTRIDGE CASE

The main purposes of the small arms cartridge case is to grip the bullet to allow an initial pressure rise in the cartridge case before the bullet in ejected, to contain the percussion cap and the discrete quantity of propellant and to provide rearward obturation. Other functions include protection of the propellant from moisture and other environmental contamination, providing a fixed initial free volume for the propellant gases and removing some of the unwanted heat from the gun upon ejection. Thus the cartridge case opened the way for revolutionary improvements in firearms and became regarded as an indispensable component of small arms ammunition.

Although the shotgun cartridge can be cheaply made from paper or polythene, the more exacting requirements of rifled weapons can be met only by metal cases, with the preferred material being 70/30 brass, although aluminium and steel are also used. This alloy is favoured because of its elasticity, hardness range, ductility and corrosion resistance. The brass cartridge case has now been in use for over a century, but in recent decades concerns regarding its use have arisen. The cost of brass, like other metals and alloys, has increased as mineral reserves become depleted, and the cost of the approximately ten energy consuming operations needed to shape it into a case has also risen. The high cost of brass encourages efforts to salvage spent cases, but this is a time consuming and, therefore, expensive exercise in itself. Furthermore brass is a fairly dense material, accounting for some 50 % of the total weight of the cartridge, and because the increased firepower of modern armed forces demands the transportation of increasingly large amounts of ammunition, the total weight of brass, which has to be carried by vehicles and soldier, has increased greatly.

Three separate solutions to the foregoing problems, as they apply to small arms ammunition, have been pursued in recent decades. One is the small calibre concept, which advocates scaling down the size of the cartridge with consequent reduction of range and barrel life. The second is the complete elimination of the metal case. The third is the replacement of the metal case by a combustible one. This latter method has been successful in large calibre ammunition, particularly for tank guns, but has proved unsatisfactory when applied to small arms ammunition. 'The two on-going solutions are not mutually exclusive; the caseless concept can be, and nowadays is, allied to that of the small calibre.

12.4.1 The Design of the Caseless Small Arms Round

If the cartridge case is eliminated from the weapon system it follows that the vital functions hitherto performed by the case must be transferred either to the gun or to the remaining components of the ammunition. Expanding on the foregoing paragraphs, the main functions of the case are:

1. To hold the bullet and present it accurately to the bore
2. To contain the percussion cap and provide an anvil for it
3. To contain the propellant
4. To protect the propellant from environmental contamination and accidental ignition
5. To provide rearward obturation of the gun
6. To provide a free volume for the combustion gases
7. To remove waste heat from the gun

Of these functions only (1) and to some extent (6) and (7) can be taken over by the gun. In compensation for these added requirements of gun design, there is no spent case to be extracted so the mechanical action can be simpler and faster. All the other functions have to be provided by the ammunition, which

comprises, essentially, only a bullet, propellant and ignition system. Since the bullet cannot be radically modified from its evolved shape and size, the propellant is required to fulfil functions (1) to (4) in addition to its basic one of providing the hot gases for propulsion. Clearly the propellant has to be changed from its traditional form of an aggregate of loose grains into a block of strong materials to grip the bullet and to provide a firm, sheltered recess for the percussion cap. It must also withstand the high stresses imposed by automatic handling at high rates of fire.

Although the propellant must exist as a firm, cohesive body up to the moment of firing, no known propellant has a sufficiently fast mass-burning rate in that condition to set up the required pressure time cycle in the gun. It must be broken up to achieve an adequate specific surface in order to increase its mass-burning rate. Hence the ignition system is in two parts. The percussion cap is situated at the rear of the round in the conventional way. Between it and the bullet is a booster explosive, part of which is in the form of a heavily compressed pellet which acts as an anvil for the cap, and which contains fire holes. When the cap is struck it ignites the booster explosive, which burns to a detonation. This provides a carefully optimised brisant effect that shatters the propellant in a consistent way. It also pushes the bullet further into the bore, providing forward obturation. The fragments of the propellant then burn in the free volume thus produced, as would a conventional granular propellant. The manufacturer claimed that there was no more than the normal round to round variation in peak chamber pressure. This was quoted as 380 MPa at 21 °C imparting a muzzle velocity of 930 m s^{-1} to the 3.4 g bullet. The weight of propellant was 1.6 g. Since the round is not required to supply the rearward obturation of the gun there is no need for the propellant block or the chamber to retain the traditional circular cross-section. The original cartridge section for the first production caseless small arms round, the Heckler and Koch G11 was rectangular. This was later modified to a bevelled shape for storage in boxes or for fitting the magazine of the rifle. A complete round showing these various features, in diagrammatic form, is illustrated in Figure 12-5. The propellant block was made in separate lateral halves, formed under pressure. The bullet and booster charge were placed between them and the halves were joined with adhesive. The block was then lacquered and when dry the surplus lacquer was machined off. The cap composition was inserted as a wet mix and was covered with a disc of the propellant material. The whole block was then given a final coat of lacquer, which completed its short-term resistance to contaminants such as moisture and oil.

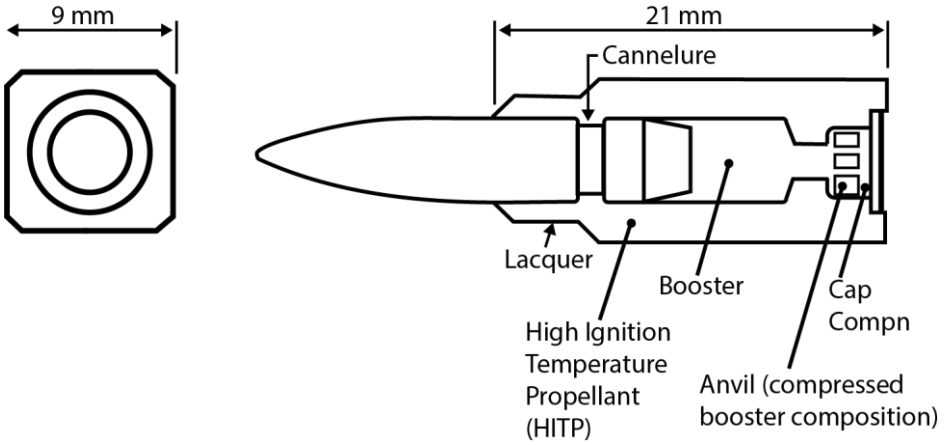


Figure 12-5 Caseless 4.7 mm round for an automatic rifle (diagrammatic)

The propellant for the G11 was originally a granular NC (single-base) type in a combustible plastic matrix, but, this was particularly prone to premature ignition due to conducted and radiated heat known as ‘cook-off’ when the cartridge was left in a hot chamber, since NC propellant ignites in the region of 170 °C. The US researchers encountered the same problem when attempting to develop caseless rounds in the late 1960s. They then sought a propellant composition which would not self ignite in a chamber below 300 °C. Such a composition was designated ‘high ignition temperature propellant’ (HITP), but this was considered not sufficient: it was required also to be resistant to accidental ignition outside the chamber, e.g. from flash or sparks, and this was described as ‘self extinguishing at ambient pressures’ (SEAP). A number of ideas were tried, including a resistant outer covering around an NC core, an HMX/polyurethane propellant and combinations of HMX, TAGN (triaminoguanidine nitrate) and plastic matrix. Some of these experimental compositions achieved the heat resistance requirements but failed on internal ballistic properties and residue free combustion. It was this failure to develop a completely satisfactory HITP/SEAP on which the US development programs for caseless small arms ammunition foundered at that time.

Furthermore, it appears that even the resistance of a caseless round to cook off at 300 °C may not be adequate, as experiments showed that the chamber temperature of a light support weapon may reach 400 °C in battle conditions. It is doubtful whether any viable propellant could reach this degree of insensitiveness to heat (see 5.1.1.1) while still remaining susceptible to ignition by the normal process, and retaining its ability, once ignited, to burn rapidly and completely.

12.4.2 Combustible Charge Containers (CCC)

It has been shown that the increasingly serious disadvantages of the metal cartridge case constitute a major reason for the persistent attempts to develop the caseless small arms round. For weapons of larger calibre, there are similar arguments in favour of eliminating the metal case but the possible solutions are different. It is difficult to imagine, for example, a block of propellant, 10 cm or

more in diameter, being broken up by a booster charge into ballistically consistent pieces. Ordnance varies greatly in size and purpose and, therefore, employs many different cartridge systems. The very largest guns, such as those formally installed in capital ships and coastal batteries, were never loaded with metal cartridge cases. Instead, the propellant was loaded in combustible bags. This system is referred to as the BL system, which originally signified 'breech loading' but which nowadays implies that obturation is chiefly a function of the gun rather than of the ammunition. The BL system still applies to medium calibre equipment (120 mm to 175 mm), both tank guns and indirect fire weapons. There are two other basic cartridge systems. That known as the QF system, employs a metal case which serves to obturate the breech, whilst the RCL (recoilless) system also uses a metal case, but one which is modified to vent at a fixed chamber pressure. It is, however, in the BL system that a significant step forward has been taken with the introduction of the combustible charge containers (CCC). The propellant is loaded into a rigid container manufactured from a mixture of NC, paper pulp and resin. Such containers are lacquered for waterproofing and replace (or in some instances complement) the fabric charge bags, over which they have the following advantages:

1. They are more easily handled than bagged charges.
2. They give better protection to the propellant in storage and transportation.
3. They contain an energetic material (NC) which contributes to the internal ballistic performance of the round.
4. They form, on firing, a boundary layer of comparatively cool gases that helps to preserve the internal surface of the chamber and bore against erosion.

When carried in an Armoured Fighting Vehicle, CCCs are kept in bins that are surrounded by a pressurised water jacket. They are thus protected against an outbreak of fire in the fighting compartment. If an enemy projectile penetrates the jacketed bins the water immediately floods the CCC and propellant in case they are ignited by the impact. The CCC shares its main disadvantage with the caseless small arms round; it is susceptible to accidental causes of ignition, including cook off in hot guns and such random hazards as lighted cigarettes. The CCC is not seen as a straight substitute for a metal cartridge case but rather as an improvement on the bag charge for the BL system.

12.5 Performance Parameters

A gun, regardless of its size, is a device for converting the chemical energy of the propellant to kinetic energy in the projectile. The propellant must be carefully matched to the ballistic requirements, to its limitations of mechanical strength and to its resistance to corrosion and erosion, so as not to compromise its safety, degrade its performance or shorten its useful life.

The propellant is loaded into the gun at the required charge weight in a cartridge case or other container. When the gun is actuated the charge is

ignited by means of a primer, a device designed to produce an explosive burst of flame. This ignites the propellant, effectively within a few milliseconds, and the flame rapidly burns over the entire surface of the charge. Hot gases are generated from the burning surface of each grain, and the pressure in the chamber, already raised by the functioning of the primer, continues to rise rapidly. Most projectiles offer considerable resistance to propulsion, because some part of their periphery has to be engraved by the rifling of the bore to impart rotation. This is not the case for smooth-bore guns. For fixed rounds, considerable extra force is necessary to affect projectile pull, i.e. to separate the projectile from its case. Because of this resistance the chamber pressure becomes quite high, say 20 MPa to 80 MPa, before shot-start occurs. The burning rate of the propellant is dependent on chamber pressure, so although the available volume increases as the projectile moves along the bore, the rate of gas production is so rapid that the pressure continues to increase until the projectile has moved approximately 10 % of the bore length. The peak pressure reached can be as high as 600 MPa. The pressure then drops and by the time the projectile has reached the half-way point of the bore in most gun types, the propellant has been entirely consumed. The pressure continues to fall, but the fall is less rapid because the acceleration of the projectile is now less pronounced. At the instant the projectile leaves the muzzle, the pressure has dropped to about 20 % of its peak value and the acceleration is insignificant due to continuing friction which has had to be overcome. From the foregoing, it will be understood that the pressure/time curve (Figure 12-6) gives the impulse, which is exerted by the hot gases on the base of the projectile. The work done on the projectile, and hence the muzzle velocity, is determined by this impulse.

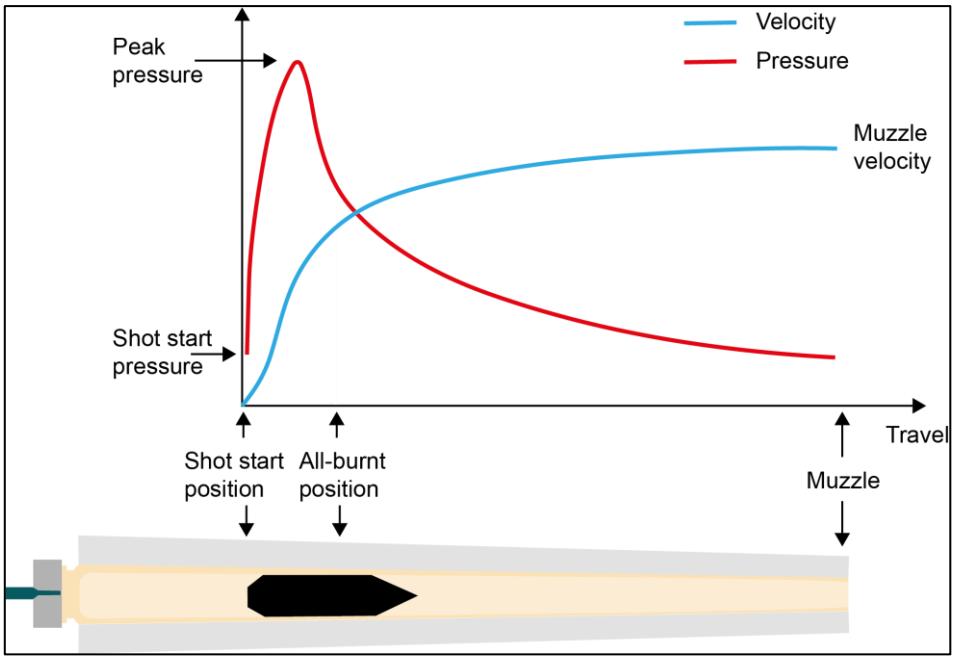


Figure 12-6 In-bore pressure versus distance travelled by the projectile

12.6 GUN PROPELLANT THERMODYNAMICS

12.6.1 Specific Energy F

The work capacity of a propellant is called the specific energy or force constant ('impetus' in the USA) and is designated F. Its value is calculated from Equation **Error! Reference source not found.**.

where n is the number of moles of gas produced by 1 g of propellant, $\overline{M}$ is the mean molar mass of the gas produced (g mol^{-1}), R is the gas constant (J K^{-1} mol^{-1}), and T_o is the adiabatic flame temperature (K).

The force energy is not measured in units of force but in units of energy per unit mass, or 'specific energy'. These are the same units (J g^{-1}), which are used to quantify Q, the heat of explosion, but the value of F for a given propellant is much smaller than Q. The work capacity depends on the quantity of the essential working fluid produced (in this case a mixture of gases) as well as on the heat available. However carefully the respective output of heat and gas is optimised for a given application, the resulting internal energy of the gas cannot be entirely converted into the work done on the projectile and hence into kinetic energy. Nevertheless, the thermal efficiency of a modern gun, when expressed as energy absorbed in to kinetic energy of the projectile (32 %) compares well with that of an internal combustion engine (20 %), as illustrated in Table 12-10.

Table 12-10 Energy Conversion Values for a Typical Medium Calibre Gun

Energy Conversion	Energy Absorbed %
Translation of projectile	32.00
Rotation of projectile	0.14
Frictional losses	2.17
Total work done on projectile	34.31
Translation of recoiling parts	0.12
Translation of propelling gases	3.14
Heat loss to gun and projectile	20.17
Sensible and latent heat losses in the propelling gases	42.26
Total	100.00

The chemical energy of the propellant gives an approximate indication of the resulting velocity imparted to the projectile. If the efficiency of the gun is expressed in a simplistic way as η then:

$$WQ\eta = \frac{mv^2}{2} \qquad \textbf{(12-2)}$$

where Q is the total chemical energy of the propellant, in J kg^{-1}, W is the propellant mass in kg, m is the projectile mass in kg, v is the muzzle velocity of the projectile in m s^{-1}.

Rearranging this equation gives:

$$v = \frac{2WQ\eta}{m} \qquad \textbf{(12-3)}$$

The range of velocities required for different kinds of weapon is from about 300-1500 m s^{-1}. The value of Q for various propellants differs by a factor of no more than 1.5 and the same is true of η, for rifled weapons. It follows that the ratio of propellant mass to projectile mass must widely vary. In fact it ranges from 1:50 in pistol cartridges to nearly 1:1 in high velocity tank gun rounds.

12.6.2 Calorimetric Value and Flame Temperature

The parameter Q of a propellant, hitherto referred to as the heat of explosion (see 4.4.2), can be calculated in the same way as that of a single high explosive, as shown in Chapter 4. The symbol Q denotes a modulus value of the net heat lost to the surroundings by the explosion process, or in other words it is the heat of combustion ΔH with the sign removed. Thus:

$$Q = |\Delta H| = \Sigma\Delta H_f \text{ (products)} - \Sigma\Delta H_f \text{ (propellant ingredients)} \qquad \textbf{(12-4)}$$

where $\Sigma\Delta H_f$ refers to the sum of the standard heats of formation of the compounds involved. Strictly, the value of Q should be called the 'heat of explosion' if calculated or 'calorimetric value' if measured experimentally. The latter term will be used for simplicity. From thermochemistry, the process of propellant combustion can be represented thus:

$$\text{Propellant} \rightarrow \begin{cases} \text{gaseous products} \\ \text{water (treated as liquid by convention though gaseous in fact)} \\ \text{heat energy Q} \end{cases}$$

It can be seen that the force (F) of a propellant is proportional to the product of the pressure of the gas mixture and the volume which it occupies, i.e. F = PV.

In turn, the value of PV is given by the basic equation of state for an ideal gas at up to moderately high temperatures.

$$PV = nRT \qquad \textbf{(12-5)}$$

where n is the amount of gas (moles) produced by unit mass of propellant, R is the molar gas constant, T is temperature (K).

In order to conform to usage in internal ballistics, the symbol T becomes T_o. It represents another important parameter of a propellant, the adiabatic flame temperature (again expressed in Kelvin). This is defined as the maximum

thermodynamic standard state temperature ideally achievable under adiabatic conditions.

The value of T_o for a given propellant composition is related to the chemical energy Q by the equation:

$$T_o = \left(\frac{Q}{\Sigma \overline{C_v}} \right) + 298 \qquad \textbf{(12-6)}$$

where $\Sigma \overline{C_v}$ is the sum of the mean molar heat capacities of the combustion products (at constant volume). For conventional propellants the value of the expression $\Sigma \overline{C_v}$ does not vary greatly, so T_o is approximately proportional to Q. The value of T_o is of considerable importance to the ballistician as a factor in the calculation of the force constant. Moreover, to the gun systems designer it is of importance in itself because it plays a large part in determining the characteristic performance of the gun in relation to heat transfer, bore erosion and muzzle flash. Therefore, since T_o depends on Q it is necessary to understand the way in which this is controlled by the combustion chemistry.

12.6.2.1 Oxygen Balance

All the major ingredients of propellants are essentially organic in nature, and are composed of carbon, hydrogen, nitrogen and oxygen. Thus the atomic composition of the propellant can, like that of its constituents, be represented by the general formula $C_aH_bN_cO_d$.

This implies that 'd' moles of oxygen atoms are available to oxidise the fuel elements present, namely 'a' moles of carbon atoms and 'b' moles of hydrogen atoms, more or less completely to oxides of carbon and to water respectively.

The dominant term in the thermochemistry Equation (12-4) is $\Sigma \Delta H_f$ (products). In fact, if small quantities of methane, ammonia, nitrogen dioxide etc. are ignored, this term comprises:

$$p\Delta H_f (CO) + q\Delta H_f (CO_2) + r\Delta H_f (H_2) + s\Delta H_f (H_2O)\ (liq) + t\Delta H_f (N_2) \qquad \textbf{(12-7)}$$

where p, q, r, s and t are the numbers of moles of CO, CO_2, H_2, H_2O and N_2 that make up the composition of the products.

The ratios p:q and r:s vary with propellant composition and are chiefly dependent on the oxygen balance (see 4.3.1). If the oxygen balance is high, these ratios will be smaller, and vice versa. The heats of formation of CO_2 and H_2O are considerably higher than those of CO and H_2 respectively. Hence a high oxygen content increases the value of Q, as shown in Figure 12-7.

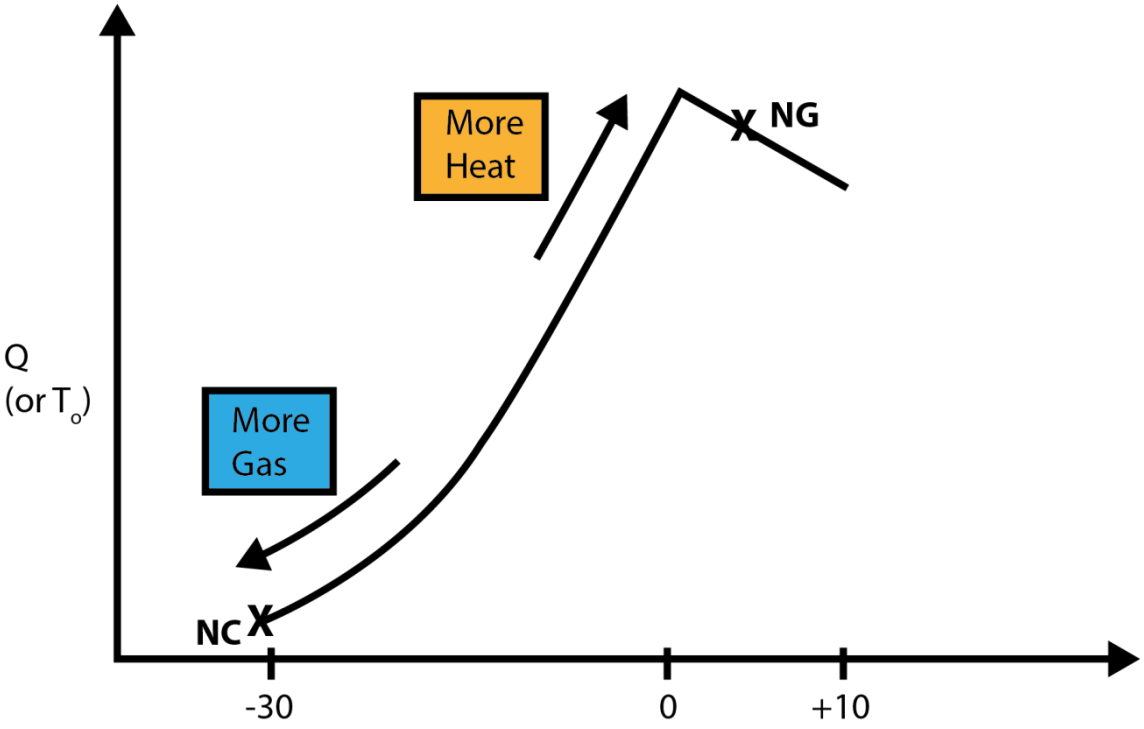


Figure 12-7 Comparison between oxygen balance and Heat of Explosion Q

It follows that single-base propellants derived from NC with 13.3 % N will be correspondingly richer in oxygen, and more energetic, than propellants derived from NC of lower N content. In some compositions a compromise requirement is achieved by blending two different grades of nitrocellulose.

In fact, all gun propellants are formulated to be deficient in oxygen and normally have oxygen balance values within the range -20 to -40 %. The reason for this is to ensure that the flame temperature is not too high, as it would be if the propellant had a zero oxygen balance, and that not too much hydrogen gas is produced, thereby increasing both flash and barrel erosion.

Of the three traditional basic ingredients of gun propellants, NC and NQ are heavily oxygen-deficient but NG has a slightly positive oxygen balance. The oxygen balance of double- and triple-base propellants is therefore very sensitive to the percentage of NG present and the adjustment of this percentage provides a second way of obtaining the required oxygen balance. An example of this can be seen with propellant types cordite-N and NQ. A difference of 2 % in the NG content causes a difference of 15 % in the respective calorimetric values.

A third way to adjust the calorimetric value (Q) of a propellant is by the use of an appropriate additive. Such additives are called coolants. A coolant, in this connection is a substance that absorbs heat when it decomposes during combustion. The original stabiliser, mineral jelly, doubled in this role and so does carbamite. Dinitrotoluene represents 10 % by mass of the artillery propellants NH and FNH and this accounts for the conveniently low flame temperatures of these compositions. Dinitrotoluene also imparts a moisture-repellent quality to propellants. The liquid plasticisers such as dibutyl

phthalate, diethyl phthalate and glycerol triacetate double as coolants and are sometimes referred to as coolant-plasticisers.

To summarise the calorimetric value of a gun propellant composition can be adjusted by:

1. Varying the nitrogen content, and hence the oxygen content of the universal ingredient NC
2. Varying the proportion (if any) of NG
3. Including small amounts of non-explosive additives called coolants

12.7 Burning Characteristics

12.7.1 Propellant Ignition

The Ignition of solid propellant charges in guns is achieved by the direct impingement of hot gas as a flame on the surface of the propellant. The ignition process is essentially a thermal phenomenon, in which the propellant surface is heated from its initial temperature, Tp, to the ignition temperature, T_i, which is typically in the range 160 -175 °C. At this point explosive burning develops, with the rapid liberation of heat and gas. The initial heating is the result of conductive and radiative heat transfer from the primer flame to the hot surface of the propellant, aided by the contact of hot particles with the surface.

When propellant charges are ignited there are additional considerations, the main one being the ability of the flame front to move through the bed of propellant in a cartridge case or charge bag. For small charges such as found in small arms ammunition this poses little problem and the flash of flame from the percussion cap can reliably ignite the propellant in a controlled manner.

When large charges are considered such as in 105 and 155 mm ammunition a method must be found to assist in the flame front moving through the propellant bed in a controlled and consistent manner. This has led to two methods being employed, the first is to use a primer tube that is situated within a cartridge case and allows flame to be introduced throughout the propellant bed through holes along its length. An example of this arrangement is shown in Figure 12-8. This is particularly suited to propellant beds that are made from granular propellant where there will be a complex pathway between the packed grains. Ignition from one end, for example with a base pad igniter, can cause impinging flame fronts moving around the grains to produce localised pressure increase that affect the burning rate in an uncontrolled manner.

The second method allows a base pad igniter to be employed by having a bed of stick propellant with a structure of uncooked spaghetti. The flame can easily flow through the propellant following the channels between the grains. This is known as stick propellant.

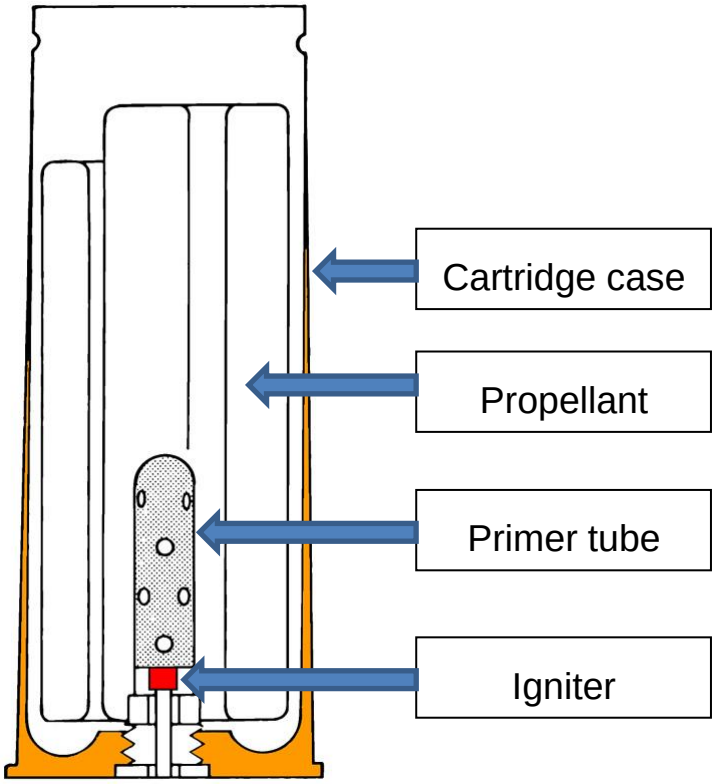


Figure 12-8 Cartridge case with primer tube

12.7.2 The Rate of Burning

The burning process for explosives, which includes gun propellants, is introduced in Chapter 7 for non-porous grains (see 7.2.4.1). The majority of propellants are non-porous in order to provide the utmost ballistic regularity. Certain types of small arms propellant, however, are manufactured by processes designed to produce porosity in the grains. When such a propellant is ignited, the flame penetrates the pores of the grains and so the rate of burning increases rapidly. This property is necessary in short-barrelled weapons such as pistols, and also in blank cartridges, which offer little resistance to the escape of gas and so cannot produce the pressure rises in the chamber necessary for fast burning.

As noted in Chapter 7, Vieille's Law can be described by equation:

$$r = a\,P_c{}^n \qquad \textbf{(12-8)}$$

where a is the pressure index. If Vieille's equation is written in the form:

$$\log r = \log a + n \log P_c \qquad \textbf{(12-9)}$$

and values of log r are plotted against the corresponding values of log P_c, then the pressure index, a, is given by the gradient of the resulting straight line and n is the antilog of the intercept. In order to obtain the values of burning rate (r) and pressure (P) to construct such a graph, an experimental method is required to measure the burning rate of a given propellant at various pressures. Clearly a compact grain, such as a sphere, is unsuitable for this purpose. If, however, the propellant is produced in the form of a 'cord', or 'strand', e.g. by extrusion, it can be burned from one end under controlled conditions. Suitable sensing devices will provide the time (t) taken by the burning surface to recede by a distance L so that the burning rate is given by: r = L/t.

In practice the 'strand' of propellant is inhibited by coating its surface with a flame-resistant film, leaving only the end exposed. Burning rate measurements are made in a strand burner. This consists of a closed, isobaric bomb, filled with an inert gas, such as argon, at a predetermined pressure and provided with electrical ignition and a means of measuring the time taken for the flame to travel down the strand. The propellant should be conditioned to a standard temperature (298 K) before use, because the rate of burning has a small but significant temperature dependence.

It should be noted that the parameter r is sometimes called the 'linear burning rate' to distinguish it from the 'mass burning rate', in the sense of units. However, unless the value of the pressure index, a, is exactly unity, the relationship of r to P_c is clearly not linear in the mathematical sense. In fact the value of a is not exactly 1 for most conventional propellants, as shown in Table 12-11, so the use of the prefix 'linear' can be misleading and is perhaps best avoided In this context. A more accurate interpretation of the word 'linear' in this context is that it represents the speed at which the flame front of an ignited surface travels in to the bulk of the propellant.

Table 12-11 Values of pressure index a for some propellants

Propellant	Pressure index a
WM	1.05
SC	1.04
N	0.93
NQ	0.89
NH	0.99
FNH	1.02

Given the burning rate, r, for a particular pressure it is possible to calculate the rate at which a grain of a particular shape and dimension will be consumed under (hypothetical) isobaric conditions, assuming also that ignition occurs instantaneously over the entire surface. The critical dimension, in the case of common shapes other than multi-tubular, is the 'ballistic size' (designated D), which is defined as the least thickness to be burnt through for complete combustion of the grain. For propellant in the form of ribbon and flake, D is the thickness. For cord, D is the diameter. For tube and slotted tube, D is the annular thickness. In all these cases the time taken by the combustion process is that in which the burning surface recedes by a distance of D/2, i.e. t - D/2r. However, recognised values of the burning rate coefficient (n) are based on the fact that the grain is burning all over and that its thickness is therefore decreasing at twice the rate of regression of a single area of surface. Therefore the 2 disappears from the denominator of the fraction, and t = D/B.

The French ballistician H. Muraour, prominent during the inter-war period, made several important contributions to the study of burning rates. One was that the burning rate equation $r = a\,P_c^{\,n}$could be replaced, for the high-pressure conditions obtaining in guns, by the linear relationship:

$$r = X + YP \qquad \textbf{(12-10)}$$

where X and Y are constants for a particular propellant. In practice, Vieille's equation is frequently changed to linear law for a maximum_pressure of 340 MPa, and the value of the burning rate coefficient (β) calculated for this purpose is denoted by β_1 where r is the total rate (mm s^{-l}) of reduction of thickness during burning.

Then:

$$r = \beta_1 P \qquad \textbf{(12-11)}$$

Table 12-12 Typical Values of β and β_1 for Some Propellants

Propellant	Non-linear burning rate coefficient, β	Coefficient in the linear law, β_1
	(r/P^2)	(r/P)
WM	1.81	2.02
SC	1.60	1.76
N	1.32	1.11
NQ	1.72	1.32
NH	1.37	1.34
FNH/P	1.20	1.25
AX	-	0.95

In Chapter 7 the mass rate of burning (see 7.2.2) was shown to be given by:

$$m^* = A_t \,.\, r \,.\, \rho \qquad \textbf{(12-12)}$$

where A_t is the burning surface area at time t.

Vieille's equation can now be adapted to the mass-burning rate to give:

$$m^* = kP^{\alpha} \qquad \textbf{(12-13)}$$

where k is a constant that takes into account the values of β_1, At and ρ.

When the parameter m* is applied to the gun, the isobaric condition under which the fundamental parameter r was measured no longer exists. By the time the propellant is ignited the pressure has already been raised by the explosion of the primer, and it continues to rise rapidly as the propellant releases heat and gas, until relieved by shot travel and completion of burning. The value of m* will therefore also change with time, but its rate of change will be related to the original parameter r.

For a given propellant burning at a defined pressure P, the values of r and ρ are constant. Therefore, it follows that:

$$m^* \;\alpha\; A_t \qquad \textbf{(12-14)}$$

It can be shown mathematically that by subdividing the volume of a given solid shape into a number of smaller shapes of the same proportions, a considerable increase in the total surface area is obtained. The effect of this increasing surface area by sub-division of grains is conveniently measured by the 'specific surface' of the charge.

$$\text{Specific surface} = \text{Total surface area of the grains}/v_o \qquad \textbf{(12-15)}$$

where v_o is the initial net propellant volume, i.e. mass of propellant/density.

For surface area in cm^2 and v_o in cm^3, specific surface is expressed in cm^{-1}. As the degree of sub-division of the charge increases, as measured by the number of grains per unit mass, the specific surface also increases, for a given grain geometry. In turn, this will increase the initial mass rate of burning. Thus finely divided charges burn more rapidly than coarsely divided ones, and their rate of gas output is correspondingly higher.

The foregoing treatment of burning rates applies to an idealised condition known as 'non-erosive burning'. This simplifying assumption is not strictly true. In practice the turbulent flow of hot gases over the burning surface can erode it faster than the normal rate of regression and at the same time the enhancement of heat conduction and radiation at the edges causes them to be rounded off as burning proceeds. These local accelerations in the burning rate are called 'erosive burning', but in proceeding to discuss grain geometry it is necessary to ignore this phenomenon and to maintain the original assumption.

12.7.3 Effect of Propellant Temperature on Burning Rate

The burning rate equation is more correctly written as:

$$^{[r]}T_p = \beta P^{\alpha} \qquad \textbf{(12-16)}$$

since the value of r is dependent on the initial temperature T_p of the propellant as well as on the chamber pressure. (This important discovery was made by Muraour). As the flame front travels into the propellant, each successive layer ahead of it is heated by radiation, conduction and the heat of its own decomposition until the ignition temperature is reached. The higher the initial temperature, the less heat is required to raise unit mass of propellant to its ignition temperatures so the values of r and m* will increase.

To determine the temperature dependence of the burning rate, r, an empirical equation is used:

$$r = \beta P^{\alpha} f(T_p) \qquad \textbf{(12-17)}$$

where $f(T_p)$ is an increasing function of T_p.

This function is approximately linear over the range –40 °C to +60 °C. Then:

$$f(T_p) = 1 + c(T_P - x) \qquad \textbf{(12-18)}$$

where T_p is in Kelvin, c is the temperature coefficient of the particular propellant composition, x depends on the reference temperature applying to β. Values of c are of the order of 0.002 per °C at 300 MPa.

The effect of charge temperature on burning rate is small in relation to the pressure dependence, but it is large enough to cause an appreciable difference in gun chamber pressures, and hence in muzzle velocities, at extremes of charge temperatures. For an indirect fire weapon of, say, 105 mm calibre, there

would be a difference of several hundred metres at extreme range. In the field, efforts are made to protect artillery cartridges against extremes of ambient temperature and the actual temperature of the charges is monitored and used in the computation of trajectories.

12.7.4 Grain Geometry and Surface Effects

The precise geometric form of the individual propellant grain in its unburned state is of great importance to the internal ballistics of the gun. The grain geometry governs the following factors:

1. Mass burning rate (m*)
2. Loading density (Δ)
3. Ignition efficiency

The dependence of mass burning rate on grain geometry is considered in the following sub-paragraphs.

- Solid forms. It is evident that solid propellant grains in the form of spheres, flakes or cord will undergo a decrease in surface area during burning. This behaviour is termed ‘degressive burning’ (sometimes called ‘regressive burning’), and it results in a decrease of m* with time at a theoretical constant pressure.
- Single-perforated forms. A tubular grain of propellant burns with maintenance of approximately constant burning area, because the surface of the perforation is increasing at approximately the same rate as that at which the outer surface of the grain is decreasing. This form of grain geometry is said to have a ‘neutral burning’ characteristic, resulting in a constant value of m* at a (theoretical) constant pressure. Tubular propellant is unsuitable for use in the form of long grains (sticks) because of the initial slowness of the inner surface to ignite, the erosive burning which occurs when it finally does so and the fact that it chatters due to pressure in its bore during burning.
- Slotted tube. The disadvantages of tubular grains can be overcome by slotting the tube during the extrusion process of manufacture. There is then no problem in using the propellant in the form of long sticks, which is common UK practice. However, the neutral burning characteristic is lost because the onset of burning widens the slot and decreases both the outer and inner burning surfaces. Slotted tube therefore behaves like a curled ribbon shape and burns degressively.
- Multitubular grains. The single perforation can be replaced by a larger number of holes, usually seven. In all multitubular grains, when the burning reaches the stage at which the perforations meet, the grain disintegrates into a number of longitudinal slivers. This is known as sliver-point, and the type of burning then changes from progressive to degressive. Like single-perforated (tubular) grains, multitubular ones are limited in their ratio of length to diameter because of ignition and erosion problems. The usual limiting ratio in 2.25:1.

12.7.4.1 The form function

The way in which the surface area, and hence the mass burning rate, of a particular shape of grain changes with time during burning can be calculated. The mathematic function that describes the process is called the 'geometrical form function'. Its standard expression is:

$$z = (1- f)(1 + \theta f) \quad \textbf{(12-19)}$$

where z in the fraction of grain mass burnt at a given instant, f is the fraction remaining, at the same instant, of the least original thickness, θ is the 'form coefficient' relating to the particular shape of the grain.

The numerical value of θ is positive for a degressive grain, zero for a neutral grain and negative for a progressive grain. Examples are +1 for long cord, zero for long tube and -0.172 for multitubular. Values of θ for other common shapes including slotted tube, ribbon and square flake, depend on the magnitude of their dimensions. Using these standard or calculated values of θ, the values of z for particular shapes of propellant can be calculated. This enables the ballistician to estimate the rate of gas production for any instant during combustion, and hence to predict the shape of the pressure/time curve for the propellant/gun combination. If the values of z are then plotted against the value of the changing surface area, A_t, at the corresponding instant (expressed as a fraction of the original area A_o) the characteristic burning behaviour of the various shapes is clearly seen (Figure 12-9). The curve for multitubular propellant does not show the change to degressive burning on slivering because it is based on a theoretical value of θ determined only up to sliver-point.

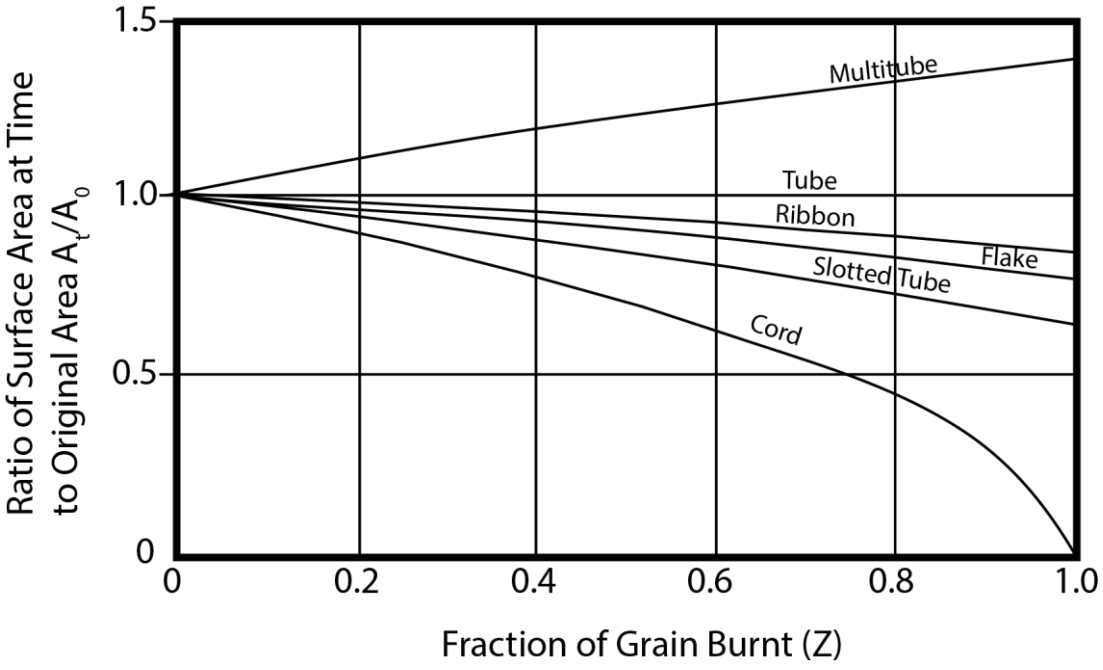


Figure 12-9 Variation of A_t/A_o with fraction of grain burnt

12.7.4.2 The choice of grain geometry

From the range of available shapes the ballistician selects one which, combined with the thermochemical and burning rate parameters of the composition, will give the required pressure/time curve in the gun. There are further considerations in making a choice between certain shapes. For small arms cartridges, small, compact grains make for easier and more compact loading than sticks, so SAA propellants are manufactured in the form of spheres, flakes or short, single-perforated grains. For larger calibres there is a choice between sticks and compact grains of the single- or multi-perforated type. Compact grains give a higher loading density, which is necessary for a gun designed to work at high pressure but there is a penalty of slower ignition because the flow of hot gas and particles from the much larger igniting device are impeded. Stick propellant is preferred in the UK for bagged charges because it imparts a rigid shape to the bag, thus assisting handling, and requires a smaller ignition device. For large calibre charges the diameter and cross-sections of the sticks can be mixed as an additional means of obtaining the optimum pressure/time curve in the gun.

12.8 CLOSED VESSEL TESTING

12.8.1 Determination of Force Constant

Although the force constant and other parameters are ultimately required for use in the design of guns and propellant charges, the gun itself is not a suitable apparatus to use in determining transient high pressures and their rate of change with time because of the rapid forward movement of the projectile, gas and burning propellant. A constant volume condition is required, and the apparatus that provides this is the 'closed vessel'. The current standard UK vessel consists of a thick steel cylinder, threaded and plugged at both ends and having a lined interior volume of some 700 cm^3 (Figure 12-10). A sample of propellant, usually up to about 140 g, is filled into the cavity, which also contains an electrical initiating device. A piezo-electric transducer that is connected to an oscilloscope gives a record of pressure vs. time, from which the maximum pressure P_{max} can also be read (Figure 12-11).

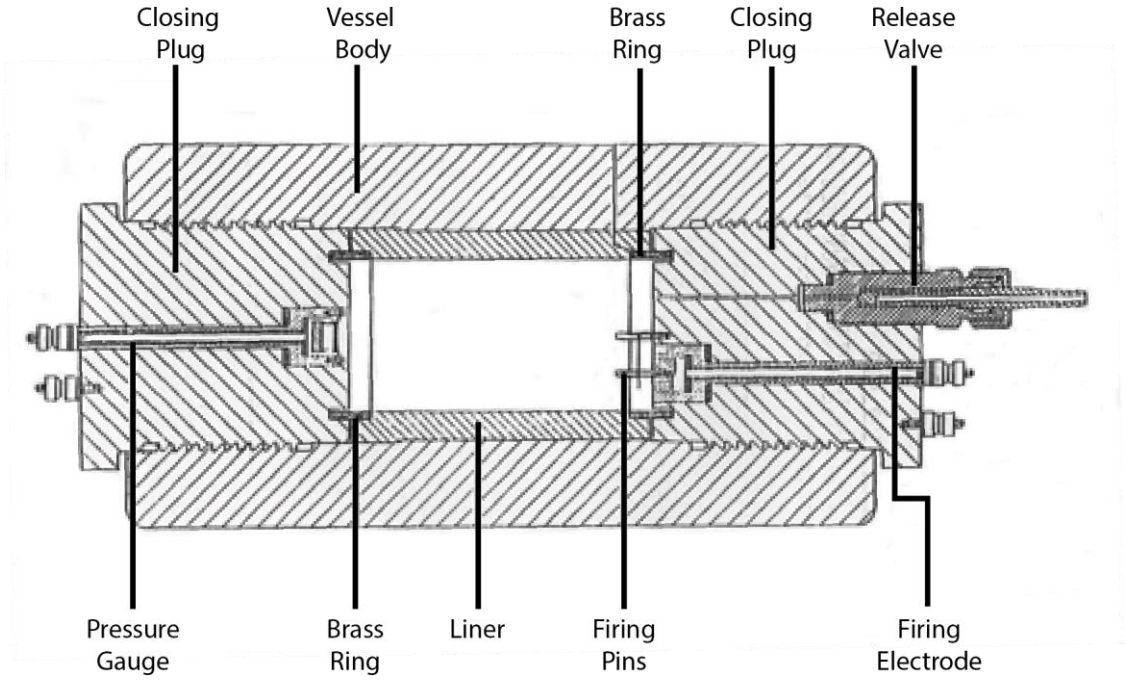


Figure 12-10 Diagram of Closed Vessel (UK Standard CV21)

More recently, smaller capacity closed vessels (100 cm^3) have been constructed with a modified internal geometry to improve signal output quality.

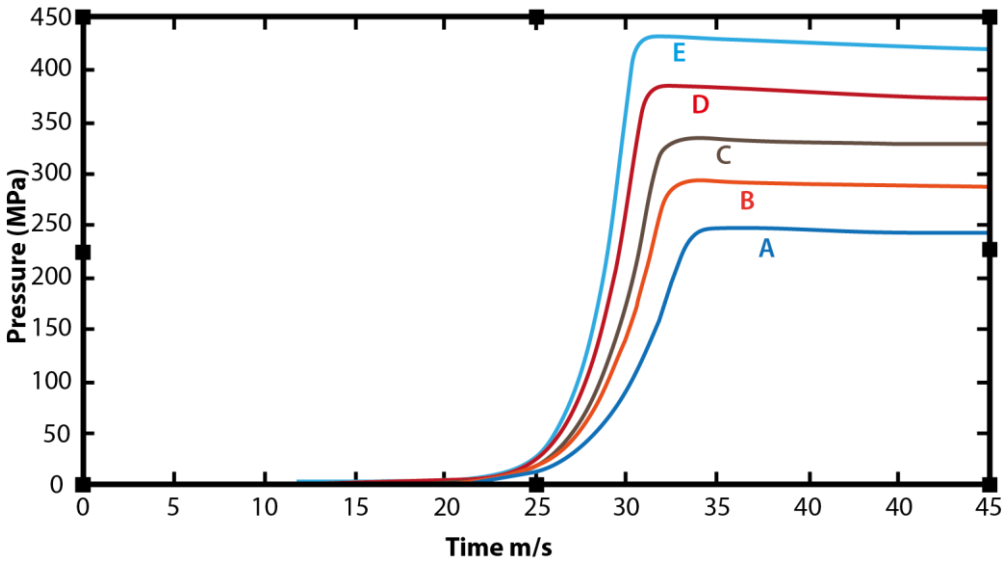


Figure 12-11 Example Pressure time curves at different loading densities[1].

The force constant F for a particular propellant can be calculated using the ideal gas law, Equation **(12-5)**. However, the simple gas law is not a suitable Equation of State (EOS) for conditions found in a gun or closed vessel. At high pressures it is necessary to take into account the volume of the gas molecules

themselves. A suitable EOS for closed vessel purposes is the Nobel-Abel equation:

$$P(V - b) = nRT \quad \textbf{(12-20)}$$

Where b is the co-volume (volume of gas molecule per gram). Substituting in the Force constant the equation becomes:

$$F = P_{max}(V - b) \quad \textbf{(12-21)}$$

where P_{max} is the maximum pressure produced by burning an accurately weighed sample of propellant in a confined space. Then V is the specific volume, i.e. the volume of the interior per unit mass of propellant, normally expressed in $cm^3\ g^{-1}$.

The Noble-Abel equation of state shown above has to be modified by a correction term for the heat lost to the vessel during propellant combustion:

$$F = \left(1 + \frac{k}{100}\right) P_{max}(V - b) \quad \textbf{(12-22)}$$

where k is the percentage of heat lost to the vessel at P_{max}.

A typical value of P_{max} in closed vessel work would be 240 MPa, so if (V - b) is equal to, say, 4.1, then F is in the region of 1000 $J\ g^{-1}$.

The closed vessel (CV) is used routinely for the quality control of 'lots' of propellant during manufacture. The force constant is markedly affected by small variations of moisture content and residual solvent. In order to check whether the effect of such variations has been nullified by adequate blending, samples of the propellant are tested in the CV and parallel tests are done on a standard sample.

In order to obtain an absolute value for the force constant of a propellant the modified Noble-Able equation is first rearranged to give:

$$\left[P_{\max}\left(1 + \frac{k}{100}\right)\right].\frac{1}{\Delta} = b.P_{\max}\left(1 + \frac{k}{100}\right) + F \quad \textbf{(12-23)}$$

This expression is of the form y = mx + c and therefore a plot of:

$$\left\{\left[P_{\max}\left(1 + \frac{k}{100}\right)\right].\frac{1}{\Delta}\right\} \text{ against } \left\{P_{\max}\left(1 + \frac{k}{100}\right)\right\} \quad \textbf{(12-24)}$$

at different loading densities will produce a straight line with an intercept of F on the y-axis. The co-volume (b) of the propellant can also be determined from this plot since this will be the gradient of the line.

12.8.2 Determination of Vivacity and Quickness

The function of gun propellants is to impart kinetic energy efficiently to the projectile. The amount of kinetic energy thus acquired by the projectile determines its muzzle velocity. A plot of pressure vs. time for a particular combination of gun and propellant gives an indication of two of the parameters of the propellant, which are of importance to the ballistician and gun systems designer.

The magnitude of the impulse integral, as we have seen, gives a measure of the work capacity, or force constant, of the propellant.

The shape of the curve is determined by the way in which the mass rate of burning of the propellant varies under the changing conditions of pressure, temperature, grain size and grain shape which occur in the gun during the time between ignition and the 'all-burnt' point. This behavior, which depends in a complex way on several factors, is called the 'vivacity' of the propellant. It is not amenable to direct calculation and must be determined experimentally.

The shape of pressure-time curve, which is sought by the gun systems designer, represents a compromise between conflicting ballistic requirements. On the one hand a high ratio of energy/bulk in the propellant is necessary for compactness of the ammunition, and this entails a high force constant and the associated large impulse integral. On the other hand, the maximum permitted pressure is limited throughout the length of the gun by the need of mobility, which places a constraint on weight and hence on strength. Furthermore it is necessary to keep the all-burnt point well back in the bore to avoid the round-to-round variation of muzzle velocity that would result from a high pressure at the muzzle. In order that the curve shall conform to these constraints, careful optimisation of the force constant and vivacity is necessary, followed by rigorous quality control of the manufactured propellant. As already stated, vivacity depends on several factors, and one of these, grain geometry, has already been discussed. The form function Equation (12-19) relates only to the geometrical shape of the grains and not generally to their size. However, the grain size as well as the grain shape determines the initial burning area of a charge, which is described by the specific surface of the propellant. In general a finely divided charge burns more rapidly than a coarsely divided charge of the same composition. The ballistic size D must therefore be taken into account.

A further factor is the composition of the propellant. This determines the kinetics of propellant combustion as a function of temperature and pressure. The rate constants for thermal decomposition, which apply to the main propellant constituents, and their heats of explosion, are the determining factors. Broadly, in the absence of reliable kinetic data in the burning phase, we can predict that high vivacity will be found in more energetic propellants.

In the expression of the burning rate law of Vieille, Equation (12-8), the index n is approximately 0.9 for conventional gun propellants, but for the present purpose it is taken to be 1.0 and the coefficient is changed to β_1 to denote the

change to linear law. Then at a selected pressure P_s (the action pressure), which is less than P_{max}:

$$\beta_1 \ P_s = -D\left(\frac{df}{dt}\right) \quad \textbf{(12-25)}$$

Therefore:

$$\frac{\beta_1 P_s}{D} = -\left(\frac{df}{dt}\right) \quad \textbf{(12-26)}$$

The term df/dt is related, as seen earlier, to the form function z and β_1/D is the vivacity of the propellant sample. Rearranging the form function equation [z = (1-f) (1+θf)] and solving the quadratic for f gives:

$$\mathrm{f} = -\frac{1}{2\theta} + \frac{1}{2} \pm \frac{\sqrt{(1+\theta)^2 - 4\theta \mathrm{z}}}{2\theta} \quad \textbf{(12-27)}$$

Differentiating with respect to time t then gives:

$$\frac{\mathrm{df}}{\mathrm{dt}} = \frac{-\mathrm{dz}}{\mathrm{dt}} \cdot \frac{1}{\sqrt{(1+\theta)^2 - 4\theta \mathrm{z}}} \quad \textbf{(12-28)}$$

From a consideration of the pressure in a closed vessel as a function of the fraction of propellant consumed, it can be shown that:

$$z = \frac{(1+x)P}{(P_{max} + xP)} \quad \textbf{(12-29)}$$

where $x = \frac{b - 1/\rho}{1/\Delta - b}$

Most propellants have co-volumes (b) of approximately 1 $cm^3\ g^{-1}$ and densities (ρ) of about 1.5 g cm^{-3}. Therefore, for typical Closed Vessel loading densities (Δ) x is very much less than 1, and hence:

$$\mathrm{z} = \mathrm{P}/\mathrm{P}_{max} \quad \textbf{(12-30)}$$

Therefore, at a pressure P_s:

$$\frac{\mathrm{dz}}{\mathrm{dt}} = \left[\frac{\mathrm{dP}}{\mathrm{dt}}\right]_{\mathrm{P_s}} \cdot \frac{1}{\mathrm{P}_{max}} \quad \textbf{(12-31)}$$

and

$$\frac{\mathrm{df}}{\mathrm{dt}} = -\left[\frac{\mathrm{dP}}{\mathrm{dt}}\right]_{\mathrm{P_s}} \frac{.1.}{\mathrm{P}_{max}} \frac{1}{\sqrt{(1+\theta)^2 - 4\theta\, \mathrm{P_s}/\mathrm{P}_{max}}} \quad \textbf{(12-32)}$$

Therefore Vivacity is expressed as:

$$\frac{\beta_1}{D} = \left[\frac{dP}{dt}\right]_{P_s} \frac{.1.}{P_s P_{max}} \frac{1}{\sqrt{(1+\theta)^2 - 4\theta P_s / P_{max}}} \quad \textbf{(12-33)}$$

The expression $[{}^{dP}/_{dt}]_{P_s}$ is deduced from closed vessel results, as follows. The closed vessel gives a curve of pressure vs. time as shown in Figure 12-11. The differential of this curve, dP/dt, is then plotted against P, giving a new curve $\frac{{}^{dP}/_{dt}}{P}$ as shown in Figure 12-12.

At pressure P_s, (the action pressure) which is selected with regard to the particular gun/propellant combination concerned, the value of $[{}^{dP}/_{dt}]_{P_s}$ is obtained as shown in Figure 12-12. The value of P_s, P_{max}, $[{}^{dP}/_{dt}]_{P_s}$ and θ can then be substituted into the above equation to give the vivacity. In fact for most propellant grain shapes of interest θ = 0, and the expression for what is termed the 'dynamic vivacity' then simplifies to:

$$Dynamic\ Vivacity = \left[\frac{dP}{dt}\right]_{P_s} . \frac{1}{P_s P_{max}} \quad \textbf{(12-34)}$$

(units of $Pa^{-1}\ s^{-1}$)

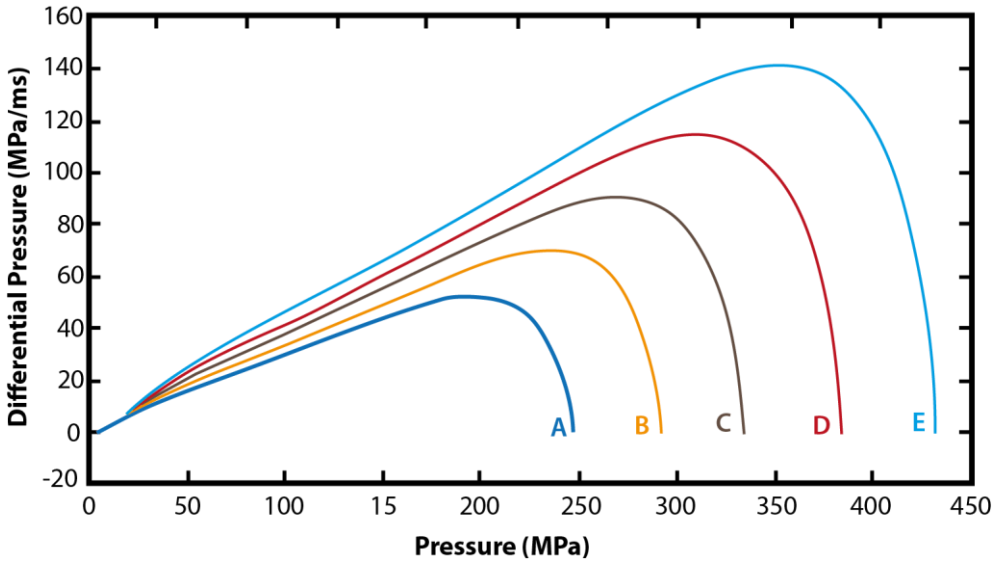


Figure 12-12 Example plot of differential pressure versus pressure curves at different loading densities(1).

A more general vivacity that is easy to determine using a closed vessel can be defined thus:

$$Vivacity = \left[\frac{dP}{dt}\right]_{mean} . \frac{1}{P_{max}} \quad \textbf{(12-35)}$$

(units of s^{-1})

where the mean value of the differential is measured over a defined pressure range below P_{max} (usually 0.25 P_{max} to 0.55 P_{max}).

When the closed vessel is used routinely for comparing the vivacity of a propellant lot with that of a standard sample, a 'relative vivacity' is determined. This is usually expressed as a percentage, in the following way:

$$Relative\ Vivacity = \frac{vivacity\ of\ propellant\ x100}{vivacity\ if\ standard\ propellant} \quad \textbf{(12-36)}$$

A further propellant parameter sometimes required is called 'quickness'. This word is sometimes used, erroneously, as being synonymous with vivacity. In fact, quickness is the product of the two parameters already described, i.e. force constant and vivacity.

$$\text{Quickness} = \frac{\text{F x } \beta_1}{\text{D}} \quad \textbf{(12-37)}$$

When closed vessel expressions for relative force constant and vivacity are multiplied together, the P_{max} term disappears. Therefore CV testing thus can establish the relative quickness of two propellants:

$$\frac{\text{Quickness of propellant X}}{\text{Quickness of propellant Y}} = \frac{[dP/dt](X)}{[dP/dt](Y)} \quad \textbf{(12-38)}$$

A closed vessel can also be used to determine burning rate (r) at high pressures by measuring P_{max}, P and dP/dt and substituting the values in an expression for r derived from the fact that:

$$r = -D . \frac{df}{dt} \quad \textbf{(12-39)}$$

12.9 PROPELLANT NOMENCLATURE

The examples of propellant compositions in this chapter are limited to British or imported types, but the nomenclature of even this small number is a complicated subject. In dealing with British propellants a clear distinction must be made between small arms types and artillery types. In small arms types the

frequently recurring letter N has a separate act of meanings. Thus NRN is Nobel Rifle Neonite, NNN is Nobel Nitro-Neonite and NPP is Nobel Parabellum Powder.

In the designations of post-1941 British artillery propellants the letter N is again commonly found, but has a different and unambiguous meaning. It signifies that the composition contains nitroguanidine (picrite), generally to the extent of 55%, and is therefore classed as ‘flashless’. Hence it may be helpful to remember N as being an abbreviation of ‘nolite’, which is its origin. Various letters prefixed or suffixed to N by Land Service or Naval Service users have specific meanings as follows:

Prefix:

M ‘modified’ and as applied to N-type propellants in Naval Service this means that the propellant is made by the semi-solvent process.

Suffixes:

F	containing nitrocellulose made from wood
/K	containing potassium cryolite
L	lower calorimetric value then the standard N composition
/P	containing 1 % potassium sulphate
/2P	containing 2 % potassium sulphate, and so on
Q	higher calorimetric value than the standard N composition
B	blended nitrocellulose

Propellants N and NQ both contain 55 % (w/w) nitroguanidine, NQ having the higher calorimetric value. As another example, the naval propellant MNF/2P has the following composition, some of which is deducible from the designation.

Parts by weight:

16.5	nitrocellulose, made from wood and contains 12.2 % nitrogen
21.0	nitroglycerine
55.0	nitroguanidine
7.5	carbamite
2.0	potassium sulphate

It should be noted that the original American propellants NH and FNH, although having been given British suffixes such an P or 3P, were not designated in accordance with the basic British system and do not, in fact, contain nitroguanidine. Propellants NH (Non-Hygroscopic) and FNH (Flashless NH) were manufactured in the United Kingdom by Nobels Explosive Company Limited under the more modern designations M6 and M2 respectively, for use in US-manufactured guns, some of which are British army equipment.

The latest British Gun propellants, the X series, mostly contain RDX and the basic designations are in both alphabetical and chronological order, followed by the letter X, e.g. AX, BX etc. The whole series are sometimes called Rowanites, a name derived from the initials of Royal Ordnance Waltham, Abbey.

In both the N series and X series a second suffix is separated from the composition designation by an oblique stroke, and denotes the geometrical shape of the grain, except in the case of cord, which has no such suffix. The meanings of the second suffixes are as follows:

/MT or
M multitubular. A number may be added, e.g. MT7 or MT19, to denote the number of holes in the grain
/R ribbon
/S slotted tube
/T tubular, i.e. single-hole
/Z scroll, which is paper-thin sheet of double-base propellant, usually SC.

To give an indication of the most ballistically important dimension of the grain, i.e. the thickness that must be burned through for complete combustion, some digits are added after the grain geometry suffix. Until a few years ago grain size was generally indicated in thousandths of an inch. Thus cord was expressed as the diameter (e.g. WM 029), tube and slotted tube by the external and internal dimensions (e.g. N/S 164-048), multitubular by the space between the holes, i.e. 'web size' (e.g. N/2P/M 055), ribbon by the width and thickness (e.g. MNQF/R 032 x 160) and scroll by the thickness of the sheet. Certain double-base small arms propellants were expressed in hundredths of an inch (e.g. CDT 5-2). Because ammunition is stored for many years in peacetime, much of it will continue to carry such markings long into the future.

More recently, however, propellant sizes have been metricized by the use of a two-digit centimetre system prefixed 'M' to distinguish it from the three-digit inch system. In both systems the existence of a decimal point before the digits is assumed. An example of the metric systems is N M04, i.e. propellant N of cord diameter 0.04 cm. Some examples of inch sizes and their metric equivalents are shown in Table 12-13.

Table 12-13 Comparison of Imperial Vs. Metric Propellant Nomenclature

Propellant	Size	
	Imperial	Metric
MNF/2P/S	164-048	M43-12
MNLF/2P/M	032	M08
NQ/S	207-047	M53-12
NQ/M	047	M12
NQ/M	044	M12
N	017	M04
SC/Z	008	M02
HX MT19	-	M05

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CHAPTER 13
ROCKET PROPELLANTS

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13 ROCKET PROPELLANTS

Authors – D Fossey (The Falcon Project Ltd) and P P Gill (Cranfield University)

13.1 AWARENESS SUMMARY

Solid rocket propellants consist of a polymer (either nitrocellulose or polyurethane) plus additional explosives and additives, carefully formulated to burn smoothly without detonating to produce hot gases to propel a rocket.

All present day solid rocket propellants are more energetic than the best liquid monopropellants, and are fully capable of providing the main propulsion for all kinds of rockets and missiles up to and including ICBM and satellite launch vehicles. In terms of energy the best solid propellants are almost equal to the best packageable bipropellants, though not to the cryogenic ones. For military purposes the advantages of solid propellants outweigh their disadvantages, and for that reason the vast majority of military rockets, whatever their size and purpose, utilise solid propellants. In space applications the balance is more even.

The general advantages of solid rocket propellants are as follows:

a. They favour simple and lightweight designs of motor.
b. They permit instant readiness of a missile system.
c. They present little or no toxic vapour hazard and are therefore safer to store and handle than liquid propellants.
d. They have good chemical and thermal stability, and therefore long shelf life (routine surveillance is necessary however).
e. They are of high density, giving a good energy/bulk ratio ('volume impulse').

The general disadvantages of solid rocket propellants are as follows:

a. They are expensive, being complex mixtures which require lengthy manufacturing processes.
b. Once ignited, solid propellant motors cannot be shut down, and it is difficult to change the level of thrust during the burning time.
c. Solid propellants cause extremely severe heating of the exhaust nozzle, necessitating either the use of expensive nozzle materials or the suppression of the maximum achievable combustion temperature and therefore maximum specific impulse (see 13.6.3).
d. The rocket motor is also the propellant container; therefore the amount of propellant contained in a missile may be limited by the overall system design requirements.

As with liquid propellants, the physical and chemical characteristics of solid propellants vary considerably and each type has its own additional disadvantages.

Apart from categorisation by the method of fabrication, solid rocket propellants fall into two broad divisions according to their chemistry; Double-base (alternatively called 'homogeneous' or 'colloidal') and are nitrocellulose (NC) based, and composite propellants. Historically, the Double-base type propellant evolved from cordite gun propellants in the 1920s, and was followed by composite propellants some twenty years later. Vast amounts of research and development have been carried out on both types since then to improve their safety, reliability and performance.

Double-base propellants, in their simplest forms, are very similar to those of the same name used in ammunition for certain small arms and guns. One of the base ingredients is the nitrated natural polymer nitrocellulose (NC) and the other is an energetic plasticiser, normally nitroglycerine (NG), both of these substances being nitrate esters. Certain additives are normally required, the most essential of which is a chemical stabiliser. Nitrocellulose burns smokelessly, if formulated correctly the Double-base propellant will also burn smokelessly. This smokeless burn enables stealthily rocket systems to be manufactured. The disadvantaged of Double-base propellants are: (i) they have low energy density and therefore performance; (ii) the nitrocellulose polymer has poor strain capability, particularly at low temperatures, meaning the mechanical properties of Double-base propellants can be a key failure mode for the rocket; and (iii) NC propellants have poor vulnerability characteristics in storage and use.

Composite propellants are two-phase mixtures comprising a synthetic polymeric matrix (usually a polyurethane) which serves both as a fuel and a binder, together with an oxidant, usually the inorganic salt ammonium perchlorate (AP). The advantages of composite propellants are: (i) they have a high energy density and therefore performance; (ii) the polyurethane polymer has a very good strain capability meaning composite propellants have much better mechanical properties than Double-base propellants; and (iii) composite propellants have very good vulnerability characteristics in storage and use. The disadvantage of composite propellants is that they are not stealthy. The combustion of ammonium perchlorate generates hydrogen chloride (HCl), a white smoke. An ammonium perchlorate composite propellant was used as the solid rocket boosters for the US Space Shuttle systems, and produced tonnes of white HCl during launch.

In order to achieve a high performance with reduced smoke, propellants using nitramines (RDX and HMX) have been developed. These propellants typically contain no aluminium, a low AP content ~10 % (w/w), 50-85 % (w/w) nitramines, with hydroxyl-terminated polybutadiene or polyurethane as a binder. These low smoke or reduced smoke propellants produce no primary smoke, while secondary smoke (created when water vapour is present) appears only at low ambient temperatures. The two disadvantages of reduced smoke are: (i) the burning rate of the nitramines are much lower than ammonium perchlorate, this means the range of the rocket is likely to be limited compared to a composite

propellant; and (ii) the high energy reduced smoke composites such as the nitrate ester plasticised elastomers (NEPE) have poor vulnerability characteristics.

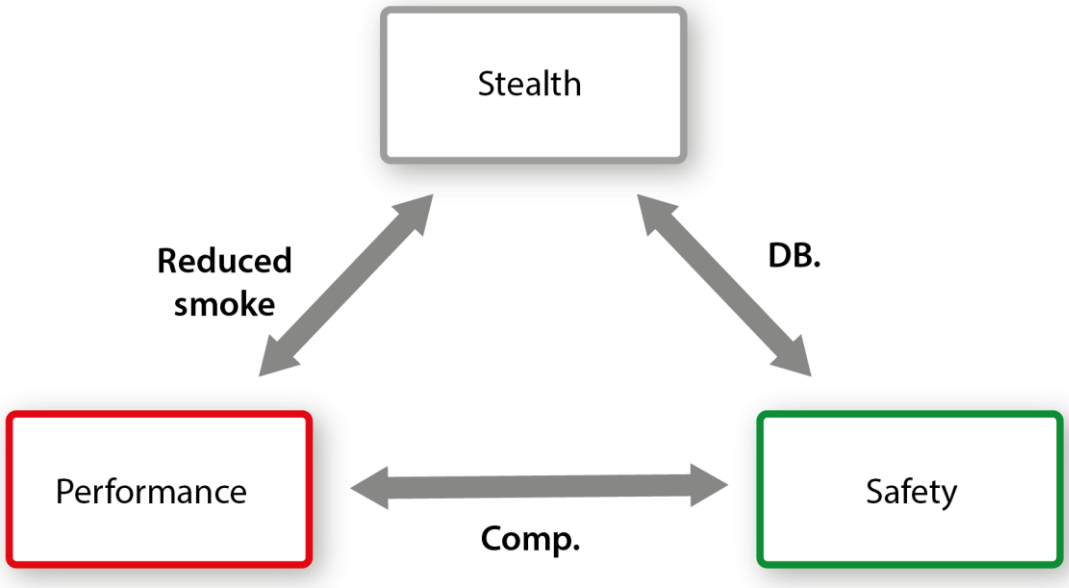


Figure 13-1 Diagram showing the design compromises of solid rocket propellants and the roles of the three main types of solid rocket propellants

Today the rocket propellant chemist must make a design compromise and choose any two of the three requirements stealth, performance or safety. Figure 13-1 shows that Double-base propellant are the best choice for stealth and acceptable safety; composite propellants are best for high performance and safety; and reduced smoke composites are best for high performance and stealth. No single propellant can fulfil all three requirements.

13.2 SOLID ROCKET PROPELLANTS

13.2.1 Grain Shape and Inhibition

All solid rocket propellants are mixtures formulated and manufactured in such a way that they will burn smoothly within the motor, without any tendency to detonate. Their mode of combustion is similar to that of gun propellants, but the rate of burning, in terms of both linear regression and mass burning rate (see 7.2.2), is much lower, mainly because of the lower operating pressure in a motor (~10 MPa) compared with a gun (up to 600 MPa). Like gun propellants, rocket propellants are manufactured in the form of geometrical shapes called grains, regardless of size. Almost all rocket propellant grains are basically cylindrical in shape. They may contain one or more lengthwise perforations called conduits. In a small, simple missile for use at short range the charge may consist of a bundle of tubular grains (sticks) which burn all over their surface.

The motor case is therefore exposed to the flame but in the short time of burning (<1 second) it will not be burned through.

Alternatively, the same large surface area can be provided by one suitably perforated grain of equal weight, and the larger the missile and the longer its burning time, the more likely this is to be so. A single grain is not usually intended to burn on its outer surface, but only in its conduit(s) and/or on its rear surface. In this way the head end and sides of the motor case are protected from the flame until the last fraction of a second of burning time. To achieve this the outer surface of the grain is prevented from igniting, in one of two ways:

a. The grain can be bonded to the motor case (case bonded).
b. It can be contained in a tight fitting, non-flammable sheath, called an 'inhibitor' which is bonded to the grain and is a sliding fit within the motor case.

The first method is preferable, because less of the valuable space inside the motor is wasted by holding a volume of non-energetic material, in this case an adhesive. There is, however, a difficulty in that the rocket may become conditioned to any ambient temperature from –55 °C to +70 °C, and the coefficient of thermal expansion of the case is very different from that of any solid propellant. Therefore case bonding is practicable only if the propellant material is sufficiently elastic or plastic to conform to the changing dimensions of the bonding surface without either itself cracking or shearing the bond. In the event of either mode of failure, the extra area of propellant surface thus allowed to burn would increase the mass burning rate to well above its designed level, the chamber pressure would exceed the relatively narrow safety margin and the motor would burst.

For all but the smallest missiles the propellant charge is likely to consist either of one case bonded or otherwise inhibited grain, or of two such grains in tandem. A single grain, or the rearmost of a pair, is required to have a high mass rate of burning so that the motor provides high thrust for the launch of the missile. It therefore has one or more conduits, perhaps of complex cross section, in order to provide adequate burning surface area in addition to the rear surface, which is not usually inhibited (Figure 13-2).

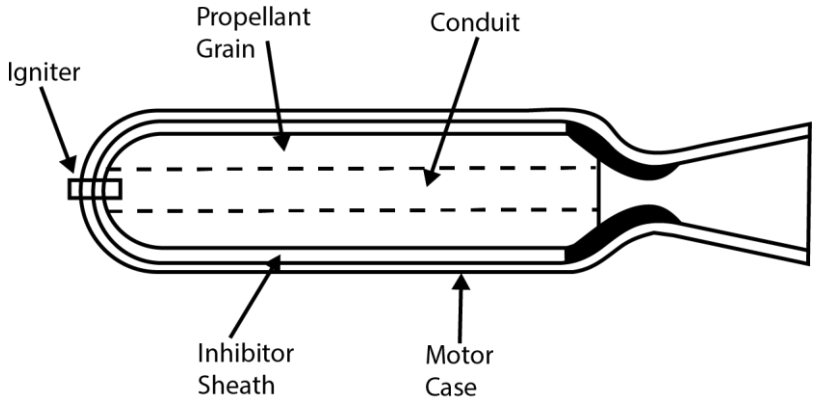


Figure 13-2 Rocket motor containing inhibited radial burning propellant grain (diagrammatic)

Since the burning surfaces within the conduit(s) regress in mostly radial directions, such a grain is called radial burning. If the motor contains a second grain this is likely to be for sustaining the speed of the missile over a longer period of thrust. A sustainer grain may not have any conduits, being intended instead to burn on its rear surface only. This is called ‘end burning' or 'cigarette burning’. A pair of grains, boost and sustainer may consist of the same propellant composition or may be chemically quite different. They may be separately loaded into the motor, or joined together end to end. Alternatively, one grain may serve as both boost and sustainer, having a conduit and/or slits at the rear end but not in the front portion.

Not all propellant grains are cylindrical. Certain boost grains, for example as found in shoulder launched anti-tank or surface to air missiles, which burns out in tenths or hundredths of a second are made of thin layers of propellant combined together in such a way as to expose a maximum surface area to the igniter flame. This type of configuration is used if the grain is required to burn out before the missile has left its launch tube and before the sustainer grain (if any) is fully ignited. This type of grain or motor is designated ABOL (all burnt on launch).

Cylindrical grains vary greatly in their diameters, from a few centimetres to over a metre, and their weight varies accordingly by five or six orders of magnitude.

13.2.2 Double-base Propellants

13.2.2.1 Extruded Double-base (EDB) propellants

Double-base propellants consist of mixtures of nitrocellulose and nitroglycerine and take the form of a fairly rigid, colloidal material of density ~1.6 g cm^{-3}. As used in guns, such propellants are manufactured by extrusion, and this process can be applied to rocket motor grains up to a limiting diameter of about 35 cm. Such extrusions are suitable for air-to-air missiles (~5 cm), decoy types (~8 cm) and Giant Viper (13 cm). Typically, an extruded Double-base propellant (Table 13-1) has a lower specific impulse (see 13.6.3) than aluminised composites (Table 13-10) and moreover has the disadvantage that it cannot be case bonded.

Table 13-1 A Typical Extruded Double-base (EDB) Propellant (Solventless)

Ingredients	% (w/w)	
Nitrocellulose (13.25 % N)	51.5	Specific impulse 2320 N s kg^{-1} (for a typical expansion ratio)
Nitro glycerine	43	
Diethyl phthalate	3	Q_p = 5110 J g^{-1}
2-Nitrodiphenylamine	1	Burning rate 15 mm s^{-1} at 5.9 MN m^{-2}
Potassium sulphate	1.25	

Carbon black	0.25	
Wax	0.05	

The additives employed in EDB propellants are mostly similar to those in gun propellants. In Table 13-1 diethyl phthalate is a plasticiser to supplement the plasticising effects of the NG. 2-Nitrodiphenylamine (2-NDPA) is the stabiliser. Potassium sulphate is a flash suppressant and also promotes smooth burning at low temperatures. Carbon black is an opacifying agent which prevents the radiant heat of the combustion from penetrating deep into the grain where it might cause sub surface ignition. The wax is added to act as a die lubricant during extrusion.

13.2.2.2 Cast Double-base (CDB) propellants

The alternative method to extrusion for the manufacture of Double-base propellant grains is casting. Cast Double-base (CDB) propellants can be made in grain diameters from 5 cm upwards, and the maximum diameter is, in theory, unlimited, as is the length. Other advantages which they have over extruded Double-base (EDB) propellant types are a better capacity for very complex cross sections, greater precision of dimensions for longer grains, and in manufacturing processes. There are two essential components used in the process, a casting powder and a casting liquid. The casting powder is an aggregate of small, cylindrical grains of gelatinised nitrocellulose, similar to a small arms propellant. It may contain a proportion of nitroglycerine. Some of the additives required in the final composition, are incorporated in the casting powder before it is extruded and chopped into the form of granules. Table 13-2 shows the composition of a typical Single-base casting powder.

Table 13-2 A Typical Single-base Casting Powder (Solvent Processed)

Ingredients	% (w/w)
Nitrocellulose (from paper, 12.2 % N)	88
2 Nitro-diphenylamine	2
Lead stearate	5
Di octyl phthalate	5

In the foregoing composition the 2-nitrodiphenylamine is the stabiliser, lead stearate is the platonising agent and di octyl phthalate is the plasticiser. The composition of a typical casting liquid is given in Table 13-3.

Table 13-3 A Typical Casting Liquid Composition

Ingredients	% (w/w)
Nitroglycerine	72
Triacetin (glyceryl triacetate)	27
2 Nitro-diphenylamine	1

In this composition the Triacetin is a desensitiser and the 2-nitro-diphenylamine is a further increment of stabiliser. The casting process commences with the filling of the powder into a mould, in which inserts are made for any conduits required. The casting liquid is then added under vacuum and as it is absorbed into the grains of the powder, they swell and eventually coalesce into a solid mass, which is then consolidated by applied pressure. No chemical reaction takes place during this process, it is a physical one and there is virtually no mould shrinkage. The curing process normally takes a few days at a temperature of 60 °C.

Ordinary cast double-base (CDB) propellants tend to contain a relatively high percentage of non-energetic additives (Table 13-4) and therefore provide an even lower specific impulse (see 13.6.3) than the extruded type. However, they have the advantage over extruded double-base (EDB) propellant types that they can be case bonded, because they are heavily plasticised, and this to some extent counterbalances the low volume impulse. Furthermore, like EDB types they can be platonised (see 13.2.4.1.1) and they give relatively smokeless burning. The low specific impulse of unfilled CDB propellants is not a serious disadvantage in one of their main applications, which is in motors for anti-tank guided weapons (ATGW), since such missiles are not required to exceed velocities of about 200 m s^{-1}. CDB grains for ATGW have a weight of the order of 1 kg and cost several hundred pounds each, a small fraction of the unit cost of the missile. British rocket motors containing CDB propellants included the Cadiz and Titus in the Seawolf missile and the US Javelin anti-tank missile. The motor grains are inhibited by either Hypalon or ethyl cellulose sleeves. The French SNPE Artus sustainer motor for the Milan ATGW was also a CDB propellant type and was inhibited by polyurethane.

Table 13-4 A Typical Unfilled Cast Double-base (CDB) Propellant (Semi-Solvent Processed)

Ingredients	% (w/w)	
Nitrocellulose (12.6 % N)	59	Specific impulse 2060 N s kg^{-1} (for a typical expansion ratio) Qp = 2930 J g^{-l}
Nitro glycerine	24	
Triacetin	9	
Di-octyl phthalate	3	
Stabiliser	2	
Lead Stearate	3	

13.2.2.3 Filled cast double-base (CDB) propellants

Cast double-base propellants can be modified by filling them with RDX or HMX, analogously to high-energy gun propellants (see 12.2.2). The capacity for platonisation is retained and there is no increase in smokiness but the quality of the plateau might be impaired. CDB propellants cannot be energised by the

addition of aluminium alone, because of the low oxygen balance of the nitrocellulose content. If, however, ammonium perchlorate is introduced into the composition via the casting powder, the oxygen balance is thereby increased and aluminium can then be added with advantage. This latter type of filled CDB propellant is called 'composite modified CDB (CMCDB).

Such compositions may also contain RDX or HMX. In any case the specific impulse of CMCDB (Table 13-5) is considerably higher than that of unfilled CDB. Their density is also better than that of CMCDB, which is ~1.78 g cm^{-3}. There are however, penalties incurred by the addition of ammonium perchlorate and aluminium; the capacity for platonisation is lost and the additives give rise to smoky burning. The propellant in the British boost motor for the Sea Dart missile, Chow, was a case bonded CMCDB type.

Table 13-5 Two Typical Composite Modified Case Double-base (CMCDB) Propellants

Ingredients	% (w/w)		
	(a)	(b)	
Nitrocellulose (12.5% N)	20	22	(a) Specific impulse = 2630 N s kg^{-1} (for typical expansion ratio) Q_p = 7718 J g^{-1} (b) Specific impulse = 2600 N s kg^{-1} (for typical expansion ratio) Q_p = 7438 J g^{-1}
Nitroglycerine	30	30	
Triacetin	6	5	
Ammonium perchlorate	11	20	
Aluminium	20	21	
HMX	11	-	
Stabiliser	2	2	

13.2.2.4 Slurry cast double-base propellants

Cast Double-base rocket propellants may also be manufactured by slurry casting. This process has the advantage of not requiring a pre-formed casting powder, the propellant grain being made in a single stage operation from granular nitrocellulose. It is therefore faster than the powder casting technique but is, in general, less flexible in terms of the size and type of grain it can produce. In the slurry casting process, the solid ingredients, which may include a nitramine or ammonium perchlorate in addition to the granular nitrocellulose (approx. 0.25 mm particle size), are simply added to a liquid plasticiser mixture (stabilised nitroglycerine plus, for example, Triacetin). The resulting slurry is stirred for some minutes, then poured into the rocket motor case and cured. The second stage motor in the Polaris SLBM contained a slurry cast CMCDB propellant (DDP 880) with the composition shown in Table 13-6.

Modifying the CDB colloidal matrix by the introduction of an elastomer, creates as elastomer modified CDB (EMCDB). Its low temperature strain capability is claimed to be comparable to the polyurethane composites, giving an extensibility of 20 % at -40°C and unfilled EMCDB propellants share the

advantages of unfilled CDB propellants, such as platonisation, case bonding and long shelf life.

Table 13-6 A Typical Slurry Cast CMCDB Propellants

Ingredients	% (w/w)
Nitrocellulose	14.4
Nitroglycerine	32.4
Aluminium	18
Ammonium perchlorate	5.1
HMX	25.9
2 nitro-diphenylamine	1
Resorcinol	0.7
Triacetin	2.5

13.2.2.5 Elastomer modified cast double-base (EMCDB) propellants

The following are performance figures for a non-aluminised EMCDB propellant:

- Burning rate 5 mm s^{-1} to 25 mm s^{-1} on plateau
- Plateau pressure range 20/35 MPa to 90/200 MPa
- Density 1.59 g cm^{-3}
- Specific impulse 2300 N s kg^{-1}

EMCDB propellants can be filled with aluminium and ammonium perchlorate and/or nitramines without undue loss of their main advantage, i.e. the low temperature elasticity. In general, the formulation of filled CDB propellant is governed by the principle of energising with aluminium for applications where smoke creates no problem, or using a nitramine where smoke would be disadvantageous. The propellant used in the British surface to air missile, Rapier, is an RDX filled EMCDB.

13.2.2.6 Advantages and disadvantages of double-base propellants

The general advantages of double-base rocket propellants, taking cast and extruded types together, are as follows:

- They have high mechanical strength.
- Complex cross sections can be produced, by casting or extrusion.
- They are relatively smokeless, provided they are not filled with ammonium perchlorate and aluminium.
- They can be platonised, provided they are not filled with ammonium perchlorate and aluminium.

- They can be filled with RDX or HMX, giving higher impulse without loss of platonisation or low smoke characteristics.

The general disadvantages of double-base rocket propellants are as follows:

- They tend to crack at low temperatures, unless elastomer modified, or highly plasticised.
- They cannot be case bonded, unless heavily plasticised as in CDB types.
- They tend to exhibit resonant and therefore unstable burning, but additives or motor design can suppress this.
- Chemical decomposition of the nitrate esters produces gas in storage which can cause 'gas cracking' in large webs during high temperature storage.
- Double-base propellants cannot be energised by aluminium, unless ammonium perchlorate is also added.

13.2.3 Composite Propellants

13.2.3.1 Binder requirements

Composite propellants are subdivided into three classes; 'plastic', 'rubbery' and 'pressed'. Pressed propellant comprises ammonium nitrate as the oxidant and guanidine nitrate or wax as the fuel. This class is not widely used. The following paragraphs refer to plastic and rubbery composites.

The binder makes up only 10-15 % (w/w) of a composite propellant but determines its mechanical properties. Such properties need to be considered carefully when a motor is designed, because the problem of differential thermal expansion entails that the binder must remain elastic over a wide temperature range (-55 °C to +70 °C). From the manufacturing point of view an ideal binder should be a liquid in the prepolymer (uncured) form with a workable viscosity (1-10 N s m^{-2} in the temperature range 20 °C to 70 °C), which can accept a high solids loading and be capable of conversion by a suitable process (cooling or curing) into an elastomeric material with high tensile and compressive strength and good elasticity.

For most applications a composite propellant binder will need to be non-hygroscopic, be compatible with other propellant ingredients and have good storage stability. For reasons of rocket motor performance, the binder, on combustion with the oxidant, should yield species having low molar mass and/or high heats of formation. In general, for a binder it is necessary to strike a balance between high propellant performance and good mechanical properties. The importance of the latter is demonstrated by the fact that most composite propellants are not formulated at the binder proportion which corresponds to maximum performance (~9 % w/w) but at a higher proportion (~12-15 % w/w), conducive to better mechanical properties and processing characteristics.

13.2.3.2 Oxidant requirements

The oxidant constitutes the major proportion by weight of a composite propellant and largely determines the specific impulse (see 13.6.3) and the burning rate of the propellant. From the view point of safety, manufacture and storage, an oxidant should have low sensitiveness (see 20.2.1) to initiation by impact and friction, and high thermal stability. It should be non-hygroscopic and should be chemically compatible with the propellant binder and other ingredients. To ensure good propellant performance an oxidant should ideally have a large, positive heat of formation and should produce gases of low molar mass. High density is also a desirable feature of an oxidant.

13.2.3.2.1 Ammonium perchlorate

Ammonium perchlorate (NH_4ClO_4) is currently the most widely used oxidant as it meets most of the desired requirements. It is a white, odourless, crystalline solid with a crystal density of 1.94 g cm^{-3} and has low hygroscopicity. Contact of the material with the human skin causes irritation, as does its inhalation to the mucous membranes. Ammonium perchlorate is moderately sensitive to initiation by impact (F of I= 95) (see 20.10.2.1), shock or external heating. The unmixed salt is likely to deflagrate if initiated in these ways, but if it is mixed with any combustible substance initiation may lead to explosion or even detonation, the likelihood of which increases as the mixture approaches the stoichiometric proportions.

13.2.3.3 Plastic composite propellants

Plastic composite propellants were the favoured British rocket propellants in the 1950's and 1960's and were used in, for example, the boost motors for the now obsolete Thunderbird surface to air missile, the Gosling boost motors for Bloodhound (reproved 1987) and the sounding rocket motors Raven and Stonechat. Much research was carried out in the United Kingdom up to the late 1970s to improve plastic propellants but by that time rubbery composites had been found superior, especially in their low temperature mechanical properties. Consequently, plastic propellants now have few applications in military rocketry.

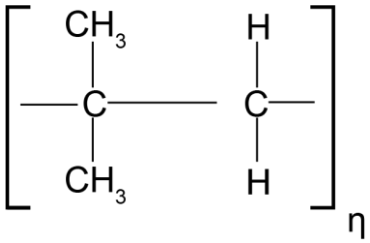


Figure 13-3 Chemical structure of polyisobutene (PIB)

Plastic propellant consists of a thermoplastic fuel/binder and the oxidant ammonium perchlorate. The usual fuel/binder is polyisobutene (PIB) (Figure 13-3), sometimes with the addition of ethyl oleate as a plasticiser to improve the low temperature mechanical properties. Some plastic composites have contained polyvinylchloride (PVC). To manufacture PIB and PVC plastic

composites the polymer is first dispersed in a heated plasticiser such as di-octyl-sebacate to give a mixture known as a plastisol, which is then mixed with the oxidant prior to extrusion and cooling. The plastic propellant is extruded into the motor case, leaving a small axial conduit which is then enlarged often to a star cross section, or some other fairly simple shape, by forcing an appropriately shaped mandrel through the centre and then withdrawing it. Plastic propellants have densities between 1.65 g cm^{-3} and 1.75 g cm^{-3}. The maximum practical grain size is limited by the tendency of the propellant to deform under its own weight. Grains up to 57 cm diameter and weighing one tonne have been made in the UK. At ordinary humidity levels, plastic propellants produce a moderate amount of smoke containing hydrogen chloride. Plastic propellants burn reliably at temperatures down to –30 °C although their performance is somewhat degraded below about 0 °C.

An oxygen-balanced mixture of PIB and ammonium perchlorate would contain 9 % (w/w) PIB and 91 % (w/w) ammonium perchlorate by weight. The maximum obtainable specific impulse, of about 2400 N s kg^{-1} is however, given by a 10/90 mix and this may be further altered to 12/88 to improve the mechanical properties. The burning rate in this range is too high for practical purposes and most UK plastic propellants have had ammonium picrate added as a coolant and burning rate modifier. This has the disadvantage, if the picrate is present in large proportion, of reducing the specific impulse (see 13.6.3). It also increases smoke. Ammonium picrate (Ammonium 2,4,6-trinitrophenolate) is an insensitive explosive in its own right. Table 13-7 gives some typical compositions of plastic composites. Basic copper chromate and titanium dioxides are catalysts which steady the burning rate at low temperatures. Oxamide $(CONH_2)_2$ is a fuel and a coolant which has a slightly platonising (see 13.2.4.1.1) effect on the burning rate/pressure curve but, in general, plastic composites cannot be platonised as can double-base composites. Lecithin is a surface acting agent (surfactant) but has now been almost entirely superseded by di-2-ethylhexyl sebacate. Plastic propellant grains can be case bonded because the strain on the bonding caused by unequal expansion at extreme temperatures is relieved by irreversible viscous flow of the propellant material.

Table 13-7 Typical Plastic Propellant Compositions

	Compositions % (w/w)					
	1	2	3	4	5	6
Ammonium perchlorate	64	84.5	82	74	70	42
Ammonium picrate	10	-	5	-	-	42
PIB (plasticised)	11	13.5	12	11	11	13
Aluminium	15	-	-	14	18	5
Basic copper chromate	-	2	-	1	-	-
Titanium dioxide	-	-	2	-	1	-
Oxamide	-	-	-	-	-	2

13.2.3.4 Rubbery composite propellants

The advantages of plastic propellants for small rocket motors, namely their simplicity of manufacture and the fact that no potentially hazardous exothermic reaction or toxic curing agent is involved, are offset by their poor physical properties from the point of view of rocket propellant requirements. Furthermore, plastic propellant suffers from an inadequate ‘solids capacity' (achievable ratio of oxidant to binder) and, therefore, has not attained the specific impulse of which it is theoretically capable, while still retaining acceptable mechanical properties.

Most composite rocket propellants in use today (2017) are of the rubbery type. These propellants were originally developed for casting into large grains, but recent advances in processing have led to the development of extruded rubbery propellants (the so called extrudable curables) so that even the smallest motor, which might previously have employed plastic propellant, can now benefit from the superior mechanical properties of rubbery composites. This sequence of development is in the reverse order to that of double-base propellants.

The main types of rubber which are mixed with ammonium perchlorate in present day rubbery composites are as follows:

- Polyurethane (PU)
- Polybutadiene (PB)
- Polybutadiene acrylic acid acetonitrile (PBAN)

A former elastomer, the polyalkyl sulphide or polysulphide type, is now obsolete for this purpose. The manufacture of a rubbery composite propellant, particularly when compared with that of a double-base propellant, can be a relatively simple process, and cast rubbery composites are cheaper than cast double-base (CDB) types. The crystalline oxidant, of an appropriate particle size, is mixed with the prepolymer and the curing agent. Other materials such as a burning rate catalyst and a fuel element (usually aluminium) may also be added at this stage. The mixture is heated and carefully agitated to ensure complete mixing. It is then degassed and cast or extruded into the desired grain shape. Curing takes place over several weeks at an elevated temperature (~60 °C) in the case of the cast propellant grain. Extrudable curables require a very much tighter control over viscosity during the mixing stage, but if this is achieved and extrusion is successful, curing can be carried out over a much shorter period of time (3-4 days) at the same temperature. The mechanical properties of the product are determined by the degree of polymerisation and cross-linking achieved in the final curing stage.

13.2.3.5 Polyurethane (PU) composite propellants

Polyurethane composite propellants are polymerised from di-isocyanate/glycol type monomers, producing a polyurethane chain of the type shown in Figure 13-4, which has the molecular composition $(C_6H_{10}O_4N_2)_n$.

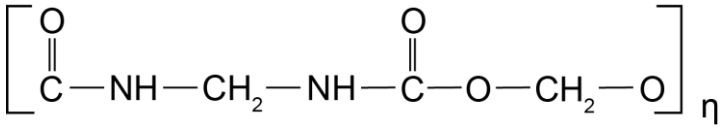


Figure 13-4 Chemical structure of a polyurethane chain

PU composite propellants originated in the early 1950's, and the cancelled British artillery missile Blue Water (1958-62) contained a PU propellant. The first stage motor of SLBM Polaris, developed in the same general period, contained a PU composite (ANP 2969). Its composition is shown in Table 13-8.

Table 13-8 A Typical Polyurethane Composite Propellant

Ingredients	% (w/w)
Ammonium perchlorate	55.0
Polyurethane	12.5
Aluminium	20.0
Nitro-plasticisers	12.5

13.2.3.6 Polybutadiene (PB) composite propellants

Polybutadiene propellants were developed in the late 1950's. Polybutadiene consists of the polymer chain (Figure 13-15) which can be either carboxyl terminated (CTPB) or hydroxyl terminated (HTPB). The two types differ in the method of cross-linking, and HTPB propellants have longer shelf lives for this reason.

$$(\text{-}CH_2\text{-}CH{=}CH\text{-})_n$$

Figure 13-5 Chemical structure of polybutadiene binder

HTPB propellants are the most widely used composites, examples of their use include: ASRAAM (Advanced Short Range Air-to-Air Missile); SEA Viper (Surface-Air ship launched missile); the Hoopoe motor for Sky Flash (air to air missile); and the motor for the LAW 80 light anti-tank weapon which burns for only 12 milliseconds. CTPB propellants have been used in the Linnet and Sparrow motors. Cast HTPB propellants have the best low temperature strain capabilities of all solid propellants. They have an extensibility of up to 40 % between +20 °C and -20 °C and this falls only to about 30 % at -60 °C, so they can be safely case bonded for any ambient temperature likely to be encountered. Typical compositions for the two PB types, with corresponding performance figures, are shown in Table 13-9, together with a PU and a PBAN type propellant.

The particular manufacture of HTPB propellants serves to illustrate the general principles of modern rubbery propellant production. The liquid prepolymer for HTPB propellants consists of a mixture of polybutadiene prepolymer molecules, each with either two, three or four hydroxyl end groups, i.e. HO-($CH_2CH{=}CH$

$CH_2)_n$-OH etc., such that the overall functionality (number of hydroxyl groups/number of molecules) is about 2.5. The actual functionality is very important in determining the physical properties of the manufactured propellant and needs to be chosen so that the propellant is as lightly cross linked as possible but has good low temperature elasticity and can withstand the stresses arising from temperature and pressure increases when the motor is fired.

Table 13-9 Typical Compositions and Properties of Rubbery Composite Propellants

	PU % (w/w)	**PBAN % (w/w)**	**CTPB % (w/w)**	**HTPB % (w/w)**
Ammonium perchlorate	70	69	63	70
Fuel/binder	21	11	10	12
Aluminium	8	15	17	18
Di-octyl adipate	-	4	-	-
HMX		-	10	
Other	1	1	-	
Specific impulse (N s kg^{-1})	2400	2600	2600	2550
Heat of explosion Q_p (J g^{-1})	4540	5970	-	6450

The hydroxyl-terminated polybutadiene (HTPB) prepolymer is mixed with the curing agent, ammonium perchlorate (~70 % w/w), aluminium powder (~15-20 % w/w) and other minor additives in the manner described. The curing agent, normally a di-isocyanate, is added in a precise concentration so that the ratio 'isocyanate groups/hydroxyl groups' in the prepolymer mix is within very closely controlled limits. This ratio, like the prepolymer functionality, is critical in determining the mechanical properties of the final propellant. The curing reaction (Figure 13-6) which takes place between the isocyanate and hydroxyl groups, following casting or extrusion of the propellant, produces no elimination products.

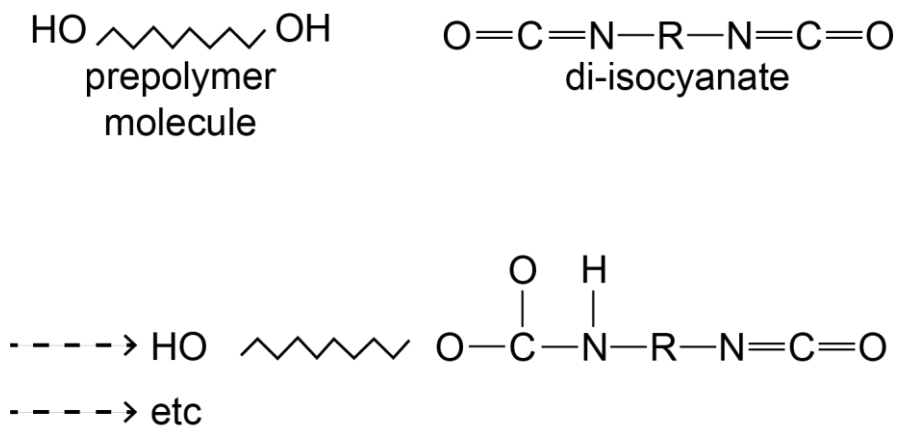


Figure 13-6 Hydroxyl terminated polybutadiene curing reaction

Besides the components already mentioned, a number of other materials are added to HTPB propellants. One such, an antioxidant (e.g. a hindered phenol), is important in prolonging the storage life, while others, (e.g. iron oxide and copper salts) affect the ballistic properties. Further additives may be present to attenuate electromagnetic radiation (e.g. MoO_3) and, as pot life extenders, to reduce the curing rate (e.g. catechol). A bonding agent is also essential to improve the physical properties of the propellant.

In carboxyl terminated polybutadiene (CTPB) the prepolymers are cured by reaction with epoxides or aziridines. PBAN, which is a terpolymer of polybutadiene acrylic acid acetonitrile formed by free radical copolymerisation, is also cured by reaction of the carboxyl groups with epoxides or aziridines.

13.2.3.7 Reduced smoke nitramine propellants

In order to achieve a high performance with reduced smoke, propellants using nitramines (RDX and HMX) have been developed. These propellants typically contain no aluminium, a low AP content ~10 % (w/w), 50-85 % (w/w) nitramines, with hydroxyl-terminated polybutadiene or polyurethane as a binder. These low smoke or reduced smoke propellants produce no primary smoke, while secondary smoke, created when water vapour is present, appears only at low ambient temperatures. Removing the aluminium from the composite will significantly reduce the performance and density of the composition. This is offset somewhat by the replacement of AP with RDX/HMX. The Evolved Sea Sparrow (Surface to Air) Missile is an example of a reduced smoke composite propellant. An energetic plasticiser such as nitroglycerine can also be added to give a modest increase in performance. These nitrate ester plasticised elastomers (NEPE) almost match the performance of an aluminised composite propellant Table 13-10, but with the reduced smoke nature of a double-base propellant. The major design compromise with using these propellants is safety. They have poor safety and vulnerability characteristics compared to composite propellants, which means their use is normally limited to small rocket motors where the required critical diameter for detonation is less likely to be achieved. The Hellfire missile (Air-Surface missile) is an example that employs a nitrate ester plasticised elastomer (NEPE) propellant.

Table 13-10 Comparison of Typical (a) Aluminised (Smokey) Rubbery Composite and (b) Reduced Smoke NEPE Propellant

Ingredients	% (w/w)		
	(a)	(b)	
HTPB	15	12	(a) density x specific impulse = 4300 N s dm^{-3} (for typical expansion ratio)
Nitroglycerine	-	25	
AP	70	10	(b) density x specific impulse = 4110 N s dm^{-3} (for typical expansion ratio)
Aluminium	15	-	
RDX	-	53	

13.2.3.8 Advantages and disadvantages of rubbery composite propellants

The general advantages of rubbery composite propellants are as follows:

- They have good mechanical properties over a wide temperature range
- They can be satisfactorily case bonded
- They can be energised by aluminium
- They can be energised by RDX or HMX
- They burn smoothly, especially if aluminised
- They have high characteristic velocity (c*) (see 13.6.4) values

Their general disadvantages are as follows:

- They have a smoky exhaust
- They require careful curing
- They cause interference with Electromagnetic (EM) radiation
- They may undergo stress cracking on storage
- They cannot be platonised (see 13.2.4.1.1)

Figure 13-7 summarises the various types of solid rocket propellant.

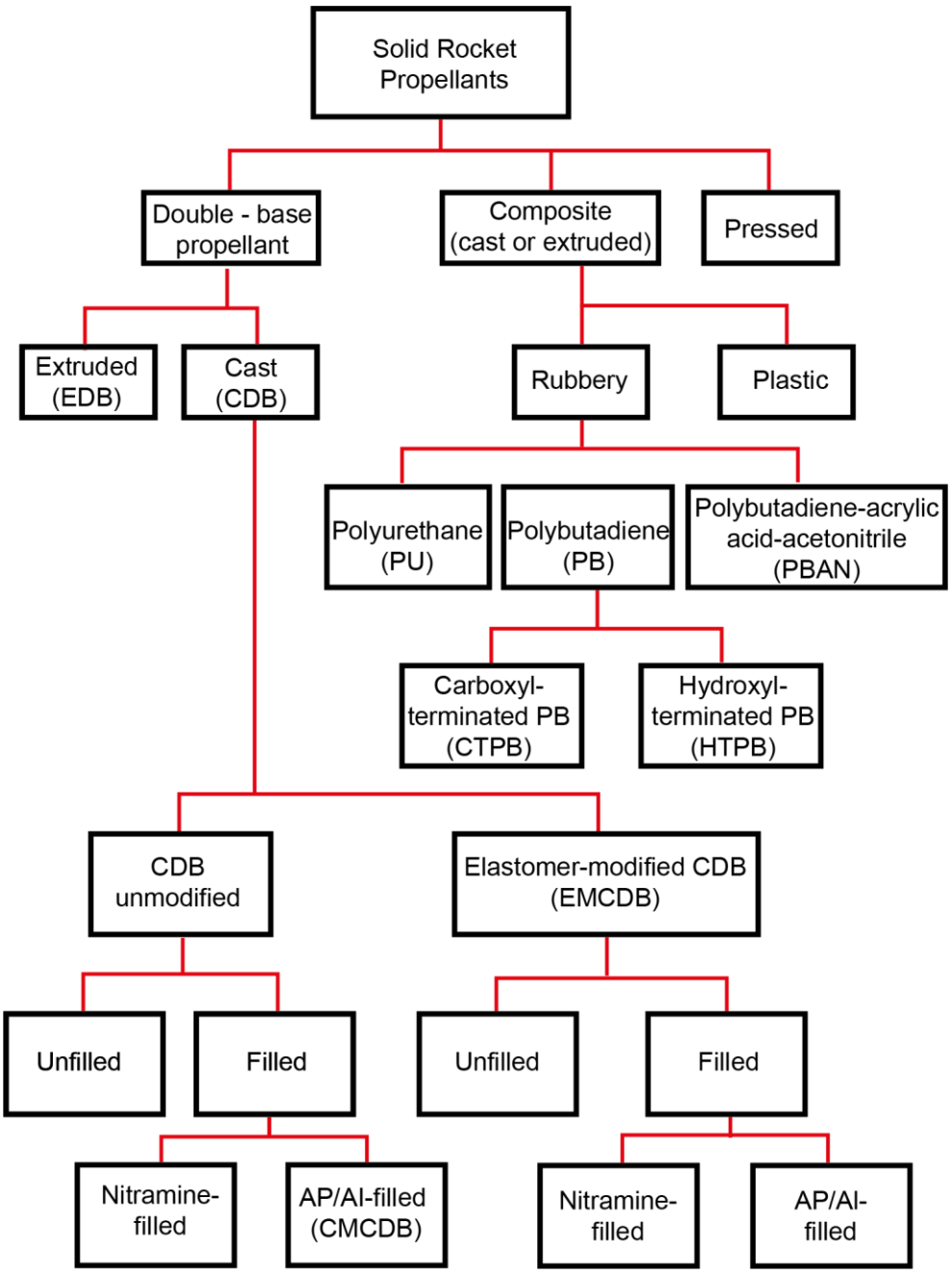


Figure 13-7 Types of solid rocket-propellant

13.2.4 DB Propellant Combustion

The burning surface of a double-base propellant (see 7.2.4.1) is known as the 'foam zone'. It is about 1 mm thick at rocket chamber pressures and its temperature is up to 300 °C. The chemical reaction mechanism in this zone is the breaking of the O-N bond in the R-O-NO_2 structure of the nitrate esters, followed by the formation of aldehydes, alcohols etc. Above the foam zone is a non-luminous gaseous reaction zone called the 'fizz zone, or 'dark zone', about

0.05 mm thick and at about 1200 °C, where the decomposition products are converted into compounds of lower molar mass including the gases CO, CO_2, H_2O, N_2 and NO_2. Finally, in the 'flame zone', which is approximately 0.01 mm thick and at 1200 °C to 3000 °C, all the compounds are converted into the final gaseous species as the foregoing, but with little or no NO_2.

As the pressure increases, the thickness of the 'fizz' and 'flame zones' is decreased and more of the generated heat is conducted or radiated back into the outer layers of propellant, causing them to reach the ignition temperature more quickly. Hence the rate of regression, the linear burning rate (r) (see 7.2.2) is dependent on the chamber pressure (P_c). The relationship is expressed in Vieille's law shown in Equation (13-1), where a is the pressure index and n is the burning rate coefficient. The value of n for double-base propellants is between 0.8 and 1.0; that for composite propellants is usually between 0.4 and 0.6. This relationship, when plotted, gives curves of the form shown in Figure 13-8 and Figure 13-9.

$$r = a\,P_c^{\,n} \qquad \textbf{(13-1)}$$

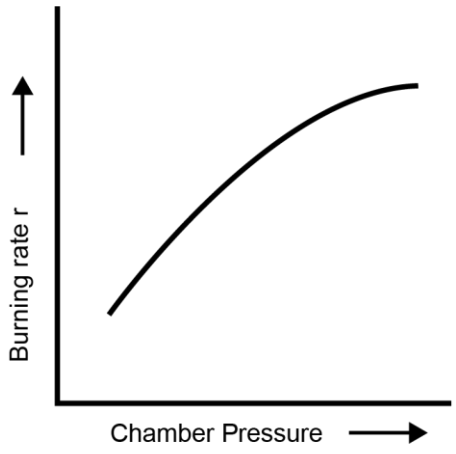


Figure 13-8 Burning rate (r) versus chamber pressure (n < 1.0)

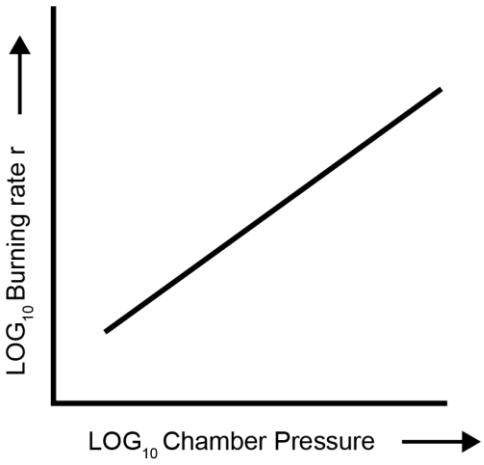


Figure 13-9 Log10 burning rate (r) versus Log10 chamber pressure

An important parameter of a solid propellant is its rate of burning at chamber pressure. In order to achieve the required mass-burning rate ($\dot{m}$) for a particular application it is necessary to obtain the optimum values for the expression:

$$\dot{m} = A_s \dot{x} a P_c^{\,n}\, x\, \rho \qquad \textbf{(13-2)}$$

where ρ is the propellant density and A_s is the burning surface area. The value of A is important to the efficient functioning of a rocket motor. The combustion chamber pressure is given by:

$$P_c = k \left(\frac{A_s}{A_t}\right)^N \quad \textbf{(13-3)}$$

where A_t is the nozzle throat cross-sectional area and k and N are characteristic of the propellant in use. The value of N is greater than unity and is related to n by the expression:

$$N = \frac{1}{1-n} \quad \textbf{(13-4)}$$

Hence a large value of n implies excessive sensitivity of chamber pressure to variation of burning surface area. This is difficult to avoid in practice, but under no circumstances must n exceed 1.0.

One reason for the variation of burning surface area is a phenomenon known as erosive burning. Within the motor the pressure is highest at the head end, but the gas velocity is greatest at the nozzle end. Although pressure affects the burning rate, a stream of hot gas passing rapidly over the burning surface causes a greater effect. Hence the grain burns away faster at the nozzle end than calculations would predict, especially in the early stage of the combustion when the conduit is still narrow. Erosive burning can be limited by keeping the cross-sectional area of the conduit(s) adequately large in proportion to the nozzle throat area, but this imposes a limit on the impulse/total bulk ratio achievable in a radial burning grain.

13.2.4.1 Platonisation and mesonisation

Values for the linear burning rate of double-base propellants range between 5 mm s^{-1} and 20 mm s^{-1} at commonly encountered pressures, depending largely on the percentage of nitroglycerine present. It is possible to produce an important alteration in the burning rate/pressure curve by introducing small amounts (1 – 5 % w/w) of certain lead or copper compounds into the propellant composition. This reduces the value of n to zero over a limited range of pressure, typically 7 MPa to 14 MPa, making the burning rate virtually independent of pressure within this range. The burning rate, and hence the thrust, will therefore be as constant as the grain geometry allows, provided the plateau covers the operating pressure of the motor (Figure 13-10).

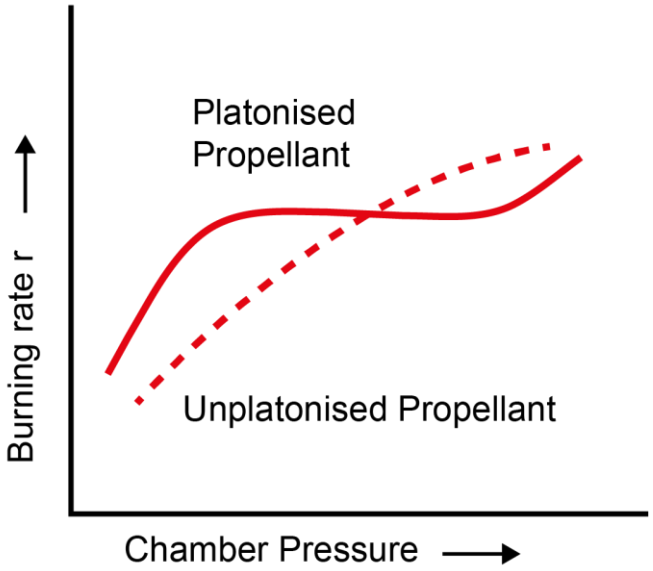


Figure 13-10 Burning rate (r) versus chamber pressure, for platonised and unplatonised propellants

The platonisation effect was discovered accidentally in the US about 1950, when they used lead stearate as a component of a die lubricant and thus contaminated a sample of propellant. The mechanism of catalysis in platonisation is imperfectly understood and differing accounts are found in the literature. It is currently believed that the lead compounds act as positive catalysts of the burning process at low rocket pressures and that the effect disappears as the pressure increases, the plateau marking the limiting pressure range for the catalysis. Lead stearate, the original agent, is still among those in use, but to be effective it must be well dispersed throughout the composition. Lead acetyl salicylate and lead ethyl hexoate are more effective, since they are soluble in nitroglycerine. Lead stannate produces high plateau rates of burning at acceptable pressures. Other platonising agents include lead resorcylate, white lead (basic lead carbonate), and a few copper compounds. Lead and copper compounds are often used in combination. Lead salts also increase the rate of regression before the onset of platonisation (i.e. a super-rate at lower pressures).

Other particulate materials, including inorganic salts such as ammonium perchlorate, tend to destroy the plateau. The type of nitrocellulose used in double-base propellants has an effect on the plateau characteristics.

A variation of platonisation, called mesonisation, is sometimes encountered and is illustrated at Figure 13-11. The burning rate at the base of the hump (mesa) may be below that of the matrix.

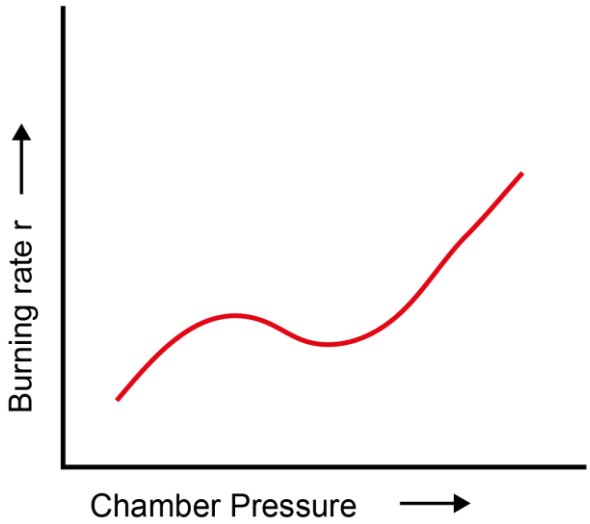


Figure 13-11 Burning rate (r) versus chamber pressure for a mesonised propellant

The advantages of platonising double-base rocket propellants can be summarised as follows.

- It minimises the effect of pressure fluctuations on linear burning rate.
- It enables the linear burning rate at given pressures to be increased by up to 100 %.
- It reduces the effects of manufacturing tolerances and grain geometry on the burning rate.
- It reduces the dependence of linear burning rate on conditioned grain temperature.

The disadvantages are as follows:

- The presence of a platonising agent, which is a non-energetic material, lowers the calorimetric value of the propellant.
- The presence of a platonising agent may increase the production of smoke.

13.2.5 Composite Propellant Combustion

13.2.5.1 Ammonium perchlorate combustion

Combustion of ammonium perchlorate in the unmixed state causes decomposition into entirely gaseous products with considerable evolution of heat:

$$2NH_4ClO_4\ (solid) \rightarrow N_2\ (gas) + Cl_2\ (gas) + 4H_2O\ (gas) + 2O_2\ (gas)$$

$$\Delta H = -193\ kJ\ mol^{-1}$$

When burnt with a hydrocarbon fuel, ammonium perchlorate yields hydrogen chloride gas, which is toxic and corrosive and which forms a smoke cloud in the atmosphere if a normal amount of moisture is present.

In composite propellants the rate of burning (r) (see 7.2.2) for a fixed Q_p (see 13.6.2) value and combustion pressure depends on the particle size of the ammonium perchlorate, as measured by its specific surface (S_o). The value of r increases with decreasing particle size and increasing specific surface. The normal specific surface requirement for ammonium perchlorate in composite propellants is ~2000 cm^{-1}. This corresponds to a rate of burning of ~18 mm s^{-1} (at 6.9 MPa) for a standard plastic composite propellant containing 85 % (w/w) of ammonium perchlorate. The same propellant composition, containing ammonium perchlorate milled to a specific surface of 8000 cm^{-1} gives a rate of burning of 38 mm s^{-1} (at 6.9 MPa).

13.2.5.2 Combustion of aluminium

The mechanism of combustion of composite propellants differs from that of Double-base propellants. It is believed that the primary reaction zone lies almost entirely in the gas phase, which is less than 0.1 mm thick at rocket pressures. The ammonium perchlorate particles and the fuel matrix are decomposed mainly by the heat conducted from the gas phase, and pockets occur in the surface, their size being related to that of the original particles. Many composite propellants contain aluminium, incorporated primarily to increase the calorimetric value. As the surface recedes during burning the metal accumulates on the surface to form molten droplets up to 20 times the diameter of the original particles. The oxidation of these particles to Al_2O_3 occurs during their passage from the surface to the nozzle throat. They tend to promote smooth burning by suppressing resonance within the chamber.

Aluminium can be added to composite propellants up to an optimum 22 % (w/w). Its inclusion reduces the number of moles of gas produced but, beneficially, it also lowers the mean molar mass $\bar{M}$ of the gaseous products by reducing the gaseous water to hydrogen, which has a molar mass of only 2 g mol^{-1}. Aluminium also increases the value of T_c by virtue of its high heat of combustion. The overall reaction in a typical aluminised composite may be expressed as follows:

$$NH_4ClO_4\,(solid) + (CH_2)_n\,(solid) + 2Al\,(solid) \rightarrow$$

$$CO\,(gas) + 2\,½\,H_2(gas) + 1/2\,N_2(gas) + HCl\,(gas) + Al_2O_3\,(solid)$$

13.2.5.3 Combustion of nitramines

The highly energetic nitramine explosives RDX and HMX are added to some cast Double-base (CDB), extruded Double-base (EDB) and composite propellants for several reasons. In modified CDB propellants they are better gas producers than the nitroglycerine which they partly replace, but with somewhat lower heats of explosion (Q_p). When burning in a propellant composition, RDX and HMX melt as the temperature of the propellant rises with the regression of

the burning surface. The melting process absorbs latent heat from the system, thus slowing its temperature rise and reducing the burning rate. When present in composite propellants RDX and HMX replace part of the ammonium perchlorate, thus lowering the burning rate with little reduction of the specific impulse (see 13.6.3). The capacity of the nitramines to reduce burning rates applies only at low combustion pressure; at higher pressures RDX and HMX exhibit increasing values of α which may exceed unity and compositions containing them would, therefore, tend to give unstable burning.

13.2.6 Grain Geometry

The three types of burning (progressive, neutral, degressive) give rise to different shapes of thrust/time curve (Figures 13-12, 13-13 and 13-14). In all three cases it is an important feature of grain design to achieve an abrupt burn out, because any slivers or other remnants of propellant which burn at a greatly reduced pressure are virtually wasted.

In order that the missile follows a predictable trajectory, neutral burning is often a desirable property of a propellant grain. There are several apparent ways of achieving this. One is an uninhibited tubular grain (which could be multiplied within a single motor): this is feasible for very short-range missile, but the flame impinges directly on chamber walls, which would quickly fail. The same applies to the serrated cruciform section grain which was used in some British rockets of World War II. Most rocket-motor grains are therefore designed to burn only in the conduits and/or on the rear surface.

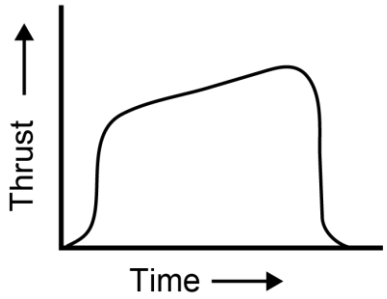


Figure 13-12 Thrust versus time for progressive burning

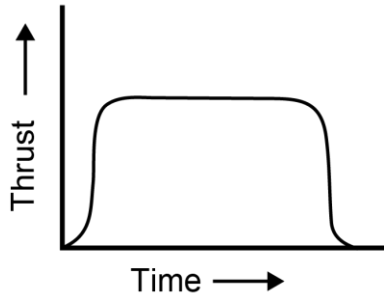


Figure 13-13 Thrust versus time for neutral burning

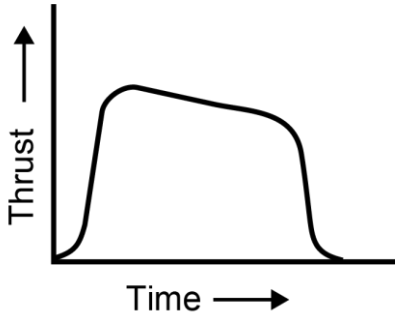


Figure 13-14 Thrust versus time for degressive burning

Neutral burning of an inhibited grain can be achieved in several ways. The simplest is the cigarette burning or end burning grain, which is inhibited at the circumference and head end, burning only at the nozzle end. A plain cylindrical grain is easy to produce, but has two disadvantages. One is that its centre of gravity (and hence that of the missile) moves forward as burning proceeds. The other is that there is insufficient burning area to give a high boost thrust. The latter disadvantage can be overcome by forming radial slots and an axial conduit at the nozzle end, thus giving large surface area for the boost phase followed by neutral and slower burning for the sustain phase. This design is called a slotted cylinder (Figure 13-15).

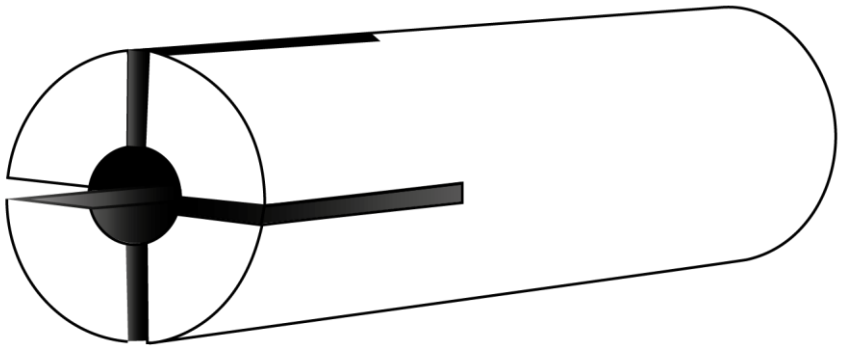


Figure 13-15 Slotted cylinder grain

Most boost grains are inhibited and radial burning. Their geometry is contrived so as to provide a large burning surface area while protecting the motor case from the high flame temperature. One way to achieve this is the 'tube and rod' design shown in Figure 13-16. The increasing outer surface of the conduits is balanced by the decreasing surface of the inner ones. This concept can be developed into more complex shapes such as Figure 13-17.



Figure 13-16 Tube and rod grain

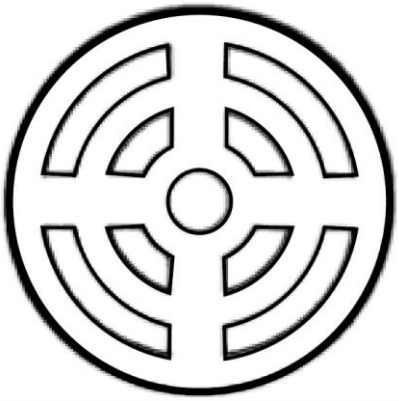


Figure 13-17 Multiperforated grain

The star centre grain (Figure 13-18) is the most commonly used design. There are many possible variations of the basic design, including both degressive and progressive shapes, but it is possible to obtain neutral burning combined with a high impulse and bulk ratio with minimal sliver formation. The star-section

imparts longitudinal strength to the grain but it is necessary to round or square the points of the star in order to distribute the stresses which are concentrated there.

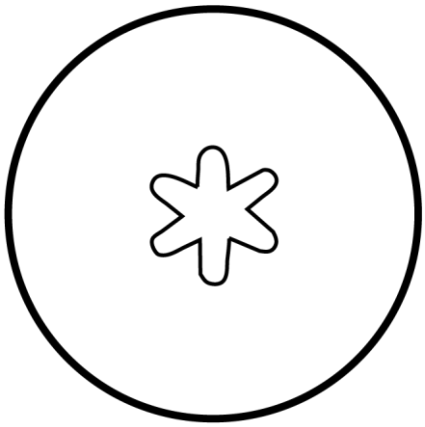


Figure 13-18 Star-centre grain

13.2.7 The Effect of Grain Temperature on Burning Rate

The burning rate of a solid propellant depends on the initial temperature (T_p) of the propellant. This is normally the ambient temperature to which the grain has become conditioned. Any change in temperature (T_p) causes a change in the rate of burning, which in turn affects the gas pressure at the burning surface and thus produces a further change in the rate of burning.

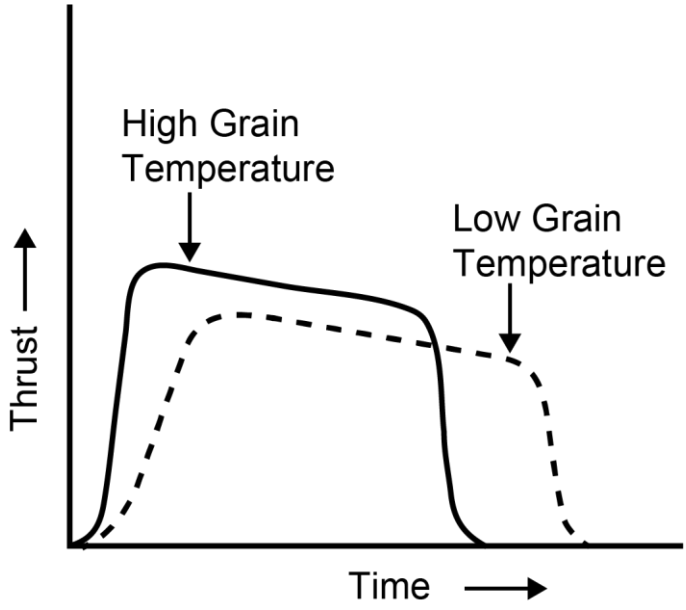


Figure 13-19 Thrust versus time for two different values of grain temperature. (degressive burning grain in both cases)

There are, therefore, two effects, the intrinsic effect of grain temperature on burning rate and the additional effect caused by the consequent increase in pressure.

Figure 13-19 shows diagrammatically the difference brought about in the thrust/time curve by different values of T_p. The ratio of the area of the burning propellant surface (A_s) to the area of the nozzle throat (A_t) is the area ratio and is given the symbol K. The chamber pressure in the rocket is P_c. At constant K the temperature sensitivity of pressure is measured by the parameter π_k which can be derived as shown in Equation (13-5).

$$\pi_k = \frac{1}{P_c} \cdot \left(\frac{dP_c}{dT_p}\right) K \qquad \textbf{(13-5)}$$

Differentiation of the equation the yields:

$$\pi_k = \frac{1}{1-\alpha} \cdot \frac{1}{\beta} \cdot \frac{d\beta}{dT_p} \qquad \textbf{(13-6)}$$

The sensitivity of burning rate to grain temperature, as measured by the π_k value, is a very important property of a solid rocket propellant. It is a fundamental design parameter, together with the rate of burning (r), density (ρ) and characteristic velocity (c*). From the view point of motor design and reliability it is clearly desirable that a rocket propellant has a low $\pi_k$value. This will reduce those differences in chamber pressure which are due to grain temperature changes, and will lead to more consistent motor performance over a wide range of conditioned grain temperatures. An important factor which helps to minimise the $\pi_k$value is a low value of the pressure index n (see Equation (13-1).

Table 13-11 Typical Values for π_k for Different Types of Solid Rocket Propellant

	Propellant	π_k.(% °C^{-1})
Platonised propellant	EDB, unfilled	<0.15
	EDB, nitramine filled	<0.15
	CDB, unfilled	0.1 - 0.2
	CDB, nitramine filled	0.1 - 0.2
	EMCDB, unfilled	0.1 - 0.25
	EMCDB, nitramine filled	0.1 - 0.25
Unplatonised propellant	CMCDB	0.5
	Elastomer modified CMCDB	0.5
	Plastic composite	0.2 - 0.4
	HTPB composite	0.2 - 0.3 and below

In platonised Double-base propellants n is zero or close to it, therefore these propellants are characterised by low values of π_k. This feature is one of the

advantages of platonisation. Table 13-11 shows the differences in π_k values between platonised and unplatonised propellants.

13.2.8 Smoke Emission

The production of smoke by a missile motor is undesirable as it may give away the firing position to the enemy, obscure the missile from the firer, or interfere with optical guidance. Some of the substances which comprise the smoke, such as HCl, can be toxic to personnel near the firing point and corrosive to equipment. Nevertheless, many types of missile produce smoke and its effects must be minimised and tolerated. The smoke consists of minute solid particles of free carbon, alumina and other metal oxides, or as mists of liquid droplets, e.g. HCl. Double-base propellants produce little smoke unless they contain a high proportion of additives.

Composite propellants produce considerable smoke, caused by the HCl produced from ammonium perchlorate supported combustion and, in many cases, by the inclusion in the composition of aluminium which is oxidised to alumina. Any other additives will tend to exacerbate the problem.

In addition to the propellant, other components of the motor may produce smoke. In inhibitor sheaths, the proportion of carbon to oxygen is a factor in smoke production. If this ratio can be kept down without prejudice to the numerous other requirements of inhibitor material, an advantage can be gained. Within the material itself, smoke-producing plasticisers may be identified. Smoke can be reduced by using aliphatic plasticisers such as ethyl carbonate (C_2H_50-CO-OC_2H_5) with a C/O ratio of 1.7 as compared to aromatic plasticisers like di-ethyl phthalate (C_6H_4 ($C0_2C_2H_5)_2$) with a C/O ratio of 3. The use of inorganic fillers in the inhibitor may also increase smoke production.

13.2.8.1 Attenuation of Electromagnetic (EM) radiation by rocket exhaust

Electromagnetic signals for missile guidance, usually of micro wavelength, beamed from a point behind the missile have to pass through at least part of the motor exhaust flame. This flame is an ionised conducting medium and therefore interferes with the signal, attenuating it and introducing noise like amplitude and phase modulations. The flame is an envelope of reacting gases, which comprise a number of species including neutral molecules, atoms, free radicals (e.g. $\cdot OH$), ions (e.g. M^+ and H^+) and free electrons (e^-). In practice it is largely the free electrons which cause electromagnetic interference. The following are some ways in which the concentration of free electrons can be reduced, but clearly some of the remedies conflict with other requirements of propellant technology.

a) Exclusion from the propellant composition of elements with low ionisation potentials, i.e. light metals. This conflicts with the use of aluminium to increase specific impulse. Other metals which may be present are potassium and sodium as impurities in ammonium perchlorate.
b) Reduction of flame temperatures by flame suppressors such as cobalt stannate, molybdenum oxide or iron penta-carbonyl.

c) Inclusion in the propellant composition of an electron absorbing species such as halocarbons. Polytetrafluoroethylene (PTFE) is a possibility.
d) Suppression of molecule dissociation by increasing chamber pressure.

13.2.9 New Solid Propellant Developments

A number of new energetic compounds have been developed in recent years and some of these are being actively considered for use in solid rocket propellants. One of the main areas of interest is the development of 'minimum smoke composite propellants' for tactical missiles. These are designed to offer comparable or better performance and mechanical properties compared to existing AP/HTPB composite propellants but with minimum smoke combustion (as in DB propellants), brought about by substituting the ammonium perchlorate oxidizer with cleaner burning components. Good Insensitive Munitions (IM) characteristics (see 2.12) are also required for modern propellant systems.

There are two types of composition being considered for minimum smoke composite formulations. One involves the use of an alternative oxidizer to AP together with an energetic fuel/binder. The oxidizer that is currently most favoured is ammonium dinitramide (ADN), with the formula $NH_4^+N(NO_2)_2^-$, which was first made and used by the former Soviet Union in the 1970s but not announced to the rest of the world until 1980s when it was independently made in the USA.

Another oxidizer being investigated is hydrazinium nitroformate (HNF), with the formula $N_2H_5^+C(NO_2)_3^-$, however, this has major stability problems at elevated storage temperatures. The binder could be a cross-linked energetic polymer such as poly-3-nitratomethyl-3-methyloxetane (poly-NIMMO) or glycidylazide polymer (GAP). A plasticiser would also be required and this again could be an energetic compound, possibly GAP-azide (a GAP oligomer) or a nitratoethylnitramine (NENA) such as ethyl NENA.

Table 13-12 Performance Comparison of Different Types of Composite Propellant

Oxidizer/ filler	Binder	Plasticizer	c* (m s^{-1})	% increase of c* over AP/HTPB
AP	HTPB	di-octyl sebacate	1511	-
ADN	polyNIMMO	GAP azide	1619	7.1
CL20	polyNIMMO	GAP azide	1645	8.9

The other type of minimum smoke composite propellant being considered is that based on an energetic compound held in an energetic binder/plasticizer matrix. The energetic compounds of most interest for this case are RDX, HMX and hexanitrohexa-azaisowurtzitane (HNIW), which is also known as CL20 (see 10.3.3.5). This is a very high density material (2.04 g cm^{-3}), which is available commercially and is being actively investigated as a higher performance alternative to RDX and HMX in high explosive formulations. A comparison of

the performance of the two types of minimum smoke composite propellant with the current AP/HTPB type is presented in Table 13-12.

While existing AP/HTPB composite propellants show acceptable response in most safety tests they are less successful in meeting the requirements of the slow cook-off test that is included in IM test specifications such as STANAG 4439. This is thought to be because HTPB propellants harden during heating under slow cook-off and are unable to dissipate energy slowly during this process. For this reason, an area of interest in composite propellant technology is the development of Hydroxy Terminated Polyether (HTPE) propellants. These propellants use polyethers as binders and do not undergo the same degradation processes as polybutadiene during slow cook-off. They soften during heating under slow cook-off and their energy is released more slowly, giving a less severe response than HTPB based compositions. However, the level of technical risk and cost required to replace HTPB with HTPE is seen as too great at this time (2017); and most nations are remaining with HTPB and using engineering controls to mitigating the risk from slow cook-off.

In recent years there has been increasing pressure to reduce propellant costs and ensure the continuity of supply of propellant ingredients. The latter point is of growing concern because of International Traffic in Arms Regulations (ITAR) issues from the USA and the introduction of stricter environmental regulations such as REACH (see 1.3.2.4.6) that limit the availability of toxic chemicals. Manufacturers are now beginning to focus on producing solid propellants for tactical systems that can meet the requirements for most applications within the limits imposed by reduced budgets and materials availability. The traditional considerations remain: maintaining high performance (c*), minimum smoke combustion, low toxicity efflux where possible, good mechanical properties and high stability/long storage life.

13.3 HYBRID PROPELLANTS

The concept of a hybrid propellant system dates back to the early years of liquid propellants. A 'normal' hybrid system is one in which a solid or gelled fuel is burned in a stream of liquid oxidant, while a reverse hybrid system employs a solid oxidant and a liquid fuel. Research on hybrids has been carried out by several US agencies since about 1950, using a variety of exotic fuels and oxidants, but little useful result emerged until recently, when the American Rocket Company (Amroc) started to test its prototype motor for the Industrial Launch Vehicle. This is a large, four stage vehicle for launching satellites into low earth orbit, and its thrust is provided by 19 nearly identical hybrid motors, each of which burns 2200 kg of solid fuel in combination with 3620 kg of liquid oxidant. There is still no military system known to be using hybrid propellants, but the prospect may have been brought closer by the foregoing commercial development. The putative advantages of military hybrid rocket systems are as follows:

a. Capability of thrust control and 'on off' functioning by control of the rate of injection of the oxidant.
b. Capability of employing very energetic oxidant fuel combinations which are incompatible under normal conditions.
c. Reduced hazard under fragment attack because oxidant and fuel are separated.

The disadvantages are:

a. Greater complexity of the propulsion system.
b. Non-uniform consumption (that is, erosion) of the fuel charge, with resulting incomplete utilisation of the charge.
c. Low performance when operating outside conditions of stoichiometric combustion.

13.4 RAMJET FUELS

13.4.1 Ramjet Propulsion

The topic of hybrid propellants for pure rocket systems is allied to that of fuels for ramjet systems, since the latter can be thought of as utilising a gaseous oxidant (atmospheric oxygen) to oxidise a liquid or solid fuel.

13.4.2 Liquid Ramjet Fuels

Liquid fuel ramjet engines have been in UK service, including Thor (Bloodhound) and Odin (Sea Dart) and were fuelled by kerosene, the heat of combustion of which is about 44,300 J g^{-1}. This was about five times better than a kerosene/LOX bipropellant system, because the oxygen consumed was not stored in the missile and therefore its weight does not enter into the calculation. On this basis, the effective specific impulse (see 13.6.3) of a kerosene fuelled ramjet motor is about 14500 MPa, compared with 2500 MPa for the bipropellant system. A disadvantage of kerosene is its low density of 0.8 g cm^{-3}. Because of this the Shell company developed a superior hydrocarbon fuel named Shelldyne H, which has the formula $C_{14}H_{20}$ and consists of reduced dimers of bicycloheptadiene. The compact molecule provides a high density of about 1.1 g cm^{-3} in the liquid, which in turn permits a more compact design of missile than one fuelled by an equal weight of kerosene. Shelldyne H is, however, much more expensive.

13.4.3 Solid Ramjet Fuels (Propellants)

In ramjet propulsion, as in pure rocketry, solid propellants have an obvious advantage over liquid propellants in that they allow the motor to be more simply designed, lighter and cheaper to manufacture. Solid fuels present no leakage or vapour hazard. Furthermore, they have a higher density than any liquid fuel. In order to burn in the ramjet however, they must, unlike liquid fuels, contain some

oxygen in their chemical structure, in addition to carbon and hydrogen. The minimum oxygen balance for this purpose is much lower than the near stoichiometric balance which is normal in a conventional rocket propellant. This rules out the use of double-base propellants for ramjets, because such propellants are capable of only limited adjustment to their oxygen balance. Instead, composite propellants are used, as these can provide a wide range of oxygen balance by variation of the fuel binder to oxidant ratio. The ammonium perchlorate content is reduced to about 30 % (w/w), making the oxygen balance heavily negative. As a result, the propellant yields under oxidised gases rich in flammable H_2 and CO. A typical composition would consist of 30 % (w/w) ammonium perchlorate dispersed in a solid fuel matrix of polybutadiene rubber 70 % (w/w). The density of the mixture would be about 1.2 g cm^{-3}.

The energy, and hence the specific impulse, of composite propellants can be improved by the addition of a fuel element which itself has a high heat of combustion. The additive commonly employed in pure rocket propellants is aluminium. An aluminised version of the solid fuel ram rocket (SFRR) composite propellant would have the typical composition:

1. Ammonium perchlorate 50 % (w/w)
2. Polybutadiene 20 % (w/w)
3. Aluminium 30 % (w/w)

This propellant would provide fuel rich gases at a higher temperature than the non-aluminised version, and furthermore the presence of hot solid particles would help to maintain steady combustion in the afterburner.

13.5 LIQUID ROCKET PROPELLANTS

13.5.1 The Uses of Liquid Propellants

Within a rocket system, propellants can be used in three fairly distinct roles:

a. In powerful rocket motors, for the rapid forward propulsion of the entire vehicle.
b. In motors which are small and of low thrust in proportion to the size and mass of the vehicle, but which are adequate, in a space environment or re-entry process, to change its course, speed or attitude (orientation). These motors are called by such names as manoeuvring systems or thrusters.
c. In small units within the system, known as gas generators, power supplies or auxiliary power units, which generate hot gas under pressure as an energy source to operate mechanical and/or electrical devices, to pressurize fuel tanks or to induce spin of the moving vehicle.

In theory all three of these roles can be performed by either liquid or solid propellant, but in practical designs the choice between the two types is made on the basis of suitability.

13.5.2 Advantages and Disadvantages of Liquid Propellants

The inherent advantages of liquid propellants are as follows:

a. Some have higher specific impulse (see 13.6.3) than solids;
b. The weight or volume of the propellants carried in the vehicle, and hence the range, is not directly limited by the size of the motor, as is the case with solid propellants;
c. The thrust can be varied by throttling, and if necessary combustion can be stopped and restarted;
d. The combustion chamber and efflux nozzle can be cooled by the regenerative method, thus reducing dependence on expensive, highly heat-resistant materials and avoiding a constraint on combustion temperature;
e. They give less smoke than some solid propellants;
f. Liquid propellants are relatively cheap;
g. Some bipropellant combinations are hypergolic (self-igniting on contact of the two liquids).

The main disadvantages are as follows:

a. The motor is much more complicated than a solid-propellant one, usually with two storage tanks, several lengths of pipe, a pump or pressurising tank, valves etc. This adds to the weight of the motor, makes maintenance more difficult and decreases reliability. A requirement of instant readiness is more difficult to meet than with solid propellants.
b. The liquid propellants are mostly of lower density than solid propellants.
c. The liquid propellants are in most cases either toxic, corrosive or cryogenic.

For main propulsion motors a small size of missile favours the use of solid propellants, to provide simplicity and lightness. As the size of the vehicle increases there is more advantage to be gained from liquid propellants. The largest civil rocket vehicles, which are used for launching large satellites or space probes, employ liquid propellants for high specific impulse and for cheapness, but in such vehicles the axially-positioned liquid-propellant motor is commonly supplemented by two or more add on' or 'strap on' booster motors to assist the launch. These parallel mounted motors have traditionally been of the solid propellant type in both medium size military systems (e.g. Bloodhound and Seaslug) and in large civil ones (e.g. the NASA/DOD space shuttle and ESA Ariane 5). In the 1980-90s there was a trend towards liquid propellants for the add on motors in the large civil systems, e.g. Arians 44L, the Soviet Energia and the Chinese Long March 2-8L.

The main propulsion of Inter-Continental Ballistic Missiles (ICBM) changed in the 1960's from the liquid bipropellants founded on the German technology of World War II towards solid propellants. This change arose from the increased need for instant readiness of ballistic missiles and was facilitated by the improvement of solid propellant technology.

Thruster motors mostly burn liquid propellants, because these provide an on off capability which solid propellants do not. Large numbers of satellites have liquid propellant thrusters, and in the same general category were the re-entry motors of the British Chevaline system for the Polaris missile and the post boost propulsion system (PBPS) of the American Minuteman III missile. For gas generators the tendency is the same as for main propulsion motors, that is, solid propellants in small rockets and liquid ones in large rockets.

13.5.3 Liquid Monopropellants

Liquid propellants are sub-divided into monopropellants and bipropellants. Monopropellants are liquids, which burn, or otherwise decompose, in the absence of external oxygen. They have comparatively low calorimetric values and provide only low specific impulse, and for this reason they are not used in the main propulsion motors of rocket vehicles, except that some monopropellants double as energetic fuels in bipropellant combinations. Instead, they are used in thrusters and gas generators. Monopropellant motors need only one propellant tank, and this permits a simpler, lighter and more reliable system than bipropellant motors. Monopropellants have to be decomposed, either on a catalyst or by heat, to provide gas at a high mass flow rate. A catalyst provides the simpler of these two systems, but care has to be taken to ensure that the catalyst does not become poisoned if the motor is required to operate intermittently over a period of months or years in a space application. Since monopropellants are reactive substances, it is also necessary to ensure that their containers are made of compatible materials. Table 13-13 shows some monopropellants, of which hydrazine is currently the most widely used.

13.5.3.1 Hydrazine

The Americans first used hydrazine as a monopropellant in the 1950's. Later it found application in the propulsion units of lunar and deep space probes, for example the U.S. Ranger. When the Shell 405 spontaneous catalyst was introduced, hydrazine replaced hydrogen peroxide in satellite thruster motors, and this use continues. It is also used in auxiliary power units and gas generators for large rockets and its use is likely to continue for some years. Anhydrous hydrazine (N_2H_4) is a colourless, mobile liquid (see

Table 13-14). It fumes in air, has a pungent, ammonia smell and is very toxic (Long Term Exposure Limit = 0.02 ppm, Short Term Exposure Limit = 0.1 ppm) (see 18.1.2.2). Its vapour damages the eyes and mucous membranes, liver and blood.

Table 13-13 Properties of Some Monopropellants

Propellant	Boiling Point (°C)	Freeze Point (°C)	$\bar{M}$ (g mol^{-1})	Combustion Temp (K)	Is* (N s kg^{-1})	Density at 25 °C (g cm^{-3})
Hydrazine	114	2.0	10.3	966	1951	1.011
Hydrogen peroxide	150	-0.4	22.7	1278	1618	1.412
Nitromethane	101	-28.5	20.3	2190	2500	1.137
Iso-propyl nitrate	102	-29.0	17.5	1252	1630	1.04
Ethylene oxide	10.7	-113.3	22.0	-	1717	0.87

* All values refer to P_C = 7 MPa and an ideal expansion to P_e= 0.1 MPa, P_e/P_c = 0.014.

Although in the future hydrazine might be used as a bipropellant fuel in the manoeuvring motors of satellites, it is currently used almost entirely as a monopropellant. It has a number of advantages in the monopropellant role:

a. It can be readily decomposed on a catalyst when required.
b. It has a high calorimetric value (Q_p) compared with some other monopropellants, the exact value depending on the particular mode in which it decomposes.
c. It can be stored, given suitable conditions, for extended periods of time without undue decomposition.
d. It is compatible with many (though by no means all) engineering materials.
e. It is readily and fairly cheaply available, being used also in the plastics and other industries.
f. It has a relatively low vapour pressure.

It has however, the following disadvantages:

a. High toxicity
b. Comparatively high freezing point.
c. High hygroscopicity.
d. Susceptibility to catalysed decomposition on various surfaces, e.g. stainless steels and many elastomers, which is increased by the presence of acidic impurities in the liquid, such as carbon dioxide.
e. Lower specific impulse than some other monopropellants.
f. Slight susceptibility to dieseling, i.e. accidental ignition by the rapid, adiabatic compression of entrained bubbles.

Table 13-14 Physical Properties of Anhydrous Hydrazine and Water

	Hydrazine	Water
Freezing point (°C)	2.0	0.0
Boiling point (°C)	114.0	100.0
Density (g cm^{-3})*	1.004	0.997
Viscosity (centipoise (cP))*	0.91	0.89
Vapour pressure (kN m^{-2})*	1.89	3.16
Heat capacity (J g^{-1} K^{-1})*	3.08	4.18
Thermal conductivity (W m^{-1} K^{-1})*	0.54	0.58

* At 25 °C

In a propulsion unit hydrazine is normally stored in a titanium alloy or stainless steel tank and is utilised by decomposition on a spontaneous (cold-start) catalyst, the most effective of which is Shell 405 containing 30 % (w/w) iridium on high-surface-area alumina. The decomposition reaction is usually considered as taking place in two steps. The initial reaction, which is exothermic, produces mainly nitrogen and ammonia and causes the catalyst to heat up:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \quad \Delta H = -157 \text{ kJ mol}^{-1}$$

Once the catalyst is at a high temperature (1500 °C) some of the ammonia is dissociated into hydrogen and nitrogen. This reaction is endothermic:

$$2NH_3 \rightarrow N_2 + 3H_2 \quad \Delta H = +46 \text{ kJ mol}^{-1}$$

13.5.3.2 Hydrogen peroxide

Until the mid-1960s, when the Shell 405 catalyst was developed for hydrazine, hydrogen peroxide was the most widely-used liquid monopropellant, as well as an oxidant in bipropellant systems. Anhydrous hydrogen peroxide is a colourless, mobile liquid with a bitter taste and an acidic smell; physical properties are given in Table 13-13. The pure substance is unstable and is readily decomposed by various impurities or reagents. Hydrogen peroxide is not as toxic as hydrazine, but its vapour causes irritation of the eyes and mucous membranes while the liquid, if it comes in contact with the skin, causes temporary discoloration and irritation. In rocketry applications an 80-90 % (v/v) solution of hydrogen peroxide in water is used, called 'high test peroxide' (HTP). At 25 °C, 90 % (v/v) HTP has a density of 1.387 g cm^{-3}, 80 % (v/v) HTP has a density of 1.334 gm^{-3}. HTP is compatible with aluminium, most stainless steels and some polymers. It is incompatible with iron, carbon steel, copper, lead, some polymers and elastomers, cork and wood.

Under the influence of a catalyst hydrogen peroxide decomposes into steam and oxygen:

$$H_2O_2 \text{ (Liquid)} \rightarrow H_2O \text{ (gas)} + 1/2O_2\text{(gas)} \qquad \Delta H = 54.2 \text{ kJ}$$

The decomposition of 85 % (v/v) HTP on metal gauze at a chamber pressure of 3 MPa gives a combustion temperature of about 1000 K and a specific impulse of about 1180 N.s.kg^{-1}. The main disadvantage of hydrogen peroxide and its solutions as monopropellants is their lack of stability in storage. They decompose relatively quickly into water and oxygen. Also, the specific impulse of hydrogen peroxide as a monopropellant is inferior to that of hydrazine, and at present the compound is little used in rocket systems.

13.5.3.3 Nitromethane

Nitromethane (CH_3NO_2) was the first successful monopropellant, its use as such having been originated by the Italian L. Crocco in about 1934. It is a colourless, mobile liquid with properties shown in Table 13-13. It is slightly miscible with water. Its vapour pressure is 81 kPa (108 mm Hg) at 10 °C. The vapour is highly toxic, being capable of damaging the nervous system, liver and kidneys. Nitro-methane can be stored in mild-steel containers coated internally with plastic. Impurities in nitro-methane may render it detonable by explosive shock; also, it will detonate regardless of its purity, if heated to 260 °C while heavily confined. Like hydrazine and HTP, nitro-methane can be used either as a monopropellant or as a bipropellant, but in the monopropellant role it cannot be decomposed by any known catalyst and has to be decomposed thermally. It is difficult to ignite, but once ignited it has a high flame temperature of 2190 K and a specific impulse of 2500 N s kg^{-1}. Despite its long history, nitromethane has not found widespread use as a monopropellant.

13.5.3.4 Isopropyl nitrate (IPN)

This substance, more correctly called 2-propyl nitrate with the formula $(CH_3)_2CHONO_2$, is a colourless, mobile liquid with properties given in Table 13-13. It is not highly toxic, and it can be stored in stainless steel or aluminium containers but is not compatible with copper or nickel. It can be detonated by an explosive shock. Like nitromethane, it cannot be decomposed catalytically, but it ignites more readily than nitromethane. It is very susceptible to detonation by dieseling, more so than hydrazine. IPN has a calculated flame temperature of 1252 K and at a chamber pressure of 2 MPa it gives a calculated specific impulse of 1630 N s kg^{-1}. An alternative to IPN is the isomer 1-propyl nitrate. IPN has found use in British Service under the acronym AVPIN, in starter capsules for gas turbine aero-engines.

13.5.3.5 Oxirane

Oxirane (C_2H_4O) a cyclic epoxide often called ethylene oxide, is a colourless, mobile liquid and has an inconveniently low boiling point for most monopropellant applications with properties given in Table 13-13. Ethylene oxide vapour has a pleasant smell but is very toxic. At low concentrations it causes nausea and loss of the sense of smell. Higher concentrations it causes irritation of the eyes and mucous membranes together with oedema of the

lungs, while very high concentrations can prove fatal within minutes. The liquid can be stored in steel, stainless steel or aluminium containers. It is readily polymerised, sometimes with explosion, by chloride or alkaline contaminants. It is insensitive to explosive shock but is easily ignited. It decomposes to carbon monoxide and methane, giving a flame temperature of 1450 K and a specific impulse of about 1600 N s kg^{-1}. It has a potential use in gas generators.

13.5.4 Liquid Bipropellants

Since liquid monopropellants do not provide sufficient specific impulse for the main propulsion of large rockets, the choice of propellants for the first stage, or two stages, of such vehicles is between liquid bipropellants, solid propellants, or a combination of both types of motor. Large rocket systems which contain liquid bipropellant main motors include the NASA/DOD space shuttle, ESA Ariane, the American Atlas, the Titan and Delta series and a number of Soviet and Chinese space launch vehicles. Liquid bipropellant systems comprise a pair of propellants, one serving as the fuel and the other as the oxidant. They are contained in separate tanks and are mixed by injection into the combustion chamber, where they either ignite spontaneously on mixing (hypergolically) or are ignited by a pyrotechnic charge. Bipropellant fuels are to some extent interchangeable, but what originally appeared to be a large number of possible fuel-oxidant combinations in the 1950's has dwindled in the course of much subsequent research, most of it carried out in the USA. The current world total of liquid-bipropellant motors now employs a very limited number of combinations.

Liquid bipropellants as a whole are divided not only by their chemical functions, but also separately by their storage characteristics. They are classed either as cryogenic ('space-storable') or packageable ('earth-storable'). A cryogenic propellant is one which must be kept at low temperatures to keep it liquid throughout the feed system. The most common examples are liquid oxygen (LOX), which has a critical temperature of –118.6 °C at 50.5 bar pressure, and liquid hydrogen with a critical temperature of –240 °C at 13 bar pressure. Non-cryogenic bipropellants are those which can be stored as liquids at normal ambient temperatures and under a pressure no greater than their own vapour pressure. If, in addition, they are chemically stable over long periods, they are classed as packageable (earth-storable). The criterion of chemical stability excludes hydrogen peroxide and its solutions from the packageable category. Hydrazine, although usually classed as packageable, is not a good example because of its high freezing point. Better examples are its derivatives, monomethyl hydrazine and unsymmetrical dimethyl hydrazine. Other packageable components include the fuel kerosene and the oxidants fuming nitric acid and dinitrogen tetroxide. The small number of substances mentioned in this paragraph comprise virtually the entire range from which present-day bipropellant combinations are selected.

A fuel-oxidant pair of bipropellants can be either of the same storability type or of different types. For example, the common oxidant LOX can be paired with the

similarly cryogenic fuel liquid hydrogen, or alternatively with kerosene, which is packageable. Cryogenic liquids are difficult and wasteful to store and handle, and are used only because they provide the high specific impulses necessary to accelerate space vehicles to their required orbital or escape velocity. The only cryogenic liquids now used in rocketry are LOX and liquid hydrogen and these are not used in ballistic missiles, because of the requirement of short-notice readiness. Liquid ammonia, formerly used with LOX by the Americans in the Bell X-15 aircraft, is now obsolete. Liquid fluorine, which boils at -188 °C though attractive on thermochemical grounds, is too reactive for practical storage purposes and liquid ozone is dangerously explosive.

The main requirements of bipropellants for a packaged military missile system are:

a. Wide operational temperature range (-54 °C to +71 °C), implying a low freezing point
b. Maximum vapour pressure of less than 3500 kPa at the upper temperature limit of 71 °C
c. Shelf life of at least two years
d. Hypergolic ignition
e. Low or zero shock sensitiveness (see 20.2.1)
f. High density

13.5.4.1 Liquid-bipropellant oxidants

The storable liquid oxidants which are used for modern bipropellant systems are few in number, and are related to each other. One is inhibited red fuming nitric acid (IRFNA) and the others are dinitrogen tetroxide (DNTO) and mixtures based on it, called mixed oxides of nitrogen (MON). The bipropellant oxidant hydrogen peroxide (HTP) which was used in British rockets of the past, including Blue Steel (1957), Black Knight (1958) and Black Arrow (1969), can now be considered obsolete for this purpose.

13.5.4.1.1 Inhibited red fuming nitric acid (IRFNA)

Nitric acid HNO_3 has been used in three forms in rocketry:

a. Anhydrous nitric acid, containing 99.0 % (w/w) of HNO_3
b. White fuming nitric acid (WFNA), containing 97.5 % (w/w) of HNO_3 and 2 % (w/w) water
c. Red fuming nitric acid (RFNA), consisting of between 82-85 % (w/w) of HNO_3, 13.15 % (w/w) dinitrogen tetroxide (DNTO) and between 2-3% (w/w) water

The most commonly used form in rocketry is RFNA, which was introduced for this purpose by the Austrian, F. W. Sander in 1931. German work on bipropellant chemistry in the fertile period of 1940-1945 was divided between three oxidants: LOX, hydrogen peroxide and RFNA, and in 1940 H. Mueller and H. Von Zborowski discovered that RFNA was hypergolic (self-igniting) with aniline, which is an aromatic amine. Later it was discovered that the tertiary amine triethylamine was also satisfactorily hypergolic with RFNA. The German

amine fuels were called Tonkas, and another class of hypergolic fuels were vinyl ethers, known as Visols. After the war Tonka and Visol development was abandoned, but the Americans persevered with the ethylaniline/furfuryl alcohol/nitric acid system for some years until mixtures of hydrazine and its derivatives replaced it.

RFNA is a brown (not red), mobile liquid with a very unpleasant odour. It is highly toxic. The vapour pressure depends heavily on the DNTO content: a typical value is 17.9 kPa, (135 mm Hg) at 25 °C. RFNA has a density of about 1.5 g cm^{-2}, the exact value depending on the composition. It freezes at between –53 °C and –61 °C. Ordinary RFNA is highly corrosive to most container materials, but it was discovered by chance in about 1950 that when at least 0.4 % (w/w) of hydrofluoric acid (HF) is added it can be safely kept for long periods of time in containers made of certain aluminium alloys or of stainless steel. The present day inhibited form of the oxidant, IRFNA, contains 0.7 % (w/w) HF. IRFNA is a dangerous material to handle: the briefest contact with the skin causes yellow staining, and longer contact causes serious burns. Hydrogen fluoride vapour is an acute poison that may immediately and permanently damage lungs and the corneas of the eyes. Aqueous hydrofluoric acid is a contact-poison with the potential for deep, initially painless burns and ensuing tissue death. By interfering with body calcium metabolism, the concentrated acid may also cause systemic toxicity and eventual cardiac arrest and fatality.

13.5.4.1.2 Dinitrogen tetroxide (DNTO) and MON

Like IRFNA, which contains DNTO, straight DNTO (N_2O_4) is not a new oxidant for bipropellant systems: it was first used as such by the Italian L. Crocco in 1930, but it was not adopted by the Germans in World War II, or by the Americans until some years after the war. At room temperature DNTO is a yellow, mobile liquid with a very unpleasant smell. It has a vapour pressure of 96.5 kN m^{-2} (724 mm Hg) at 20 °C, and 151 kN m^{-2} (1134 mm Hg) at 30 °C. It is very toxic, with an OEL of 3 ppm. It freezes at -11.2 °C to a colourless solid and boils at 21.1 °C to a red-brown gas. The density of the liquid at 20 °C is 1.45 g cm^{-3}.

DNTO poses problems of storage because when containing more than 0.2 % (w/w) moisture, it is unacceptably corrosive towards steel containers, and also the presence of dissolved oxygen in DNTO induces stress corrosion in titanium alloys, which are commonly used for rocket propellant tanks. Because of the latter problem DNTO is more often employed as the major constituent of the bipropellant oxidant called 'mixed oxides of nitrogen' (MON), which is DNTO containing a small amount of nitric oxide (NO). Nitric oxide reacts with dissolved oxygen in DNTO to give nitrogen dioxide and hence reduces the problem of stress corrosion. A particular MON mixture is identified by the weight percentage of nitric oxide which it contains, e.g. MON 3 is DNTO containing 3 % (w/w) of NO.

Although DNTO containing less than 0.6 % (w/w) NO is a yellow liquid at room temperature it is referred to as 'red brown DNTO' to distinguish it from MON,

which takes on a green colour when containing more than about 0.6 % (w/w) NO due to the formation of dinitrogen trioxide N_2O_3. MON propellants thus contain four different oxides of nitrogen in equilibrium with one another.

The corrosive effect of DNTO towards metals is not too severe provided the water content of the propellant is kept below 0.2 % (w/w), the (1987) accepted specification limit in most grades of the propellant. At water levels above this value the increase in the corrosion rate of stainless steel and titanium alloys is very steep and arises from the formation of nitric and nitrous acids in the propellant:

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

Increased iron contamination in the propellant also causes problems since the metal precipitates from DNTO at extremely low levels (0.5 ppm) as a gelatinous nitrate complex which blocks valves and other components, giving rise to a phenomenon known as 'flow decay'. In order to minimise its effect, the iron content of MON must be kept as low as possible. The (1987) specification limit for iron in MON 3 is 1 ppm (US National Aerospace Standard NAS 3620, August 1983).

Because of its strong oxidising effect, very few non-metallic materials are compatible with DNTO; of elastomers, only perfluoro-derivatives are suitable for extended periods of contact. The same arguments apply to IRFNA and in this case even glass is incompatible, owing to the presence of hydrogen fluoride (HF) in the composition.

13.5.4.2 Liquid bipropellant fuels

The number of possible bipropellant rocket fuels has always exceeded the number of possible oxidants, and in former decades even single classes of fuels, like the German Tonkas and Visols already mentioned, contained numerous member compositions. Following the rationalisation of bipropellant chemistry in recent years however, the number to be considered is very small. The best cryogenic fuel on performance grounds is liquid hydrogen, which is used with LOX in the main motors of the American space shuttle and in the upper stages of a few other space launch vehicles, but its density of 0.07 g cm^{-3} is so low that when used in large quantities this fuel adds greatly to the bulk of the system, e.g. as seen in the external tank of the US space shuttle. Added to this disadvantage its cryogenic nature renders liquid hydrogen unsuitable for military rockets. With the elimination of liquid hydrogen for this purpose the remaining current candidates are classed as packageable. These are used both in space launch vehicles and military missiles.

13.5.4.2.1 Packageable bipropellant fuels requirements

These fuels are used both in space launch vehicles and military missiles. An ideal fuel should satisfy the following requirements:

a. The fuel must give an adequate specific impulse when burned with the selected oxidant.

b. It should have a high density, to minimise its bulk and therefore that of the missile.
c. It should be of low viscosity for ease of pumping, especially at low temperature.
d. The freezing and boiling points must be compatible with the operating environment.
e. It should be capable of being stored for extended periods of time without significant decomposition.
f. It must be rapidly hypergolic with the oxidant if the design requires it.
g. It should preferably not be toxic or corrosive.
h. It should not be detonable.

In more than ninety years of liquid rocket propellant technology, no fuel has been discovered which complies with all these requirements. One example out of the many problem areas is hypergolicity. If a fuel/oxidant combination is not infallibly self-igniting within a few milliseconds of the first contact the delayed ignition may cause an explosion within the chamber of the motor. The modern candidate fuels described in the following sub-paragraphs are all descended from the German and American types of the 1930's and 1940's.

13.5.4.2.2 Kerosene

Kerosene is a mixture of alkanes, alkenes and aromatics from petroleum, its properties approximating to those of decane ($C_{10}H_{22}$). It is a colourless, mobile liquid which freezes at -40 °C and boils over a wide range, typically 150 °C to 290 °C and has a density of about 0.8 g cm^{-3}. It presents no serious toxic hazard. Kerosene has been used in rocket motors in combination with, variously, LOX, nitric acid and hydrogen peroxide. It can be seen as the logical successor to the ethanol/water mixture oxidised by LOX, as first used by the Germans Riedel and Ley in 1932, then by Von Braun in the V.2 in 1944 and later by the Americans, e.g. in the Viking (1949) and the Redstone (1953) rockets. The ethanol/water/LOX system was relatively cheap and clean burning but, like petrol/LOX and kerosene/LOX, it could not be made hypergolic despite all attempts to do so. All these fuels give very similar specific impulses with LOX, so the cheapest of them, kerosene, is now the definitive one. It was used with LOX in the American Jupiter (1954), Thor (1956) and Atlas (1957), also in the British ICBM Blue Streak (1960), and it is still used in the first-stage motors of some space launch vehicles, e.g. the US Delta and the Soyuz-2.

13.5.4.2.3 Hydrazine

The physical characteristics of hydrazine (N_2H_4) have been mentioned (13.5.3.1). Anhydrous hydrazine, unmixed with substituted hydrazines, has not, until very recently, been used as a bipropellant fuel with DNTO, partly because the reaction is extremely violent. Hydrazine has other disadvantages: its freezing point, +2 °C is far above the maximum –54 °C required of a military propellant for use in all climatic conditions. Also, hydrazine and mixtures rich in it, are apt to detonate when used in regenerative cooling systems. For these reasons, the Americans developed mixtures of anhydrous hydrazine with

substituted hydrazines, notably unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH), as bipropellant fuels. These mixtures were named Mixed Hydrazine Fuels (MHF).

13.5.4.2.4 UDMH and Aerozine-50

The unsymmetrical dimethyl derivative of hydrazine (UDMH), is a colourless, mobile liquid with a strong, unpleasant odour and has the structure shown in Figure 13-20. It has a much lower freezing point than hydrazine, -57 °C, as compared with +2 °C and in this respect, it is also much better than symmetrical dimethyl hydrazine with a freezing point of –9 °C. A compromise has to be made with regard to its boiling point of 62 °C, which is below the lower limit of 71 °C preferred for defence use. UDMH has a relatively high vapour pressure of 22.3 kPa (167 mm Hg) at 25 °C compared to the vapour pressure of hydrazine of 1.89 kPa, and it is highly toxic with a Threshold Limit Value (US Long Term Exposure Limit (see 18.1.2.2)) of 0.5 ppm. UDMH has a rather low density of 0.786 g cm^{-3}.

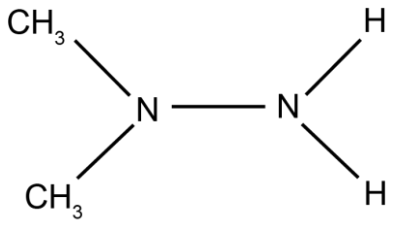


Figure 13-20 Chemical structure of UDMH

Despite its disadvantages UDMH was adopted by the Americans in the 1950's and was first used in admixture with hydrazine in the bipropellant fuel Aerozine-50, which consists of equal parts by weight of hydrazine and UDMH. In addition to having a lower freezing point (about –7 °C) than hydrazine, the mixture is safe to use as a regenerative coolant. Aerozine-50 was used in the first two stages of the Titan series of space launcher/ICBM and in the second stage of the Delta launchers, with DNTO as oxidant in both cases. UDMH, after its first employment as a constituent of Aerozine-50, became a bipropellant fuel in its own right. It was used in the second stage of the earliest Delta space launchers, in Agena and in Vanguard, oxidised by IRFNA in all cases. The Russians have used UDMH, oxidised by LOX, in at least two of their space launchers and it is currently (2017) used in the first two stages of the Soyuz-FG launcher. The Lance tactical missile, which was employed by the British Army used UDMH and IRFNA bipropellant. The Lance propellant system was fully packaged, the two propellant components being storable for several years in the sealed, aluminium tanks contained in the missile. The propellants and the tanks underwent only negligible deterioration and were proof against extreme conditions of environment and handling. The Lance missile held 170 kg of UDMH and 502 kg of IRFNA, representing together about 45 % of its launch weight. The motor gave two different levels of thrust and was able to deliver a pulsed thrust in flight, a capability not shared by solid propellant motors.

13.5.4.2.5 Mixed Amine Fuel (MAF)

In the 1960s, the Americans developed a series of rocket propellant fuels called Mixed Amine Fuels (MAF), based on UDMH and diethylenetriamine (DETA). DETA is included in the mixture to increase its density, and in some cases acetonitrile (CH_3CN) was also included, to reduce the viscosity. The composition of three of the MAF types is shown in Table 13-15.

Table 13-15 Composition of MAF Fuels

	MAF 1	MAF 3	MAF 4
UDMH (% w/w)	40	20	60
DETA (% w/w)	50	80	40
Acetonitrile (% w/w)	10	-	-

These fuels are used in hypergolic combination with IRFNA. MAF 1 was used notably in the American Bullpup family of air-to-surface missiles (circa 1960-80), one type of which was used by the Royal Navy to arm Buccaneer aircraft.

13.5.4.2.6 Monomethylhydrazine (MMH)

Another hydrazine derivative used for rocket propulsion is monomethylhydrazine (MMH), which has the formula $N_2H_3.CH_3$. It is a colourless, mobile liquid with a density of 0.87 g cm^{-3} at 25 °C. It freezes at –52 °C and boils at +88 °C. Its vapour pressure is 6.6 kPa (49 mm Hg) at 25 °C and its toxicity is intermediate between that of hydrazine and UDMH, with a Long Term Exposure Limit of 0.2 ppm.

MMH is miscible with water and forms a hydrate $N_2H_3.CH_3.H_20$ which freezes at –60 °C. The density of MMH, 0.87 g cm^{-3}, is better than that of UDME. Like UDMH, MMH has been used in mixtures with hydrazine as a propellant. The most frequently used mixture is 14 % (w/w) hydrazine with 86 % (w/w) MMH, which freezes at –54 °C. Also, like UDMH, MMH has been used extensively in its own right as a bipropellant fuel, with DNTO or MON as a hypergolic oxidant. The second stage of the Ariane 5 launcher uses monomethylhydrazine (MMH) as a fuel oxidised by dinitrogen tetroxide (N_2O_4).

Historic applications include the orbital manoeuvring system (OMS) of the American space shuttle, the post-boost propulsion system (PBPS) of the Minuteman III missile and the attitude control thrusters of many existing satellites. The MM/DNTO system provides a specific impulse of 2717 N s kg^{-1}, which is much better than a hydrazine monopropellant system at 1951 N s kg^{-1} and is therefore a competitor with it for certain space applications. However, MMH has some disadvantages, one of which is that if incomplete combustion of the mixture upon shutdown of the motor occurs, it leaves an explosive residue in the chamber which is apt to detonate at the next start-up. Table 13-16 gives the chief physical properties of hydrazine, MMH and UDMH.

Table 13-16 Physical Properties of Hydrazine, MMH and UDMH

	Molar mass ($g\ mol^{-1}$)	Density at 25 °C ($g\ cm^{-3}$)	Freeze Point (°C)	Boil Point (°C)	Vapour pressure at 25°C		
					(kPa)	(mm Hg)	TLV (ppm)
Hydrazine	32.05	1.004	+2	114	1.89	14	0.1
MMH	46.07	0.870	-52	88	6.6	49	0.2
UDMH	60.10	0.786	-57	62	22.3	167	0.5

13.5.4.2.7 Fuel tank materials for hydrazine propellants

Hydrazine and substituted hydrazine propellants are normally stored in titanium alloy or stainless-steel tanks. The incompatibility problems of these propellants with other metals relate principally to the effect of the metal in increasing the decomposition rate of the hydrazine, rather than to any gross corrosiveness of the propellant. Slow decomposition during storage is a particular problem with hydrazine whatever the nature of the storage vessel, the reaction being catalysed by trace metals and dissolved acids such as carbon dioxide. The problem is less marked with MMH and UDMH. A number of elastomeric and other non-metallic materials are not suitable for use with hydrazines because of their effect on propellant decomposition rates. However, ethylene-propylene rubber has been used successfully as a bladder material in the expulsion of hydrazine from propellant tanks in satellites.

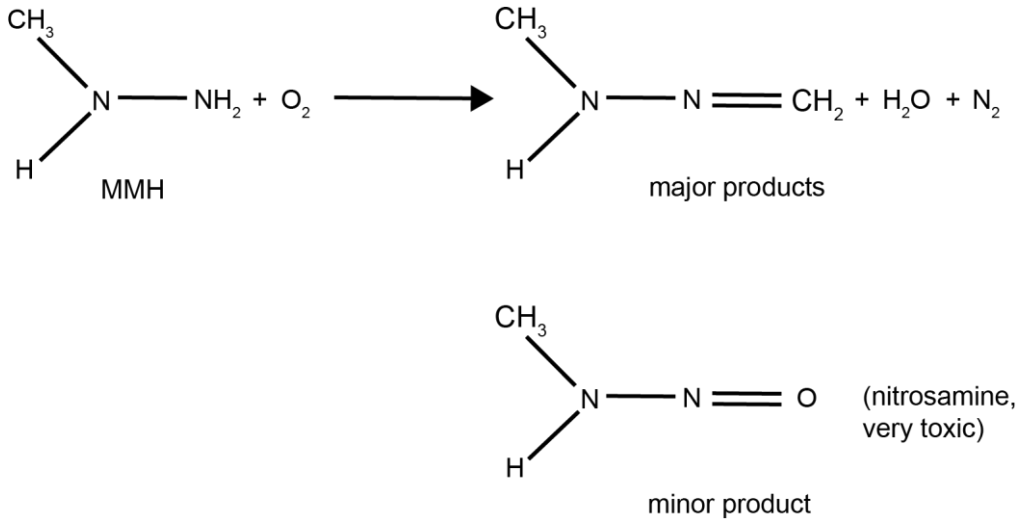


Figure 13-21 Reaction products of air and hydrazine

13.5.4.3 Liquid bipropellant performance

Table 13-17 provides details of some bipropellant performance parameters, which when compared to those of typical monopropellants given in Table 13-3 shows the far superior performance of the bipropellants.

Table 13-17 Performance of Some Bipropellant Combinations

Fuel	Oxidant	Ratio	$\bar{M}$ g mol^{-1}	Combustion Temp. (K)	I_{sp}* (N s kg^{-1})	Density (g cm^{-3})
Hydrogen	Oxygen	4.00	10.0	2980	3824	0.280
	Fluorine	8.00	12.8	4117	4020	0.460
Kerosene	IRFNA	4.80	25.7	3156	2628	1.355
Hydrazine	Fluorine	2.18	19.4	4687	3569	1.310
(N_2H_4)	DNTO	1.30	20.7	3255	2854	1.225
UDMH	IRFNA	3.00	23.7	3222	2706	1.220
	DNTO	1.30	23.5	3436	2805	1.185
MMH	IRFNA	2.60	-	3091	2659	1.230
	DNTO	-	-	3255	2717	-
Aerozine - 50	IRFNA	-	-	2997	2668	-
Aerozine - 50	DNTO	-	-	3230	2727	-

* All values refer to Pc = 7 MPa and an ideal expansion to Pe of 0.1 MPa, P_e/P_c = 0.014

13.5.5 Summary of Liquid Rocket-Propellants

The roles of the various propellants discussed in this chapter are summarised in **Figure 13-22** in the form of a 'family tree'.

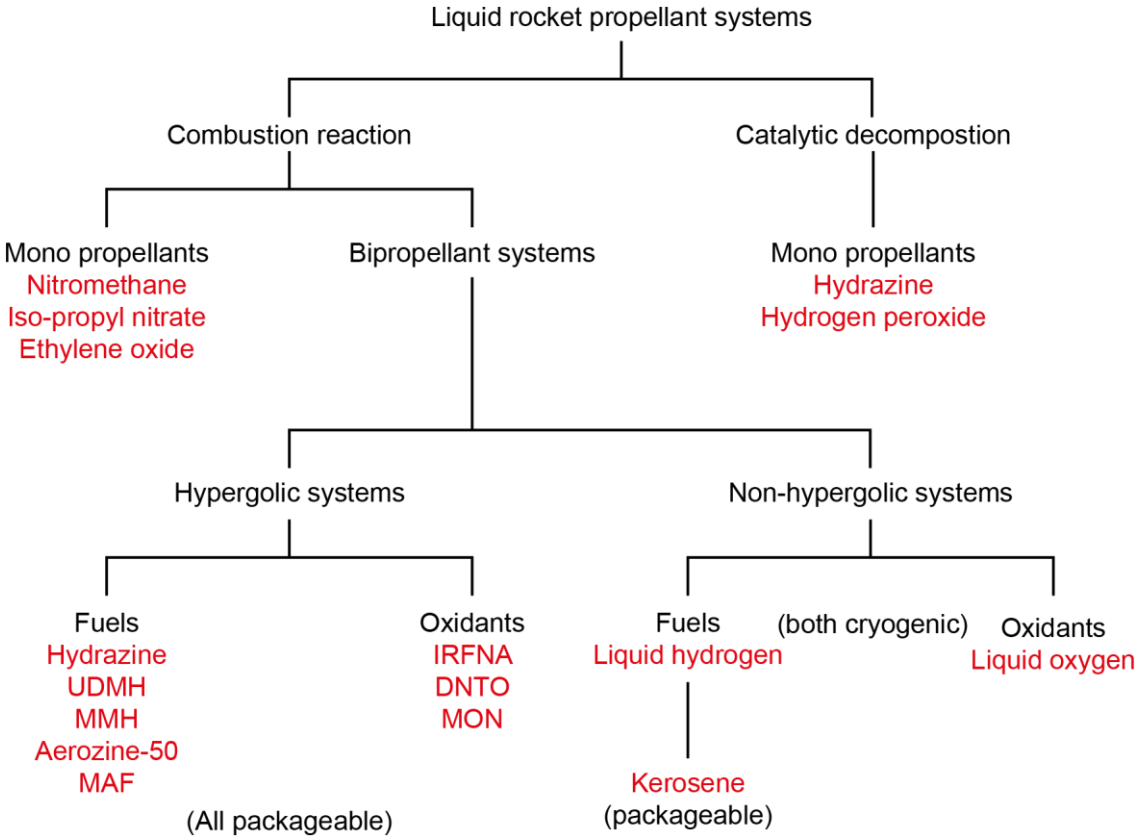


Figure 13-22 Types of liquid rocket propellant

13.6 PERFORMANCE PARAMETERS

13.6.1 Rocket Propulsion

Rocket propulsion is produced by the reaction of the missile to the thrust created by burning propellant in a combustion chamber or tube. As in the case of gun propellants, only a portion of the heat released by the combustion of the propellant can be converted into useful work, in this instance the acceleration of

the rocket and the overcoming of gravity and drag. The remainder of the heat is lost in sensible heat transfer to the hardware, in the residual heat and kinetic energy of the exhaust plume and in the emission of light and sound. The thermal efficiency of the motor is the ratio of useful work output to the chemical energy (heat of combustion, Q), of the propellant(s), and is in the region of 20 % for rockets generally. This percentage increases with the exit velocity of the gases, but is still less than the corresponding figure of >30 % for a typical gun.

13.6.2 Calorimetric Value and Gas Production

The total chemical energy of a rocket propellant, or of a bipropellant combination, is called its heat of combustion (see 4.4.2) or, as for a gun propellant, its calorimetric value. (Strictly, the latter is an experimentally determined value). It is designated Q_p, the p denoting that the value is measured under conditions of constant pressure as distinct from the (theoretically) constant volume conditions of a gun. Like its gun propellant counterpart Q_v, the parameter Q_p is measured in kJ kg^{-1}.

On combustion of the propellant its whole mass is converted (ideally) into a mixture of gases, each of which has its own characteristic molar mass (or, in older terminology, molecular weight), expressed in grams per mole. For some purposes of thermochemistry, as will be seen later, a 'mean molar mass' value, designated $\bar{M}$, for a gas mixture is used. This is simply the mass of mixture in grams divided by the number of moles of gas present. $\bar{M}$ is the inverse of the n value more commonly used in connection with gun propellants.

13.6.3 Thrust and Specific Impulse

One of the internal forces (F_1) in a motor is that acting over the nozzle exit plane (A_e) which is subject to a pressure P_e, from inside the motor (**Error! Reference source not found.**).

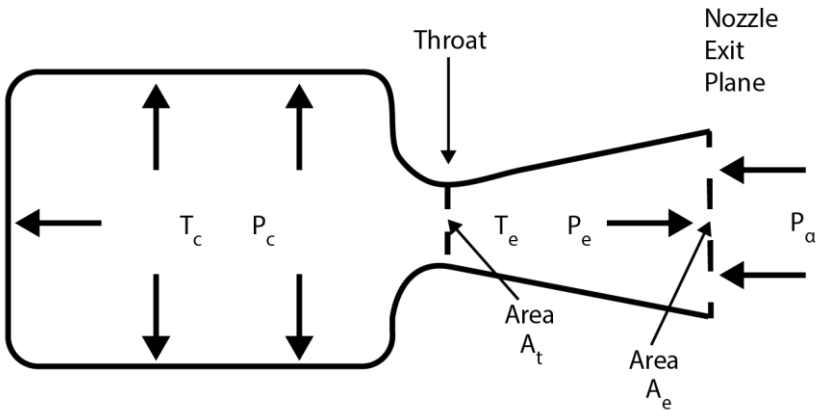


Figure 13-23 Diagram of a rocket motor

Since force = pressure × area, therefore,

$$\boldsymbol{F_1 = P_e A_e} \quad \textbf{(13-7)}$$

In addition there is a significant internal force (F_2) resulting from the change in momentum of the combustion products as they pass through the nozzle exit plane at a velocity v_e which is assumed to be constant. If the mass of the combustion gases passing through in the time interval (d_t) is $\dot{m}$, then this momentum change is given by:

$$\boldsymbol{F_2 = \frac{d(mv_e)}{d_t} = \dot{m}v_e} \quad \textbf{(13-8)}$$

where $\boldsymbol{\dot{m}}$ is mass flow rate of the combustion products through the nozzle exit, which is also the mass rate of burning for either solid or liquid propellants.

There is also an external force (F_3) which acts over the nozzle exit area (A_e) from outside the rocket where the pressure is the ambient pressure (P_a). This force is opposed to the internal forces, therefore,

$$F_3 = -P_a A_e \quad \textbf{(13-9)}$$

It is the reaction to the sum of these three principal forces which provides the propulsion of a rocket. The total force (F_T), called the thrust of the rocket motor, is therefore given by:

$$F_T = \dot{m}v_e + A_e(P_e - P_a) \quad \textbf{(13-10)}$$

The thrust of a rocket motor can be controlled in various ways, but the total impulse (thrust × time) provided by unit mass of propellant in a given motor has a finite value, known as the specific impulse (I_s). This parameter is used to assess the performance of a rocket motor, and it is defined as the thrust per unit mass flow rate through the nozzle:

$$I_s = \frac{F_T}{\dot{m}} \quad \textbf{(13-11)}$$

The SI units corresponding directly with this definition are N/kg s^{-1} which can be alternatively written as N s kg^{-1}. By taking the expression for F_T in (13-10 and dividing throughout by $\dot{m}$, it is seen that:

$$I_s = v_e + \frac{A_e\,(P_e - P_a)}{\dot{m}} \quad \textbf{(13-12)}$$

In general the second term is small compared with v_e so the specific impulse is often taken as the velocity of the combustion products at the nozzle exit. It is easy to verify that the units are consistent, as follows.

$$\text{Units of } I_s = \frac{N}{kg\ s^{-1}} = \frac{kg\ m\ s^{-2}}{kg\ s^{-1}} = m\ s^{-1} \quad \textbf{(13-13)}$$

In order to obtain an expression for specific impulse it is necessary to make a number of assumptions about the properties of a rocket motor:

i. The gas mixture produced by combustion of the propellant is of constant composition and behaves as a perfect gas.
ii. The chemical reaction within the combustion chamber takes place at constant pressure.
iii. The expansion through the nozzle is steady, is one-dimensional along the axis of the nozzle and does not involve a change in entropy.
iv. The expansion through the nozzle is adiabatic, and factors such as friction and gas viscosity can be neglected.

By making these assumptions and by using the approximate expression for specific impulse already given, it is possible to equate the kinetic energy of the gas at the nozzle exit to the enthalpy (ΔH) released in a reversible adiabatic expansion of the gas from the chamber pressure (P_c) to the nozzle exit pressure (P_e). Since this process is a conversion of enthalpy into kinetic energy it entails a fall in the temperature of the gas from T_c to T_e, where T_c is the adiabatic flame temperature of the propellant in the constant pressure condition of the chamber and T_e, is the nozzle exit temperature.

Now by definition:

$$\Delta H = \bar{C}_p(T_c - T_e) \quad \textbf{(13-14)}$$

Where $\bar{C}_p$ = mean heat capacity of the gas mixture at constant pressure, in J kg^{-1} K^{-1}.

Therefore, for unit mass of the gas,

$$\frac{{I_s}^2}{2} = \bar{C}_p(T_c - T_e) \quad \textbf{(13-15)}$$

For an adiabatic expansion it can be shown that:

$$\frac{T_e}{T_c} = \left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}} \quad \textbf{(13-16)}$$

Where γ = ratio of heat capacity of the gas at constant pressure to that at constant volume, i.e. $\bar{C}_p/\bar{C}_v$. For the majority of rocket propellants this value is in the range 1.2 – 1.3.

Substitution in (13-15) gives:

$$I_s{}^2 = 2C_pT_c\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right] \quad \textbf{(13-17)}$$

For an ideal gas $C_p - C_v = R/\bar{M}$. Where R = the universal gas constant (8.31 J mol^{-1} K^{-1}) and $\bar{m}$ = the mean molar mass of the gas (kg mol^{-1}). Approximately, therefore, in the present case;

$\bar{C}_p = \frac{\gamma R}{(\gamma-1)\bar{m}}$ and substitution in Equation (13-17) gives:

$$I_s = \left\{\frac{2\gamma RT_c}{(\gamma-1)\bar{m}}\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]\right\}^{1/2} \quad \textbf{(13-18)}$$

Alternatively, use can be made of the propellant force constant F, which is equal to nRT_o and therefore to $\frac{\gamma RT_c}{\bar{m}}$;

$$\text{Thus } I_s = \left\{\frac{2F}{\gamma-1}\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]\right\}^{1/2} \quad \textbf{(13-19)}$$

13.6.4 Characteristic Velocity and the Thrust Coefficient

The specific impulse of a rocket depends both on the combustion chamber conditions, which are determined by the propellant, and the expansion ratio, which is determined by the nozzle geometry. For this reason two further parameters are defined which enable each of these components of performance to be described separately. The characteristic velocity, c^* ('c star'), is defined as:

$$c^* = \frac{P_cA_t}{\dot{m}} \quad \textbf{(13-20)}$$

where A_t = rocket nozzle throat area in m^2. It can be shown that, for an ideal rocket;

$$c^* = \left[\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{\gamma-1}}\left(\frac{RT_c}{\gamma\,\bar{M}}\right)\right]^{1/2} \quad \textbf{(13-21)}$$

and as this expression depends only on the properties of the propellant, it is more useful than specific impulse when comparing the performance of propellants in rocket motors.

A complementary parameter to c^* is the thrust coefficient C_F, defined as:

$$C_F = \frac{F_T}{P_c\, A_T} \quad \textbf{(13-22)}$$

It can be shown that the thrust coefficient for an ideal rocket motor is largely a function of nozzle geometry. The specific impulse of a motor is then given by:

$$I_s = c^*\, C_F \quad \textbf{(13-23)}$$

13.6.5 Expansion Ratio

The expansion ratios (P_e/P_c) for many dissimilar rocket motors lie within a rather narrow range. This is equivalent to stating that C_F values do not vary greatly from one motor to another, and in fact such values are mostly between 1.3 and 1.5. This is partly because the exit pressure is invariably close to the ambient pressure, but also because it is not practicable to increase P_c greatly as this would entail adding strength, and therefore weight, to the motor. Thus it is common practice to use specific impulse as a parameter for comparing the performance of different propellants, but when this is done the relative expansion ratio strictly should be quoted.

13.6.6 Factors Affecting Rocket Propellant Performance

From the expression for c^* and that for specific impulse, I_s, it is apparent that rocket propellant performance is proportioned to $(T_c/\bar{M})^{1/2}$. Therefore a high value for the flame temperature (T_c) of a propellant increases c^*. The highest temperature which can be produced by chemical propellants is about 5000 K, but the normal combustion temperature for rocket motors is about 3000 K. The need for constraint arises from the damaging effect of extremely high temperature on the motor components, particularly the nozzle, and the difficulty of designing cooling systems for solid propellant motors. Nozzles for liquid propellant motors, however, can be cooled by the regenerative method, in which the flowing propellant passes through the thickness of the nozzle and absorbs the transferred heat.

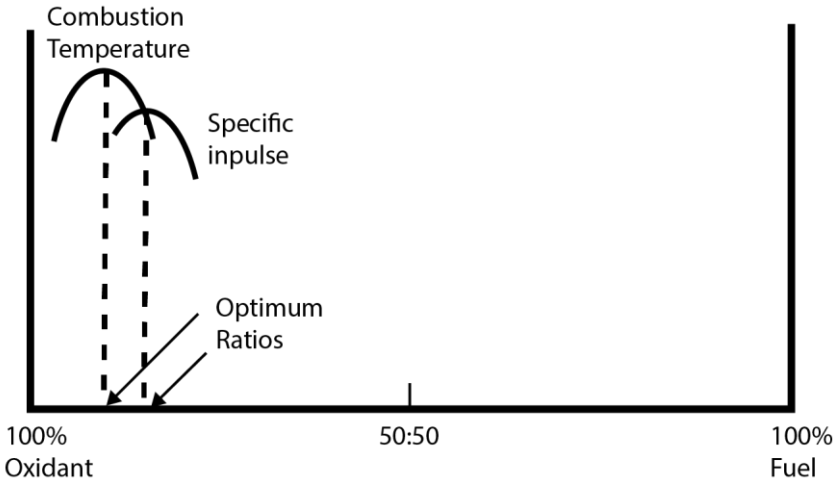


Figure 13-24 Specific impulse and combustion temperature versus fuel/oxidant ratio (diagrammatic).

From the expression in the foregoing paragraph, it can also be seen that the value of $\bar{M}$, the mean molar mass of the gas mixture, should be kept as low as possible for high c^*. This implies that no solid products should result from the combustion process, but this requirement is often compromised by other factors, as will be seen in the section on solid rocket propellant where aluminium additive is considered (see 13.2.2.3).

It is found that, for a given CHNO propellant system, the oxygen balance (see 4.3.1) figure (Ω) which produces the highest value of c^* is slightly on the fuel-rich side of stoichiometric as shown in Figure 13-24, that is, slightly negative. This is because the resulting products are slightly lower mean molar mass, e.g.:

$C + O_2 \rightarrow CO_2$ M = 44 g mol^{-1}

$C + O_2 \rightarrow CO$ M = 28 g mol^{-1}

Table 13-18 Elements in the First 3 Rows of the Periodic Table

Group	I	II	III	IV	V	VI	VII
	H						
	Li	Be	B	C	N	O	F
	Na	Mg	Al	Si	P	S	Cl

At the temperature of the exhaust gas the equilibrium tends to the formation of CO. The divergence from a zero oxygen balance should be very limited, otherwise the heat of combustion (Q_p) falls off rapidly. The requirement to optimise the $\bar{M}$ value of the gases also entails that propellants should contain only 'light' elements, that is, elements of low relative atomic mass ('atomic weight'), which on combustion give molecular and atomic species of low molar mass. In fact, all the chemical elements used in rocket propellants, except in a few special additives, are to be found in the first three rows of the periodic table, which are shown in Table 13-18.

The oxidising element is normally oxygen (Group VI) but fluorine (Group VII) is also a candidate. The oxygen can be in elemental form as a cryogenic liquid, but more often it is in the form of an acid, salt, nitrate ester, oxide or peroxide. The fuel elements hydrogen (Group I) and carbon (Group IV) are the most common, both of them giving gaseous products. Hydrogen provides a low heat of combustion with a value -240.6 $kJmole^{-1}$ compared to -393.5 $kJmole^{-1}$ for carbon when fully oxidised to CO_2.

Hydrogen, however, provides the gaseous product water with a very low molar mass of only 18 g mol^{-1} compared with 44 g mol^{-1} and 28 g mol^{-1} for carbon dioxide and carbon monoxide respectively. The two elements in Group III, boron and aluminium, are used in some rocket propellants even though they yield solid instead of gaseous products, on account of the high heats of combustion of these elements. From these various elements, or suitable compounds of them, together with nitrogen it is possible to synthesise or formulate propellants which provide the high combustion temperatures and low molar mass products required.

13.6.6.1 Dissociation products

Under the conditions of high temperature and pressure in a rocket motor dissociation takes place among the combustion products, including:

$$H_2O\ (g) \rightarrow {\cdot}H\ (g) + {\cdot}OH\ (g)$$

$$1/2\ H_2\ (g) \rightarrow {\cdot}H\ (g)$$

$$1/2\ N_2\ (g) \rightarrow {\cdot}N\ (g)$$

These reactions are endothermic, so they occur more readily at higher temperatures, in general above 3000 K. The products formed are of lower molar mass than the reactants, a fact which tends to increase characteristic velocity. At the same time, however, the reactions absorb heat from the system and the temperature is thereby lowered, in turn lowering c^*. The net result depends on the value of T_c/M for the combustion process with dissociation, compared with the value in the absence of dissociation.

13.6.6.2 The effect of specific impulse on missile performance

The performance of a rocket missile in terms of its velocity and range depends upon two factors, the specific impulse I_s of the missile's rocket motor and the mass ratio, γ, which is the ratio of the mass at launch to that at the all-burnt point. The importance of specific impulse is shown in the following generalised equations.

$$Velocity\ at\ all\ burnt = I_s\ log_e\ I_s \qquad \textbf{(13-24)}$$

Range, for an ideal ballistic trajectory,

$$= \frac{{I_s}^2 (log_{\ e}\ \gamma)^2}{g} \qquad \textbf{(13-25)}$$

where g is the acceleration due to gravity.

Range, for an airborne trajectory,

$$= \frac{V\, I_s\, log_e \gamma}{g}\, \frac{L}{D} \qquad \textbf{(13-26)}$$

where L/D is the lift/drag ratio for the missile and V is the post-boost velocity.

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CHAPTER 14
PYROTECHNICS

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14 PYROTECHNICS

Authors – G Manton (UK MOD), S G Murray and R Vrcelj (Cranfield University)

14.1 AWARENESS SUMMARY

Pyrotechnic stores were evolved in the mid-19th century, a development of the already well established fireworks industry. The first use of such stores was for signalling, however, as equipment and ordnance became more complex, the need for a much wider range of pyrotechnic stores grew. It is understandable that such military stores are considered by some to be larger versions of commercial fireworks. This, however, is not the case since most military pyrotechnics are filled with high performance compositions with large energy outputs making them truly explosive materials.

Pyrotechnic compositions can be defined as materials which when correctly initiated, burn and produce a special effect. Thus in their designed use these compositions do not detonate, however, this does not mean that certain of the compositions are not capable of detonation. Under heavy confinement or by over-stimulus, highly energetic mixtures particularly when in powder form, can detonate or explode. The second point of importance in the definition is that the pyrotechnics are designed to provide a special effect. These effects are listed in **Error! Reference source not found.** Table 14-1, together with examples of each category.

Table 14-1 Special Effects Provided by Pyrotechnic Compositions

Effect	Examples
Heat	Priming, Igniters, Incendiaries
Light	Illumination (long and short period), Tracking, Signalling, Decoys
Smoke	Screening, Signalling, Riot-control, Target marking
Sound	Distraction, Signalling, Gunfire Simulators, Maroons
Gas	Pyromechanisms, Oxygen candles
Time Intervals	Delays

Since all compositions produce heat when they burn it could be said that heat was the primary driving force for all special effects. The output of light energy, for example, comes from the very high temperatures produced by illuminating compositions. More difficult to classify by effect is signalling or coloured smoke where a heated composition vaporises a dye. However, the effects listed in **Error! Reference source not found.**the Table are generally accepted as the most convenient method of classifying the special effects produced by pyrotechnic compositions.

The distinction between pyrotechnics and pyromechanisms is not clear. Though some pyromechanisms contain true pyrotechnic compositions, it is more common to use a single-base or double-base propellant powder. The gas produced by these can be used to operate a mechanical device. Other pyromechanisms contain detonating high explosives. The need for use of propellants rather than pyrotechnic compositions in pyromechanisms is that the latter may produce large amounts of unwanted solid slag in their combustion products. The subject of Pyromechanisms is covered in Chapter 15.

14.1.1 CHEMICAL COMPOSITIONS

Chemical compositions of pyrotechnics fall into three categories. The main category is fuel and oxidant mixture (see 4.2.1) where both components are themselves non-explosive. Other additives are often included as processing and performance modifiers.

The second category is that of fuel only compositions. The most important examples of this group are white and red phosphorus, used to provide screening smoke. Phosphorus fuel whether red or white burns in air therefore no oxidant is incorporated in the store but whereas white phosphorous will ignite spontaneously on contact with air, red phosphorus requires a source of ignition.

There is also the possibility of a fuel precursor filling, where a chemical reaction releases the fuel, again to burn in air. Naval smoke marker stores have been filled with calcium phosphide which reacts with water to form phosphine gas which spontaneously ignites in air and reacts with moisture to give smoke. These fillings with no oxidant content are still considered as pyrotechnics since the special effect, production of smoke, is considered a pyrotechnic effect.

The third group comprise materials which simply react with atmospheric moisture to produce a smoke on dissemination. These are smoke producers and are also considered as pyrotechnics. Examples are titanium tetrachloride and chlorosulphonic acid which hydrolyse forming acid droplets, which have corrosive properties.

14.1.1.1 Fuel-oxidant mixtures

Many materials found among pyrotechnic compositions are fuel-oxidant mixtures, which allow for the optimisation of output for a particular effect. The fuels are usually finely divided metal powders although some metal alloys, non-metals and organic materials are also utilised. Oxidisers cover a wide range of chemical species, most of which are sources of oxygen, used to oxidise the metal or non-metal fuel. One class, however, does not provide oxygen but contain chlorine or fluorine capable of reacting with elements to form metal chlorides or fluorides, which is classed as an oxidation reaction. For example, magnesium reacts with PTFE, $(-CF_2-)_n$, to form magnesium fluoride generating around 10 kJ g^{-1} of energy.

Table 14-2 lists the more important fuel elements and oxidant types. Intimate and uniform mixing of the fuel/oxidant mixtures is essential to ensure optimum-

performance. To maximise shelf-life, ingredients should be non-hygroscopic and compatible.

Table 14-2 Fuel Elements and Oxidants

Fuel Elements			Oxidisers	
Metals	Aluminium	Al	Chlorates	$NaClO_3$
	Iron	Fe	Chromates	$PbCrO_4$
	Magnesium	Mg	Dichromates	$K_2Cr_2O_7$
	Titanium	Ti	Halocarbons	C_2Cl_6, PTFE
	Tungsten	W	Metal Oxides	Pb_3O_4, BaO_2
	Zirconium	Zr	Nitrates	KNO_3,$NaNO_3$
Non-metals	Boron	B	Perchlorates	$KClO_4$
	Carbon	C		
	Organic fuels	Lactose Hexamine		
	Silicon	Si		

14.1.1.1.1 Thermite compositions

One special group of fuel-oxidant mixtures comprises metal-metal oxide combinations. These are based on the original Goldschmidt reaction of aluminium with iron oxide as shown in Equation (14-1). Although the heat output is modest compared to the compositions described in Section 14.1.1.1, around 4 kJ g^{-1} of mixture, the heat is held within the products and temperatures in excess of 2000 ^oC are obtained.

$$8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe \qquad \textbf{(14-1)}$$

This provides molten iron in the products which has been used for onsite welding operations. This type of composition is nominally gasless.

14.1.1.2 Binders

Pyrotechnic compositions are sometimes filled into stores as loose powders particularly when very fast reaction is required. However, it is more common to find compositions consolidated into a single pellet known as a 'candle'. This consolidation may be achieved by pressing, usually with a binder included in the composition and often in increments, or by 'in-situ' polymerisation.

Table 14-3 details examples of both natural and man-made binders in use by the pyrotechnics industry. It should be noted that this list is not exhaustive

although as can be seen the range of binders is extensive. Part of the art of pyrotechnics lay in knowledge of natural binder materials; however, the move presently is towards man-made binders where quality control and availability can be more strictly governed.

Table 14-3 Pyrotechnic Binder Materials

Natural	Man-Made
Acaroid resin (Plant resin)	Carboxymethyl cellulose
Beeswax	Chlorinated natural rubber
Boiled linseed oil (Flax oil)	Epoxy resin
Carnauba wax (Palm wax)	Polyester resin
Lithographic varnish (From linseed oil)	Polytetrafluoroethylene (PTFE)
Paraffin wax (From hydrocarbon deposits)	Polyvinylacetate PVA)
Shellac (Insect resin)	Polyvinylchloride (PVC)
	Silicone rubber
	Thiokol rubber
	Viton

Binders do more than just act as a consolidating agent. When present in significant amounts they can be considered as part of the fuel components. Also, the use of chlorinated binders can enhance the performance in certain cases, such as the production of coloured light.

The other major role of the binder is in the protection of reactive components. Metal powders such as those of magnesium and aluminium react with moisture which may be absorbed from the atmosphere. Coating these particles with a waterproof material can dramatically improve storage life. Thus, it is common practice to coat the metal powder by evaporation of an organic solution of a binder, such as lithographic varnish, before incorporation into the pyrotechnic mixture.

Other modifications which occur due to the presence of binders are reduction in burning rate and reduced sensitiveness (see 20.2.1) to initiation. This latter point is particularly true for polymer bound candles making them less susceptible to accidental initiation by friction or impact. However, it must be realised that purposeful initiation is also more difficult and that good ignition

methods are required. Finally, binders can aid powder flow in filling machines, reduce segregation and increase the waterproof properties of the composition.

14.1.1.3 Burning-rate moderators

Binders will normally reduce the burning rate of a composition. If further rate reduction is required, it may be achieved by incorporating inert materials such as clays or chemicals which decompose endothermically into the composition. Care must be taken that such moderators do not adversely affect the required output of the pyrotechnic, for example, flame colour.

14.1.2 MATERIAL PROPERTIES

The majority of pyrotechnic compositions used in military stores contain finely divided metal powders as fuel. These metals are usually highly reactive, such as magnesium or aluminium which, together with the large surface area available for reactions, makes these powders susceptible to degradation. The main problem is the reaction with moisture to form metal oxide and hydrogen. The presence of this extra metal oxide may well modify the output of the store. Also, the hydrogen produced may create a pressure build up making the device unsafe to handle. Thus the control of moisture content of a composition in manufacture and when filled in a store, is of great importance. As discussed in Section 14.1.1.2, metal powders are often coated with a binder such as lithographic varnish to give protection against moisture.

14.1.2.1 Sensitiveness

The diversity in the chemical and physical properties of the ingredients of pyrotechnic compositions is reflected in a corresponding diversity in the sensitiveness (see 20.2.1) of the compositions. The sensitiveness of the compositions depends on many factors which include:

a. The proportions of the ingredients, compositions in stoichiometric proportions tend to have greater sensitiveness than those which are not.
b. Particle size and shape; the larger surfaces presented by fine particles, particularly those with flattened or irregular shapes, increases sensitiveness.
c. The intimacy of mixing
d. The hardness of the ingredients as most pyrotechnic compositions contain metal or metalloid powders mixed with a crystalline salt or metal oxide powders and thus are gritty materials. These compositions show high sensitiveness to friction.
e. The atmospheric humidity plays an important role with electrostatically sensitive mixtures. Pyrotechnics containing zirconium are especially sensitive to initiation by electric spark discharge.
f. The presence of phlegmatisers which protect the fuel particles or act as diluents, and which may absorb much of the heat generated by local friction or impact, reduces composition sensitiveness.

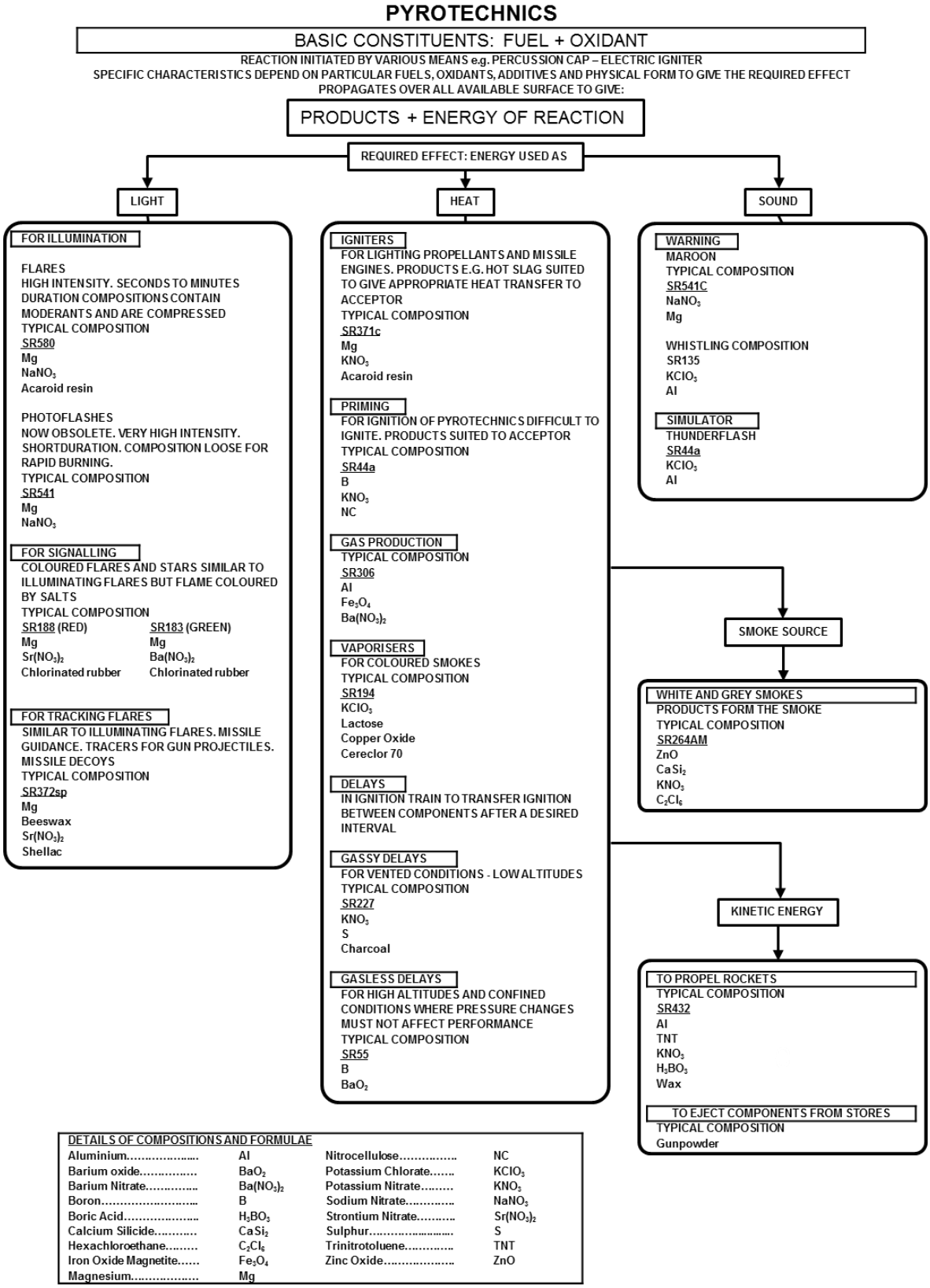
14.1.2.2 Explosiveness

Since the early 1980s the explosiveness (see 20.2.1) of pyrotechnic compositions has given rise to great concern mainly due to incidents during the processing of MTV flare (see 14.4.6) compositions. Accidental ignitions may not be more common with these compositions than with any other compositions but the explosive response (explosiveness) has been very violent and led to fatalities at production plants. The use of remote control facilities, robotics and personal operator protection is now used when these compositions are processed.

14.1.2.3 Classification of pyrotechnic compositions

The classifications of the types of pyrotechnic composition with examples are given in Table 14-4.

Table 14-4 Classification of Types of Pyrotechnic Compositions



14.2 FACTORS AFFECTING PERFORMANCE

When considering the performance of a particular pyrotechnic composition there are several factors which must be considered. The burning rate of a composition can be affected by the ratios of the ingredients (stoichiometry), by the chemical and physical characteristics of the ingredients (particle size and particle shape), presence of impurities, by the method of filling (consolidation pressure - compaction load) and the ambient temperature and pressure.

14.2.1 Effect of Ingredients – Stoichiometry

Once the particular chemical species to be used in a composition has been selected, there are many factors which can influence output. The first consideration is the ratio of reactants. If the products of the reaction are known, the optimum ratio of reactants can be chosen so that all ingredients are totally consumed. This is called the stoichiometric mix and weight percentages can be calculated from the balanced chemical equation. Stoichiometric mixtures are often the most sensitive and have the greatest heat output and for these reasons are not generally used.

The composition giving maximum heat output will also have the fastest rate of burning. This is measured in seconds per inch (s in^{-1}) and is usually the measured parameter when relating variations in composition with performance as shown in Figure 14-1. For any given grade of magnesium (0 to 5), as magnesium content increases, the luminosity and burning rate of the magnesium/sodium nitrate increase to maximum values at 60 % magnesium(1).

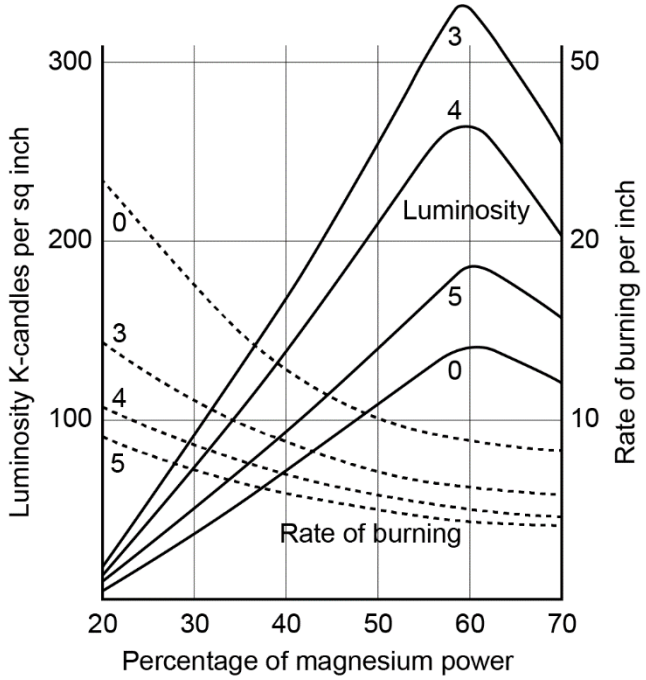


Figure 14-1 Variation of luminosity and rate of burning with grade and proportion of magnesium powder in magnesium - sodium nitrate compositions

It is of interest to note that since the maximum output occurs at 60 % magnesium, the reaction is not only between magnesium and sodium nitrate but also atmospheric oxygen. The stoichiometric mixture for the magnesium and sodium nitrate reaction would only contain 42 % magnesium based on the reaction shown in Equation (14-2).

$$5Mg + 2NaNO_3 \rightarrow Na_2O + 5MgO \qquad (14\text{-}2)$$

The heat output and, therefore, rate of burning will always be of a lower value when the composition changes from the stoichiometric mixture, either to a fuel lean or fuel rich situation. As shown in Figure 14-2, this means that two compositions will have the same heat output either side of the maximum, therefore, the composition choice for, say, a delay, could be made on economic grounds, depending on the relative costs of fuel and oxidant(1).

On practical grounds, however, the fuel rich mixture is preferable, since the slope is less steep on the fuel rich side giving more tolerance to slight changes in composition due to inhomogeneity. Also, the fuel lean compositions may well have very small amounts of fuel, making mixing difficult.

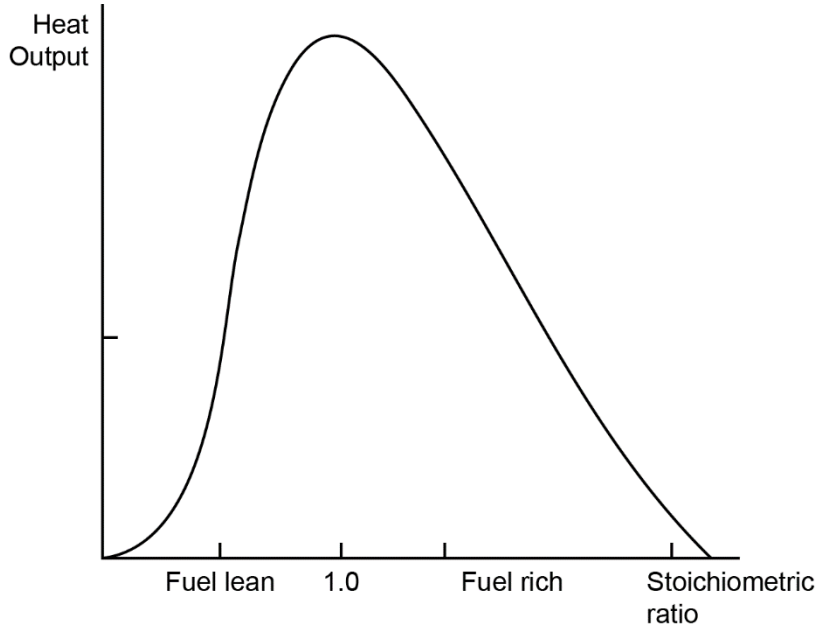


Figure 14-2 Stoichiometry versus heat output

The other method of obtaining a reduced heat output and rate of burning is to use the stoichiometric ratio or composition with the maximum values and add either an inert material or a coolant. This has the advantage that any slight change in the fuel oxidant mixture will have the least effect at this ratio being at the top of a curve. It must be remembered that the binder will probably act as a cooling moderator.

14.2.2 Effect of Particle Size and Particle Shape

Particle size and particle shape are of great importance since in most cases at least one if not all of the materials present are reacting as solids. Thus, the smaller the size of the particles, the larger the surface area per given weight at which reaction can occur. If the composition is held constant but the particle size distribution of one of the materials is changed, then performance can be modified to a large extent. Both rate of burning and luminosity of the flare composition shown in Figure 14-1 are altered markedly as the particle size changes. Metal powders can be obtained from sub-micron size called ‘ultrafine’, however, the usual range of practical use is from 5 μm to 100 μm.

For metal powders the particle shape is also very important. Metal powders are formed generally by one of two methods. Cut powder is manufactured by machining large pieces of metal whereas blown powder relies on the atomising of molten metal which is rapidly cooled and solidifies into spheres or pear-shaped particles. The cut powder being of a flake nature has a higher specific surface (area/wt) than blown metal powder. Therefore, a cut powder of apparently the same particle size distribution as a blown powder will have a larger surface area and thus react more readily. Some grades of metal powders are particularly reactive. For example, 'dark pyro' aluminium is much favoured by the pyrotechnician for its excellent performance in compositions. The shape of the particles can be assessed by measuring the apparent density, the less dense material being of the flake form whereas the higher density will be the near-spherical type.

The reactivity of solids is also controlled by strength of the intermolecular or interatomic forces that bind their crystal lattices together. These forces become weaker as the temperature is raised and atomic and molecular vibrations increase in amplitude. The strongest bonds are found in covalent lattices such as those of silicon; ionic bonds are next strongest and non-ionic lattices such as are found in organic compounds (e.g. hexachloroethane) are weakest.

Early work by Hedvall suggested that reactivity of a solid would be enhanced when the atoms or ions within the solid became more mobile. This occurs near the melting point (mpt) of the solid but also at phase changes, which occur for many solids at temperatures well below the melting point. Tammann quantified this with the coefficient α as shown in Equation (14-3).

$$\alpha = \frac{\text{Tsolid (K)}}{\text{Tmpt (K)}} \qquad \textbf{(14-3)}$$

Surface mobility becomes significant at α = 0.3 and internal mobility at α = 0.5. Thus, potassium perchlorate (mpt 588 °C) and potassium chlorate (mpt 364 °C) would have significant internal mobilities at 158 °C and 46 °C respectively.

14.2.3 Effect of Impurities

Small quantities of impurities or the presence of lattice defects due to the methods of preparation may also affect the reactivity of solids. Since pyrotechnics manufacturers are only small customers of large manufacturers it may be difficult for them to control specifications of ingredients and changes in suppliers may lead to changes in pyrotechnic composition performance.

14.2.4 Effect of Temperature

Pyrotechnics burn more slowly at low temperatures than at high temperatures, and the burning rates of the same system at two different temperatures can usually be related approximately:

$$r = r_0 \exp(bT/T_0) \quad \textbf{(14-4)}$$

Where r, r_0 are the burning rates at absolute temperature T,T_0.

14.2.5 Effect of Ambient Pressure

Pyrotechnics are burning explosives and as such are affected in their performance by ambient pressure. Vieille's Law relates the rate of burning (s in^{-1}) with pressure (atmospheres) as shown in Equation (14-5). The constants β and α (pressure index) differ from one composition to another.

$$r = a\,P^n \quad \textbf{(14-5)}$$

Where r is the burning rate at pressure P, a and n are constants for the chemical system. In general, the more gas that is produced by the pyrotechnic (how gassy) the greater the value of n (the greater the sensitivity to pressure).

If a composition's performance was independent of pressure, then n would be zero. This should occur for gasless mixtures, that is, those which produce no gas output at any stage of their combustion. This is never achieved completely and care should be taken when theoretical reactions seem gasless. The reaction between aluminium and potassium perchlorate, for example, should in principle form solid products only. However, during combustion large pressure increases can be measured.

Values of n, the pressure index, range from 0.5 for gas producing pyrotechnics such as gunpowder down to 0.05 for cool-burning 'gasless' compositions. It is important to consider that as pressure changes, the burning rate and thus performance can alter markedly. For example, gassy delays are unsuitable for delay elements in aircraft stores because of the dependence of the pressure index, and hence the burning rate, on the atmospheric pressure. At a height of 10 km the ambient pressure is 0.28 atmospheres and a pyrotechnic composition with an n value of 0.4 such as sulphurless gunpowder would have a burn 1.7 times slower than at sea level. Figure 14-3 shows the relationship between rate of burning and pressure, for five SR compositions. SR stands for 'Superintendent of Research', which was a numbering system for pyrotechnic

compositions developed at the Royal Armaments Research and Development Establishment, Fort Halstead, Kent.

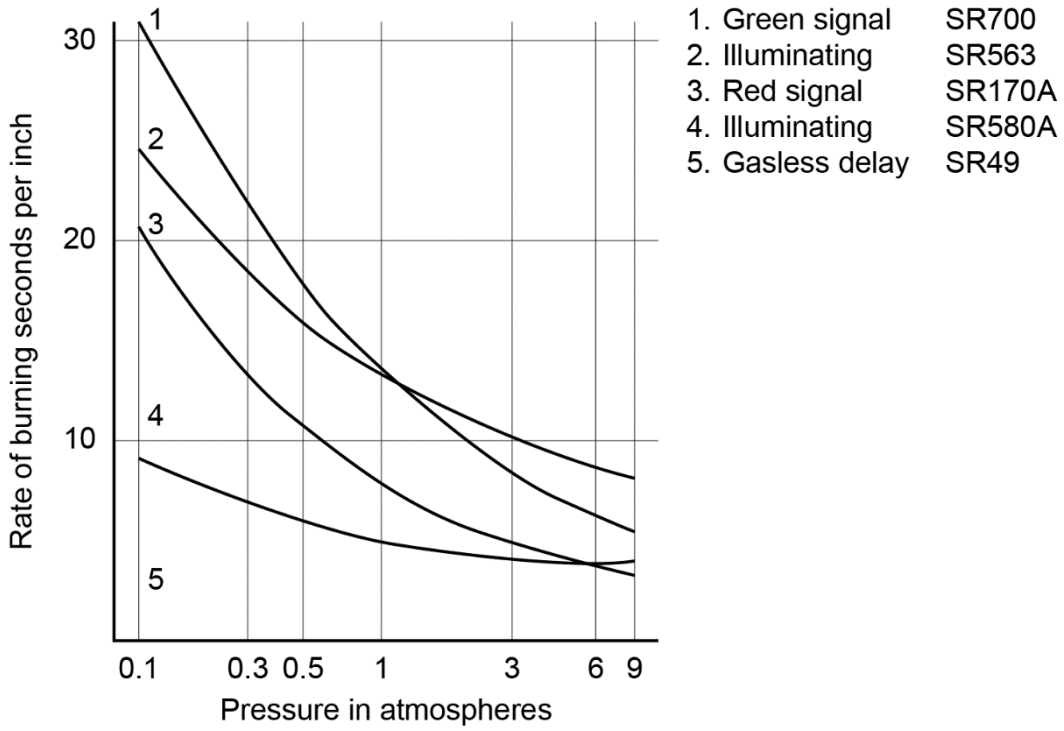


Figure 14-3 Variation in rate of burning with ambient pressure

14.2.6 Effect of Consolidation Pressure

The effect of consolidation pressure may markedly affect the burning rate, but its effect is often complex. If the combustion reaction is truly solid phase, that is no melting or vaporisation in the combustion zone, then increase in consolidation should allow better contact between the reactants, and the reaction rate should increase. If the reaction is not solid phase, then the effect is less predictable. Increasing the density decreases the porosity and thus may hinder hot gas penetrating the reactants and so reduce the burning rate. In most cases it is the linear burning rate of the pyrotechnic composition which is of interest to the designers, but the mass burning rate (kg s^{-1}) (see 7.2.2) is the real measure of the output from a pyrotechnic device. Many compositions have a lower linear burning rate at higher compaction loads, but the mass consumption rate decreases by less, or may even increase due to any increase in the density of the column.

It is unwise to attempt to predict the effect of consolidation on a new composition, as small changes in ingredient ratios and particle size can change the behaviour markedly. Except for pyrotechnic delay compositions, the effect of compaction on burning rate is usually of secondary importance, and the compaction load is adjusted to give optimum mechanical properties. Attention also must be paid to the ease of ignition, which often decreases at high compaction loads because the surface is smoother and less porous.

14.3 HEAT AS A SPECIAL EFFECT

In the following section priming, igniter, incendiary and delay compositions are considered.

14.3.1 Priming Compositions and Igniters

A priming composition is used to pick up the flash from an initiator such as an electric match-head or fuze-head and ignite the next component in the store, usually the main filling. Figure 14-4 gives an example of how a priming composition is used. In this case, two priming compositions are used, sulphurless fine grain (SFG) gunpowder composition picks up the flash from the ejection cartridge, ignites and then in turn, ignites the priming for the flare composition. This technique is used because the flare priming is not readily ignited by the cartridge flash. SFG is not suitable to ignite the flare but will readily ignite the flare priming layer.

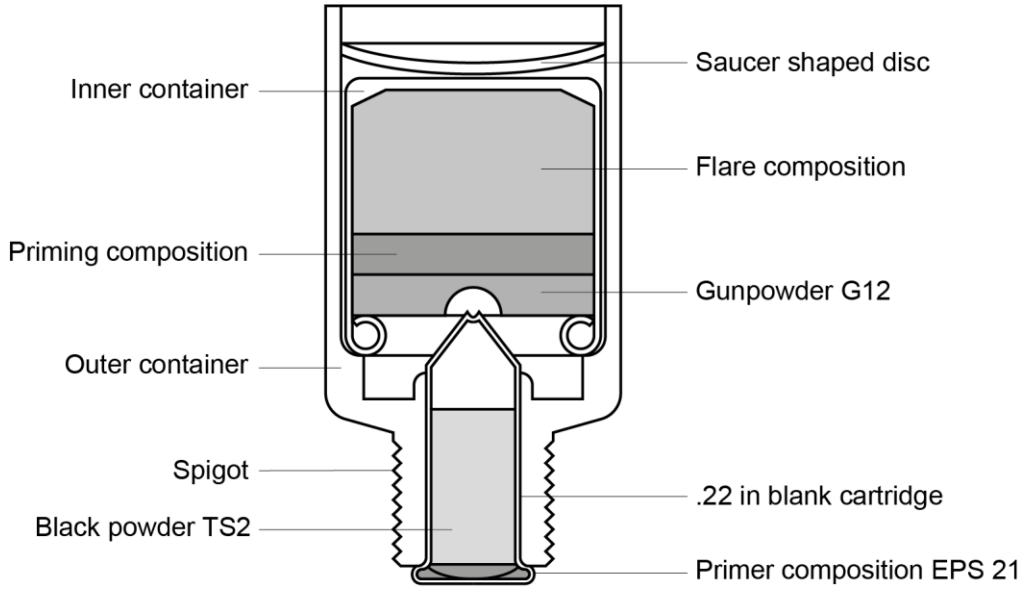


Figure 14-4 Example of a priming arrangement for a pyrotechnic store

Common terms for this type of composition are, priming composition, first fire, starter mixture and igniter. It is more usual to use the term igniter, for a store when it is used, for example to ignite rocket motors or flame-throwers. This type of igniter may well contain a pyrotechnic or propellant main filling and have an associated priming composition.

The role of a priming composition is essentially to act as a booster in a burning explosive train between the initiator and main charge. For such a composition to fulfil its role a number of requirements have to be met:

a. It should be readily ignited by flash or flame.
b. A large amount of heat must be generated but not too violently since that might throw the composition off the surface to be ignited.

c. The output characteristics should match the ease of initiation of the filling to be ignited.
d. Non-volatile products are desirable since a hot slag remains to enhance heat transfer.
e. Sensitiveness (see 20.2.1) should be compatible with safe handling.
f. The composition should be chemically compatible with the mixture to be ignited as often the priming composition is pressed directly onto the main filling and is in intimate contact.
g. The use of gassy mixtures will ensure a pressure increase aiding the ignition process.

The most important group of priming compositions are based on gunpowder since gunpowder is readily ignited by flash. Gunpowder itself burns fiercely when compressed and a layer of this alone may not ignite an underlying layer due to the rapidity at which the gunpowder is consumed. Several approaches have been used to slow the burning rate. The addition of lactose or resins will give slower burning compositions; however, a more popular method is to mix with the gunpowder, an equal weight of the material to be ignited.

The most common priming composition is SR252 based on potassium nitrate/silicon/sulphurless mealed powder. An example of its use is shown in Figure 14-4 where a first layer of gunpowder (SFG12) is used to ignite the composition which primes the main filling. Composition SR252 is used as priming in signal and illuminating cartridges, most flares and many other stores.

Other modifications are made to gunpowder. The sulphur content is often omitted to increase compatibility with other compositions. When an adjacent layer contains magnesium this alteration is a necessity due to the corrosive action of sulphur on magnesium. These materials are known as sulphurless fine grain (SFG) or sulphurless mealed powder (SMP) depending on their form. Another modification is in the way the gunpowder is supported to give a layer for priming. Cambric is a woven material on which the gunpowder is supported giving a rigid or semi-rigid layer. This is used in the priming of most screening smoke stores.

Certain compositions require a cool-burning priming layer since over-ignition may well create an undesired burning regime. Coloured smoke compositions are prone to this problem and a second type of priming composition, organic fuel plus oxidant, provides suitable mixtures. For example, SR214 based on lactose/potassium nitrate provides suitable ignition.

If ignition is to occur at high altitude where pressure is very low, then special gasless compositions are required. Gasless mixtures are used such as SR44 (boron/potassium nitrate), which is readily ignitable and burns under near vacuum conditions. This is an example of a slag producing composition which leaves a hot solid residue to enhance thermal transfer. This is a particularly important condition if ignition conditions are difficult. Another difficult ignition condition, where this type of composition is used, is that of tracer compositions as in SR370 (magnesium/potassium nitrate/charcoal) and SR867 designed as a ‘dark ignition’ for small arms tracer rounds (see 14.4.4).

Igniters for rocket motors are normally based on high heat output compositions with large amounts of solid products. A popular composition for the ignition of solid propellants in rocket motors is SR371C (magnesium/potassium nitrate/acaroid resin). Data on the compositions used for priming and ignition are given in Appendix A, Table A-1.

14.3.2 Incendiary Compositions

Incendiary compositions are used for fire raising, physical destruction of flammable materials and for the physical penetration of metals. The requirements of an incendiary composition are quite stringent. To ignite a flammable material, it is necessary first to drive off the moisture content and then cause sufficient thermal decomposition to provide flammable gases which on burning propagate the combustion. The requirements are, therefore, a high temperature, large heat output and a relatively long burn-time. The burning time is very important since massive heat flashes will rarely cause ignition of all but the most flammable materials.

To obtain large heat outputs over long time periods it is usual to use a fuel burning in air as oxidant. These are not strictly pyrotechnics; however, the incendiary effect is normally linked historically to pyrotechnics and is considered here.

There are two types of material in this category, combustible metals or alloys and liquid fuels, usually as a gel. The two metals of most use are aluminium and magnesium having among the highest heats of combustion of any element. The values are 29 kJ g^{-1} for aluminium and 25 kJ g^{-1} for magnesium, compared with 12 kJ g^{-1} for typical pyrotechnic compositions without metallic constituents. It is important to note that pyrotechnic compositions with heats of combustion approaching this magnitude burn explosively and would not be suitable as an incendiary material.

The combustible metal can be fashioned into an outer container which is then filled with a suitable igniter composition. This was the basis for the incendiary bombs which caused extensive destruction during World War II. The igniter composition is based on Thermite type materials. The conventional aluminium/iron oxide composition being difficult to ignite is modified by the addition of barium nitrate to improve ignition as in composition SR306. This composition provides over 4 kJ g^{-1} and consists of both flake and blown magnesium, hammerscale a form of iron oxide produced by hammering hot iron in air, is the oxidant, barium nitrate aids ignition and boric acid which stabilises the composition chemically against reaction of aluminium with barium nitrate in the presence of traces of moisture. The composition does not itself ignite readily from a flame and is therefore primed normally with SR252 (potassium nitrate/charcoal/silicon), with an intermediate layer of SR252 + SR306.

The other type of fuel used as an incendiary is a liquid hydrocarbon, thickened to make it adhere to target material. Various thickeners or gelling agents have been used such as rubber, Perspex and soaps. The most widely known

example of the gelled liquid incendiary is called Napalm although strictly this is the thickener, a mixture of aluminium naphthenate and aluminium palmitate. The fuel is normally petrol or kerosene.

From the point of view of an adhering incendiary liquid the Napalm based materials are not particularly effective since a fast-burning fireball is produced. This occurs because the liquid is thixotropic and thins under shear stresses such as explosive dissemination. This property, however, makes it a very good flame-thrower fuel. As it passes through the nozzle it thins for easy passage, and on relaxing thickens to hold the stream together giving good range. More suitable thickeners for a burst munition are rubbers or man-made polymers. A composition developed in the United States of America uses partially esterified polyisobutylmethacrylate as thickener.

Incendiary composition CC466 (similar to SR306) is presently used in Destructor Incendiary (DI) EOD XL5E1 and L5A1 and is intended for use by EOD and other trained users to either initiate the explosive filling in target munitions or initiate combustible materials to assist in the bulk destruction of munitions or destroy materials by heat, flame and hot metal residue (slag).

Incendiary stores have also been used to destroy documentation in an emergency. An example of which is the Document Wallet Self Destruction Incendiary. This consisted of a PVC wallet (235 mm x 170 mm) inside which is a sheet of pyrotechnic composition SRE794 attached via a delay to a friction igniter. To aid destruction the document pages are interleaved with sheets of celluloid.

Incendiary bullets and cannon-shell fillings are based on magnesium-aluminium alloy fuel with barium nitrate oxidant such as SR365 composition. A short list of incendiary compositions is given in Appendix A, Table A-2.

14.3.3 Delay Compositions

A delay element is a device filled with a flame or heat producing composition which burns in 'cigarette fashion' at a known rate so that it can be used to control the time interval between two events. Timing accuracy in some cases need only be sufficient to allow for operator safety. In more sophisticated uses the timing accuracy may be critical and timings at the millisecond level are required such as in commercial delay detonators or for function operations within missiles. Military delays are often filled into lead sheaths or tubes to achieve the required burning rate and timing accuracy.

There are many factors to be considered in the design of a pyrotechnic delay and choice of composition. Of paramount importance is the required time interval and acceptable accuracy. Compositions are available which will burn from 0.01 s in^{-1} to 40 s in^{-1}.

The volume and shape of the space available to house the delay column may affect choice. In many simple munitions the delay column can be readily incorporated. However, in complex systems the physical form of the delay may

be dictated by the space available. Delay elements often consist of the composition filled into a lead sheath or tube. Small diameters are obtained by filling a large tube and then swaging down to the required diameter. This can be wound into a spiral to be accommodated in a restricted space. Other methods of incorporating a delay are to fill a channel cut into a metal or plastic plate or to have channels within the device such as in bomb and shell fuzes.

The operating temperature of a delay column will affect its rate of burning if the composition is either gasless or low gassing. In a crowded design, heat dissipation may be poor with associated large temperature rises. It is pertinent here to make note of the relevance of available heat sinks around the composition particularly the container. If the containment is a very good conductor of heat such as copper, the composition will have a slower rate of burning than if the heat cannot escape in this fashion. The designer of a delay munition must optimise these factors to suit the situation.

A choice must be made between a vented, semi-vented or obturated (closed) system. Vented systems are used when a gassy composition such as gunpowder is employed. For a delay a constant burn rate is required. The gaseous products must have, therefore, an unobstructed vent to atmosphere. A semi-vented system allows venting from the delay element into another closed system of finite volume. Obturated systems are used for the so-called gasless compositions and are particularly important at high altitude. It should be noted, however, that no system is truly gasless. For example, PbO/Si (80/20) burns at 2 s in^{-1} in the open but in a sealed tube at 1 s in^{-1} due to the formation of lead vapour. Compositions have been developed whose burning rates are essentially independent of pressure. These compositions, based on boron fuel with either barium or lead chromate as oxidant, are prepared by a co-precipitation process. One of these, boron/barium chromate, has a burning rate 15 % slower at 0.03 atmospheres compared to that at 1 atmosphere for a mechanical mixture whereas the co-precipitated mixture shows no change in rate.

The ignition source must be considered, since some compositions may be difficult to ignite. Delays are ignited in Service stores by several methods including burning propellant, percussion cap and electric fuze-head. The delay must pick up reliably from the ignition source.

The event to be initiated by the delay requires a consideration of suitability. The delay could be chosen to provide several different outputs such as flash, heat and pressure or heat only.

The simplest delays use gunpowder as the pyrotechnic composition. Fuse Instantaneous L1A1, used in Battlefield Noise Simulators, consists of a semi-fuse made from glazed Kraft Paper twisted yarn coated with sulphurless mealed gunpowder wound with yarn and protected by an outer light polyethylene covering and burns at not less than 33.5 m s^{-1} at 16 °C. Gunpowder is the filling in Safety (Bickford) Fuze which consists of a gunpowder core enclosed in braided flax or jute and covered in rubber. Vent holes are provided to maintain an even pressure within the tube and the burning rate is 2 ft min^{-1}. The

variability of moisture content within the gunpowder due to the properties of charcoal precludes the use of the material for accurate timing although one such composition, SR227 based on potassium nitrate, charcoal and sulphur, was in Service use in the Fuze Nose Time No.390. Fuze timing for shells and bombs is now almost exclusively mechanical or electronic. However, as a safety delay as in demolition work, Safety Fuze is ideal.

To overcome the problems of moisture in the gunpowder other organic materials have been employed such as tetranitrocarbazole (TNC), nitroindene polymer and tetranitro-oxanilide. One such composition, SR12, based on TNC and potassium nitrate, is used in the Anti-riot Irritant CS Hand Grenade, L13 as delay composition. Another example of the use of organic fuel with barium and potassium nitrates, SR651, is used for the delay in some mortar systems where delay ignition is achieved from the burning propellant as the mortar bomb is fired.

Gasless delay compositions are based on metal or metalloid powders mixed either with oxidant salts or metal oxides, the latter oxidising agents giving Thermite type materials. For millisecond delays, very reactive combinations are required such as silicon or boron with an oxide of lead or bismuth, for example SR57. If the oxidant is a chromate or dichromate, the compositions will be slower giving second interval delays. One example of this type is co-precipitated barium chromate compositions with various fuels. One of these based on boron as fuel, RD1368, has been employed in the L25A5 Percussion Grenade Fuze. If lead chromate is employed the compositions become more reactive, and if the boron is replaced by titanium the burning rate is extremely rapid as in RD1370. If dichromate is used the compositions become slower as for SR67.

It should be noted that the rate of burning is dependent on exact compositions and also on pressing load. Compositions and their burning rates are given in Appendix A, Table A-3. Ambient pressure is one atmosphere and rate will alter even for the gasless mixtures, except for RD1368, as pressure changes. The factors which affect pyrotechnic performance are of particular importance in delay technology. Even small changes in stoichiometry or particle size will alter the rate of burning as will factors such as pressing load or container material (heat losses).

14.4 ILLUMINATING COMPOSITIONS (INCLUDING VISIBLE AND INFRARED EMISSIONS)

Some pyrotechnic compositions are designed to produce electromagnetic radiation. Depending on the region of the electromagnetic spectrum in which the radiation is produced, the special effect will be white or coloured light visible to the eye, or infrared radiation for wavelengths longer than 750 nm. The various regions and wavelengths of the electromagnetic spectrum are shown in Figure 14-5 and Table 14-5.

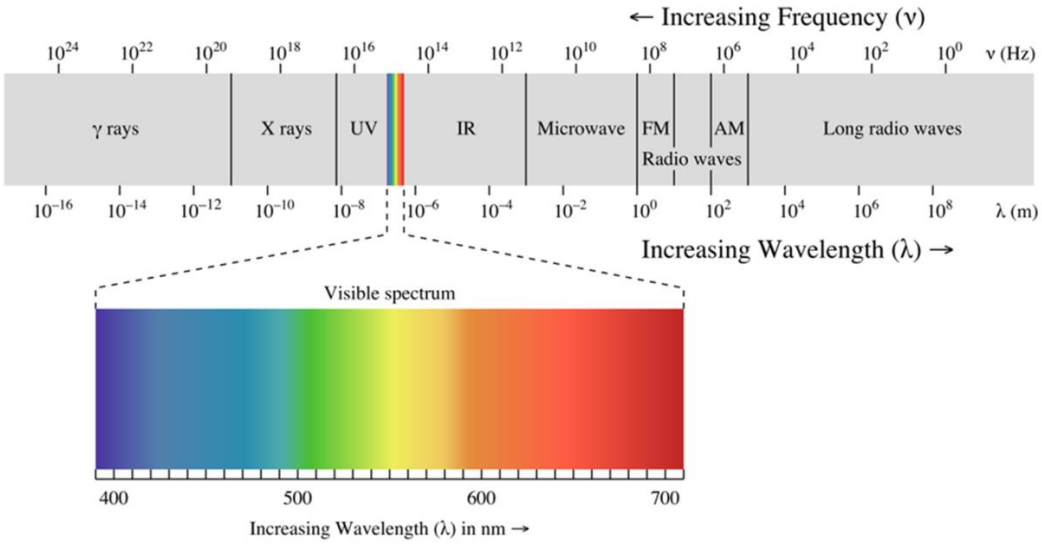


Figure 14-5 Electromagnetic Spectrum

Table 14-5 Regions of the Electromagnetic Spectrum

Region	Wavelength range
Ultraviolet	<380 nm
Violet light	380 – 440 nm
Blue light	440 – 495 nm
Green light	495 – 558 nm
Yellow light	580 – 640 nm
Red light	640 – 700 nm
Infrared	700 nm – 1 mm

The effects produced by the compositions considered in the following paragraphs are:

a. Long duration illumination for target acquisition, reconnaissance, exposure of infiltrators and emergency landing
b. Signalling with either white or coloured light
c. Decoys emitting infrared radiation

14.4.1 Radiometric and Photometric Units

Radiometric units are concerned with the transfer of all radiant energy from or to a body. The total rate at which a body emits radiation energy is the *radiant flux* which has units of power (W). Emission in a particular direction as measured

radiometrically is the *radiant intensity* which is the radiant flux within unit solid angle measured in units of power per steradian (W sr^{-1}). If the body is not a point source, then the radiance is the radiant intensity per unit surface. If the body is receiving energy, its *irradiance* is the radiant flux that it receives per unit area. It is customary to report the values within a narrow waveband centred at a wavelength of interest with the results quoted per nanometre (the energy emitted at an infinitely narrow single wavelength is zero).

The sensitivity of the human eye to visible light depends on the wavelength. For example, two monochromic sources of identical radiant intensity but different wavelengths appear to be of different brightness. Photometric units have been established that allow for this and the luminous intensity is related to the radiant flux by the sensitivity curve for a standard human eye.

The total rate at which light is emitted is the *luminous flux* from the source, measured in *lumens* (lm). The light emitted in a given direction is the *luminous intensity* measured in lumens per steradian, a unit usually known as *candela* (cd). The luminous intensity from unit area of the source (its brightness) is the luminance (cd m^{-2}) and the light falling on unit area of a surface is its *illuminance* (lm m^{-2}), also known as *lux*. If a light source emits with a luminous intensity of 1 candela in all directions, it provides a luminous flux of 4π lumens. Radiometric and photometric units are summarised and compared in Table 14-6.

Any radiating body radiates only part of its energy in the visible region of the spectrum. The fraction of the total radiation emitted as light is the luminous efficiency of the source, measured in lumens/Watt.
In pyrotechnic applications, a number of characteristics of a flare are important.
Pyrotechnic nomenclature, synonyms, units and definitions often encountered are given in

Table 14-7.

Table 14-6 Radiometric and Photometric Units

	Radiometric Units		**Photometric Units**	
Rate of energy emission	radiant flux	W	luminous flux	lm
Radiation emitted in a specific direction	radiant intensity	W sr^{-1}	luminous intensity	Lm sr^{-1} cd
Radiation emitted per unit surface area in a specific direction	radiance	W m^{-2} sr^{-1}	luminance	cd m^{-2}
Radiation striking a unit area	irradiance	W m^{-2}	illuminance	Lm m^{-2} (or lux)

Table 14-7 Additional Units Used in Light Producing Pyrotechnics

Pyrotechnic Nomenclature	Synonym	Units	Definition
Specific intensity	luminance	cd m^{-2}	Luminous intensity per unit area of source.
Specific efficiency	specific light flux	cd s g^{-1}	Total emitted light per gram of composition; compares compositions irrespective of burning rate.
Energy conversion	luminous efficiency	lm W^{-1}	Compares luminous flux with the exothermicity of the composition.

14.4.2 White Light

The radiant or luminous energy emitted from a given source is very dependent upon the temperature of the source. A perfect radiator of electromagnetic radiation is called a black body (a condition rarely achieved and certainly not with pyrotechnics) whose energy emission is proportional to temperature to the fourth power. Thus high temperature compositions are required to provide large radiant outputs.

The production of white light, often with a yellow colouration, can be achieved by several methods. Foremost is the creation of very high temperatures to give thermal excitation and cause of broad continuous emission across the visible region. Secondly, the presence of sodium, particularly with a source of hydrogen gives another broad continuous emitter, NaH^+, which emits from 550 nm - 700 nm providing the yellow colouration. The presence of organic material, as in the binder, is known to enhance luminous output of flares. Thirdly, the presence of species emitting in certain bands of the visible spectrum can further enhance performance. Examples of these species are, BaO^+, $BaCl^+$ and $SrCl^+$, the latter two used together if white light is required. Such species are only stable at very high temperatures found in burning flare compositions.

The requirements of an illuminating store are that it burns for the required time interval, that it has an appropriate luminosity and that the flame colour is as desired. These factors are achieved by a judicious choice of composition, bringing in many of the factors, previously described, which affect pyrotechnic performance. Examples of illuminating compositions showing the effects of composition modification on flare performance are contained in Appendix A, Table A-4.

The fuel used in illuminating compositions is always magnesium and the preferred oxidant is sodium nitrate. With an organic binder, this provides the very high temperatures and emitting species such as NaH^+. As shown

previously in Figure 14-1 the optimum magnesium content is 60 % in magnesium/sodium nitrate compositions such as SR580 which has by far the best performance of these compositions.

Particle size of the fuel is extremely important as shown by comparison of SR563 and SR563A compositions. Here the specific intensity is more than doubled by changing from grade 0 (coarse) to grade 5 (fine) magnesium. This is also exemplified in Figure 14-1. The burning rate of SR563A is about half that of SR563 and a smooth curve relationship exists between luminous performance of burning rate as shown in Figure 14-6.

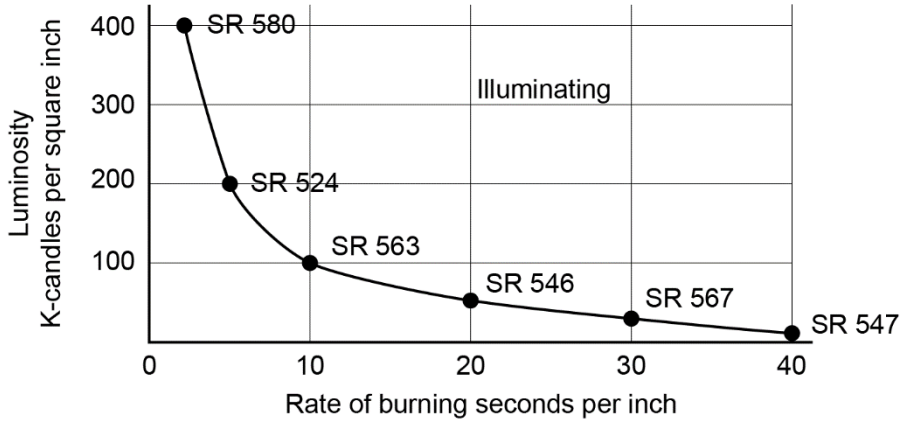


Figure 14-6 Luminosity versus rate of burning

Other modifications include the use of calcium oxalate to moderate and thus slow the rate of burning. Composition SR562 has almost the same fuel content as SR563, however, the presence of calcium oxalate (7 %) gives a rate of burning 1.5 time that of SR563 (17.8 s in^{-1} c.f. 12.0 s in^{-1}) and reduces luminous output to around 60 %. This type of modification is a useful method for increasing the endurance of a flare's illumination at the expense of luminous output.

Barium nitrate may also be employed in illuminating compositions. This increases the physical stability of the burning candle and consequently there is a lesser tendency for burning lumps to be ejected from the burning surface. The output of these compositions is less than sodium nitrate based materials, for example, compare SR343A with SR562 (see Table A-4 in Appendix A).

Choice of composition, therefore, depends on the requirements of the store. The tripwire flare, used to expose infiltrators, does not need the luminous intensity of a parachute flare operating at altitude; however, burn time is important. These needs are fulfilled by SR547. Parachute flares or stars require high intensities to provide ground illumination and thus, compositions such as SR576A in the anti-submarine aircraft flare and SR580 in the star for the 1.5 inch illuminating cartridge are utilised. Illuminating cartridges without parachutes need to produce high intensities and are relatively small since they only burn for a short time. The output from the compositions list above is given in Table A-4 of Appendix A.

14.4.3 Coloured Light

Coloured flares are known as signals and as such must be capable of being distinguished from considerable distances and against adverse backgrounds such as a bright sky. The requirements for such compositions are:

a. A good luminosity
b. A distinctive colour
c. Colour which is highly saturated

Colour is produced by the emission from molecular species over wavebands appropriate to that colour. However, to attain the temperatures required to produce these species and to give a suitable luminosity for viewing at a distance the composition will also produce a continuum of white light achieved by using magnesium as fuel. This causes unsaturation of the colour and in some cases may give poor colour recognition. The luminous output of coloured flares is significantly lower than that from illuminating compositions.

14.4.3.1 Red light

The red part of the spectrum covers the range 640 nm – 750 nm and species which emit in this range include $SrCl^+$ (620 nm – 680 nm) and SrO^+ (600 nm - 690 nm). Red flames, therefore, require a source of strontium and chlorine in the composition. This has been achieved successfully using compositions consisting of magnesium fuel, strontium nitrate as oxidant and source of strontium with a chlorinated organic material, such as PVC or chlorinated rubber as the source of chlorine. These give good colour and have a relatively slow rate of burning. For example, commercial composition CC325 used in Signal Kit Pyrotechnic 16mm.

A further example is composition SR170A which consists of a mixture of magnesium fuel, potassium perchlorate as oxidant and source of chlorine and strontium oxalate as the source of strontium. This composition was used in the, now obsolete, 1.5 inch Signal Cartridge.

14.4.3.2 Green light

It is somewhat more difficult to produce a highly saturated green emission than it is red. The green part of the spectrum covers the range 495 nm – 558 nm and emission in this region is achieved from $BaCl^+$ having a spectral band from 505 nm – 535 nm. However, BaO^+ gives a broad band emission 400 nm - 800 nm which complements the high temperature continuum of white light, adding to the dilution of the green waveband emission.

The longest established compositions which produce green flames contain magnesium as a fuel with potassium perchlorate and barium chlorate as oxidants. Barium chlorate provides the barium and potassium perchlorate the chlorine as in SR429. The presence of barium chlorate, however, makes these compositions rather unstable in the presence of moisture. A second type of composition which is much more stable in storage is based on magnesium and potassium perchlorate. In this case the barium is introduced as barium nitrate

and additional chlorine as a chlorinated organic material such as PVC. The luminous output of this second group is generally much less than those containing barium chlorate, for example SR700 used in the, now obsolete, 1.5 inch Signal Cartridge. However, the increased stability is an important factor in military stores. For green signal flares such as those used in the Signal Kit Pyrotechnic 16 mm it is more common to use commercial composition CC326 which consists of magnesium fuel, barium nitrate as oxidant and source of barium with a chlorinated organic material, such as PVC or chlorinated rubber as the source of chlorine.

14.4.3.3 Yellow and white light

The production of yellow flames requires emission in the range 580 nm - 640 nm and this is provided by the presence of NaH^+ giving a broad band emission over the range 550 nm - 700 nm. Yellow signals rely on sodium to produce the colour and use sodium nitrate as the oxidant. Sometimes they also contain barium nitrate to counter the tendency of a yellow flame to appear orange through atmospheric haze. Coolants such as sodium or calcium oxalate which decomposes endothermically producing carbon dioxide may be added to reduce desaturation of the colour whilst maintaining a sufficiently high burning rate. The emission spectra for yellow light compositions are generally similar to those of an illuminating composition. Flare Ground Indicating No.1 Yellow used during conditions of poor visibility to indicate the position of an airfield runway in use contains composition SR562H.

White light signal flares such as those used in the Signal Kit Pyrotechnic 16 mm consist of commercial pyrotechnic compositions such as CC327. These compositions contain magnesium fuel, barium nitrate and strontium nitrate as oxidant and source of barium and strontium with a chlorinated organic material, such as PVC or chlorinated rubber as the source of chlorine

14.4.3.4 Blue light

Blue signal flares are rarely used since the emission in the blue region of the spectrum 440 nm – 496 nm from pyrotechnics is weak. Furthermore, the human eye does not register blue wavelengths as readily as other colours such as red and green. The presence of a strong white continuum will “wash out” blue emissions, therefore any blue flare must be of low intensity. Blue wavebands are produced by $CuCl^+$ over the region 420 nm – 460 nm. The compositions usually have lactose as fuel with potassium perchlorate as oxidant, producing much less energetic mixtures than the magnesium fuelled systems. A copper salt and source of chlorine is then added. The luminous intensity is an order of magnitude less than for red, green or yellow flares as shown for SR405 in

Table 14-8. Blue signal flares cannot be used in daylight which restricts their use.

Table 14-8 Coloured Signal Compositions – Luminous Intensity

Designation	Luminous Intensity (cd in^{-2})
SR170A Red	92500
SR700 Green	16500
SR560 Yellow	152500
SR405 Blue	200

Typical compositions used across the spectral range are given in Appendix A, Table A-5.

14.4.4 Tracer Compositions, Tracking Flares and Target Flares

Tracer ammunition (tracers) are bullets or artillery projectiles that contain a small pyrotechnic composition contained in the base of bullets or shells. When the weapon is fired, a priming composition is ignited by hot propellant gases which in turn ignite the tracer composition. The pyrotechnic composition burns very brightly (cf. bright and subdued tracers), making the trajectory of the projectile visible to the naked eye during daylight, and very bright during night time firing. This enables the firer to make aiming corrections without observing the impact of the rounds fired and without using the sights of the weapon.

Tracer compositions must function under very demanding conditions and provide sufficient luminous output to be observed throughout the flight of the projectile. A small arms round, for example, will be spun at about 400,000 rpm and be subjected to an acceleration of 200,000 g. To provide the necessary burn time, the filling must burn 'cigarette fashion inside the container and must not crack or allow the flame front to travel down the side of the filling. This would significantly reduce the functioning time.

In flight there will be a low pressure area behind the projectile where the composition is burning. Tracer compositions must be as gasless as possible to minimise pressure effects on the rate of burning. It is usual to use a priming layer pressed onto the tracer composition which is ignited from the heat of the burning propellant. This composition must maintain combustion on the large pressure drop as the projectile leaves the barrel of the gun.

There are three types of tracer; Bright, Subdued and IR/Dim. Bright Tracers sometimes known as “Red Tracers” start burning immediately after exiting the muzzle. This has the disadvantage that the firer’s location can be given away. An example of a red tracer is composition SR390A (magnesium, linseed oil, strontium nitrate, strontium peroxide, talc). A priming composition SR370

(magnesium fuel and barium peroxide oxidant) is used with this tracer composition.

Subdued Tracers sometimes known as “Dark Tracers” burn at full brightness after a few hundred yards and avoid giving away the fire’s position or dazzling the firer during night firings. For tracers of this type there is a requirement for 'dark ignition', a priming layer which emits little light. This has been achieved by using SFG12 gunpowder which ignites an intermediate dark ignition priming layer which in turn ignites the tracer composition. Direct dark ignition priming is obtained by composition SR867.

Both bright and subdued tracer ammunition can create excessive illumination or visual interference known as the blooming effect when viewed through night-vision devices (NVDs). To counter this effect, IR/Dim tracers have been developed which emit in the near infrared region of the spectrum, which prevents the tracer from being detected by the naked eye. To meet this requirement, tracer compositions have been developed which emit in the near infrared region of the spectrum. Tracers of this type are invisible to the naked eye, but visible through NVDs and do not cause the blooming effect. Dark Ignition priming composition is used with IR/Dim tracers. Examples of typical priming compositions used with tracers are given in Appendix A, Table A-6.

Red provides good contrast against blue sky and green fields, and bright red compositions are readily made. Most visible NATO tracer compositions are red however, most visible Russian and Chinese tracer compositions are green, the reason for this is unclear but one possible explanation is that green tracer is more effective in an urban environment. Tracers are required for projectiles of all calibres, SAA (i.e. 5.56 mm) to anti-tank rounds (i.e. 120 mm). Different compositions are required for small arms and artillery ammunition.

Tracking flares for missiles have constraints similar to tracers; that is, high velocities which reduce luminosity, and low pressure behind the flare. Compositions used both for tracking flares and target flares are often based on magnesium and sodium nitrate, such as SR568A a typical white illumination mixture. The performance may be enhanced by additional components such as barium and strontium salts (both required for white light) and a source of chlorine such as chlorinated rubber. For high altitude uses the composition should be as gasless as possible. This is achieved by the use of barium peroxide as oxidant with the minimum binder. An example of this is SR399 where the rate of burning at an altitude of 60,000 ft is 5.4 s in^{-1} compared with 4.6 s in^{-1} at sea level. While for SR568A there is a change in burning rate from 6.0 s in^{-1} burning at sea level, to 12.1 s in^{-1} at 35,000 ft.

For missile tracking flares, the smoke produced by the flare may cause unacceptable levels of obscuration. This can be remedied by the use of titanium as fuel instead of magnesium. One such composition is SR699 using strontium nitrate as oxidant. Compositions that have been used for tracers, tracking flares and target flares are given in Appendix A, Table A-7.

14.4.5 Infrared Decoys

One of the most important developments in the pyrotechnics field is that of infrared decoys. As the name suggests the decoys act to protect targets which emit in the infrared region of the electromagnetic spectrum. The main use is to protect aircraft, from heat-seeking missiles. To be effective the decoy thermal output must be greater than that from the exhaust of the jet engine. Three types of pyrotechnic devices have been evaluated for Service use - pyrotechnic flares, spectral flares and pyrophoric flares.

14.4.6 Pyrotechnic Flares (MTV)

The pyrotechnic flares are based on magnesium, PTFE and Viton formulations commonly referred to as MTV compositions. These flares in essentially the same form have provided standard self-protection for all military aircraft since the 1970s. The combustion products, mainly incandescent carbon, emit grey body radiation in both the infrared and visual region of the electromagnetic spectrum. Flares of this type work by generating a heat signature in excess of the platform signature. The effect is to seduce any heat seeking missile's homing system into locking on to the flares' instead of the heat signature of the target platform. The required output is in excess of 8 kJ g^{-1} and achieved by formulating a fast burning composition with high calorific value which burns over the whole surface of the candle. It must also reach the required decoy energy output in the shortest time possible after deployment. Performance achievable from these flares is for example, time to effective output < 0.5 s and burning time 2.5 s to 3.5 s with intensities up to 35 kW sr^{-1}. Compositions of this type of flare are classified.

14.4.6.1 Hydrogen outgassing and mitigation

A major problem with pyrotechnic flares containing MTV compositions and all pyrotechnic compositions containing magnesium is that during storage they can evolve hydrogen. This is generally brought about as a result of reaction between magnesium and water:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \qquad \textbf{(14-6)}$$

This raised serious safety concerns with reported increased pressures and high levels of hydrogen in ammunition container assemblies housing MTV type flares. This resulted in the development of a suitable hydrogen scavenger, referred to as a "Hydrogen Getter" which is now used extensively in ammunition container assemblies housing MTV countermeasure flares.

14.4.7 Spectral Flares

Traditional MTV flare composition spectral distribution does not match that of a typical aerial target, whose spectral output is mainly created by burning kerosene as shown in Figure 14-7**Error! Reference source not found.**.

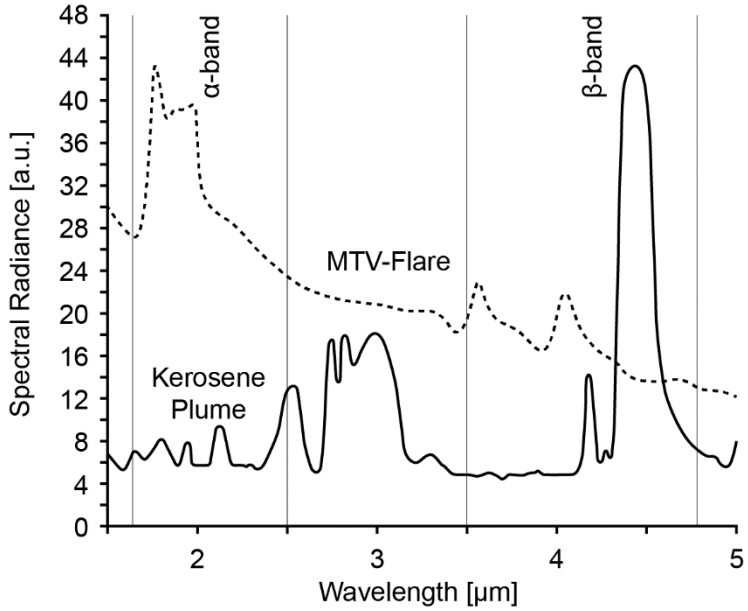


Figure 14-7 Spectral intensity of MTV flare and Kerosene plume[8]

IR missiles search out the hotter flame provided by the MTV flare which burns at around 2000 °C whereas the aircraft jet engine temperature is in the range 600-800 °C. Newer generation missile seekers can spectrally discriminate between the decoy and the aircraft exhaust plume and can compare the energy levels in two different parts of the IR waveband simultaneously. If the flare does not match certain criteria it will be rejected as a non-target.

To mitigate this problem, spectrally matched flares have been developed. The flare provides large amounts of hot H_2O and CO_2 on combustion, similar to burning kerosene aviation fuel and effectively matches the exhaust of jet engines.

Spectral flare compositions are usually based on propellant and/or high explosive rather than pyrotechnic compositions such as MTV. Compositions of this type of flare are classified.

14.4.8 Pyrophoric Flares

Pyrophoric substances ignite spontaneously in air. The main advantage of these is that they produce CO_2 and H_2O vapour as the main constituents of their combustion products and therefore match spectrally the exhaust of jet engines. The materials can be solid, e.g. iron platelets coated with ultrafine aluminium, or liquid, often organometallic compounds such as alkyl aluminium compounds, such as triethylaluminium and ignite on contact with the oxygen enriched airstream providing an alternative IR source for the missile to target. Pyrophoric decoy flares exist in various shapes and sizes to suit the appropriate flare dispenser. Pyrophoric materials have low intensity power output levels, partly due to dilution in the wind stream in which they must function. As a result, they are generally used as a pre-emptive countermeasure prior to lock on.

Some flares work on the principle of ejecting a special pyrophoric material out of an airtight cartridge. The material then self-ignites in contact with air. The main advantage of pyrophoric flares is that they are covert in nature due to the fact that only a faint glow, not a ball of flame, is produced. They are also effectively invisible to the naked eye during the day.

14.5 SMOKE COMPOSITIONS

All smokes are aerosols, suspensions of small particles in air which settle very slowly under gravity. Typical sizes for these particles which may be solids or liquids are between 0.1 μm and 5 μm. The types of smoke covered in this section are:

a. Coloured smoke for signalling
b. Smoke and flame signals
c. Irritant smoke for crowd control
d. Screening smoke

14.5.1 Signal Smokes

Coloured smokes are produced for military use by the vaporisation of an organic dyestuff, heated by a pyrotechnic composition. These smokes are used for signalling, screening and for visual displays. The main colours are red, orange, green, yellow, violet and blue. Smokes are produced by the vaporisation of an organic dyestuff, heated by a pyrotechnic composition. When the vapour leaves the exit hole of the store, it is cooled as it enters the air and condenses back to solid particles of the required particle size distribution to be a smoke aerosol. The organic dyestuff is intimately mixed with the pyrotechnic composition and ideally is should vaporise or sublime below 350 °C and have good thermal stability.

For effective smokes, chemical reactions during smoke formation should cause only minimal thermal decomposition. In order to achieve this the fuel-oxidant system must fulfil some demanding requirements. The temperature produced must be sufficient to give efficient vaporisation of the dye. However, since the dyestuff is an organic compound it can pyrolyse and the composition must, therefore, be cool enough to prevent or minimise this degradation. There should be a minimum of solid residue from the fuel-oxidant reaction because reactions can occur between the dyestuff and char. Any smoke formed other than by dyestuff vaporisation will dilute the colour and should not occur. Particle size of these components plays a very important role in determining smoke quality.

The composition of choice is lactose monohydrate as fuel and potassium chlorate as oxidant. The general reaction that occurs between the ingredients is shown in Equation **(14-7)**.

$$C_{12}H_{22}O_{11}H_2O + 8KClO_3 \rightarrow 12CO_2 + 12H_2O + 8KCl \qquad \textbf{(14-7)}$$

The stoichiometric mixture, 26 % w/w lactose, 74 % w/w chlorate, burns too hot and would decompose the dyestuff therefore; the mixture normally employed will be near a 50/50 mix (i.e. lactose 25 % w/w, chlorate 25 % w/w, dyestuff 50 % w/w). The excess fuel may lead to char formation which includes elemental carbon. At the temperatures present in the char, water may react with the carbon forming hydrogen gas. This is the 'water-gas' reaction shown in Equation (14-8). The hydrogen thus formed can react with double bonds in the dyestuff necessary to produce their colour.

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad \textbf{(14-8)}$$

This additional reaction can alter the colour of the dye, possibly making it colourless. Design of munitions which enhance dyestuff-char contact should be avoided. Examples of UK service signal smokes and smoke compositions are detailed in Appendix A, Table A-8.

14.5.2 Marine Markers

Marine markers are stores designed to produce a visible signal both day and night for prolonged periods of time. They may be dropped by aircraft, usually on a parachute, or released from submarines at depth. Stores include, Marine Marker No.4 Mk N11, Float Smoke and Flame No.1 Mk5 and N2 Mk4, Candle Smoke White N6 MOD5 and Candle Smoke Yellow N7 MOD4.

On functioning these stores provide smoke and flame, usually from burning red phosphorus or occasionally a phosphorus compound such as phosphine (PH_3). The smoke produced is based on phosphorus oxide hydrolysis products as described in Section 14.5.5. The luminous output comes from a yellow lambent flame. Being a marker the burn time is more important than smoke density; however, the density must be sufficient for visual recognition at some distance.

To obtain the necessary burn times, pyrotechnic reactions are used to vaporise excess phosphorus in the composition which burns in the air as it exits the store. For example, SR414 uses calcium silicide and magnesium as fuel with manganese dioxide as oxidant. The heat these produce on reaction vaporises the red phosphorus. This is quite a vigorous reaction which maintains pressure inside the store to counteract ingress of seawater which might extinguish the burning phosphorus flame.

A newer composition used in the Marine A/C Marker, No. 4, is SR622, and variations, based on calcium sulphate and red phosphorus. These react to produce heat to vaporise excess phosphorus plus phosphorus sulphide. This composition, which includes oxalic acid, has a very slow burning rate (240 s in^{-1}). This gives one hour of functioning from a 4.5 kg charge. The oxalic acid is present to maintain pressure inside the store by thermally decomposing to give gaseous products.

One other type of composition, not strictly a pyrotechnic, has been used. This utilises the reaction between water and calcium phosphide which releases phosphine (PH_3) and a diphosphine impurity (P_2H_4) the latter being spontaneously flammable in air. Both hydrides burn to produce a 'phosphorus' smoke. Examples of UK service Marine marker smokes and smoke compositions are detailed in Appendix A, Table A-9. A typical marine marker, Float Smoke and Flame N.2 Mk4 is shown in Figure 14-8.



Figure 14-8 Float Smoke and Flame N2 Mk4

14.5.3 Irritant Smoke

Irritant smoke used for riot control purposes can be generated pyrotechnically in a manner identical to coloured smokes. Lactose monohydrate is used as fuel with potassium chlorate as oxidant and these are intimately mixed with the chemical agent CS (o-chlorobenzalmalononitrile). A typical composition is PN700 consisting of:

a. CS (25 % w/w)
b. Potassium chlorate (30 % w/w)
c. Lactose monohydrate (30 % w/w)
d. Kaolin (15 % w/w)

PN stands for ‘Porton Number’, which was a numbering system for pyrotechnic compositions developed at the then Chemical Defence Establishment, Porton Down, Wiltshire.

14.5.4 Screening Smoke

The purpose of screening smoke is to obscure a target from an observer. This is achieved by reducing the contrast, that is the difference between irradiance falling on the detector from target and background, to a level below the threshold of the detector. This is shown in Equation **(14-9)** where R is irradiance falling on the detector and τ the transmission having a value between 1 (no smoke or atmospheric interference) and 0.

$$\text{Contrast} = \tau\,[R(\text{target}) - R(\text{background})] \qquad \textbf{(14-9)}$$

Transmission can be reduced by two processes, absorption or scattering of electromagnetic radiation. All smokes cause scattering, but absorption may or may not occur. Both depend upon type of aerosol produced and the wavelength or region under consideration. The effects of scatter plus absorption are called

attenuation or extinction equal to (1 - τ). The attenuation is a function of aerosol concentration, path length through the aerosol and smoke particle properties.

The screening effectiveness of a smoke cloud can be expressed by its mass extinction coefficient, α, which can be calculated from the Beer-Lambert law, Equation (14-10).

$$\alpha_\lambda = [-(\ln\tau)_\lambda]/CL \text{ m}^2 \text{ g}^{-1} \quad \textbf{(14-10)}$$

Where: τ_λ = transmission through a smoke cloud at wavelength λ; α_λ = mass extinction coefficient at wavelength λ; C = smoke mass concentration; L = optical path length through smoke cloud.

As can be seen, the mass extinction values relate to a specific wavelength (λ), however, average values across spectral bands such as the visible region may be used. The mass extinction coefficient is a measure of how strongly a chemical species or substance absorbs or scatters light at a given wavelength per unit mass. Therefore, the higher the mass extinction coefficient, the more effective the material is as an attenuator.

There are five basic methods by which a visual screening smoke may be generated:

a. Vaporised materials which recondense unchanged
b. Partially combusted organic materials
c. Materials which react directly with atmospheric moisture
d. Materials which burn in atmospheric oxygen
e. Pyrotechnic compositions

Type (a) includes fog oil, a liquid hydrocarbon such as diesel injected into vehicle exhausts. Type (b) is typified by stack smoke as used by large ships. Type (c) includes titanium tetrachloride ($TiCl_4$) and chlorosulphonic acid ($ClSO_3H$) which react to form acid gases which are themselves hygroscopic forming liquid droplets. These water types of smoke are not used currently in British Service.

14.5.5 Phosphorus Smokes

Phosphorus (White and Red) can be used to provide visual screening smoke and is a type (d) material. The phosphorus burns in air to produce oxides of phosphorus particularly phosphorus pentoxide (P_40_{10}) a very strong hydrating agent. This then reacts further with atmospheric moisture, forming a mixture of phosphorus acids including H_3PO_4 as detailed in the reactions shown in Equations (14-11 to 14-14) below.

$$P_4 + 5O_2 \rightarrow \ P_4O_{10} \quad \textbf{(14-11)}$$

$$P_4O_{10} + 2H_2O \rightarrow 2(HPO_3)_2 \quad \textbf{(14-12)}$$

$$(HPO_3)_2 + H_2O \rightarrow H_4P_2O_7 \quad \textbf{(14-13)}$$

$$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4 \quad \textbf{(14-14)}$$

The acids produced are hygroscopic and absorb further moisture from the atmosphere producing sub-µm sized droplets of an aqueous solution of orthophosphoric acid (H_3PO_4). It is this acid mist which constitutes the white smoke cloud and scatters both visible and near infrared electromagnetic radiation.

Atmospheric moisture is required for the formation of the droplets with the amount of smoke formed being dependent upon the relative humidity of the atmosphere. Because the composition is only a fuel with no oxidant, it is usual for the weight of smoke material produced to be greater than the weight of the filling. Under high humidity conditions it is possible to achieve “Yield Factors” of 4 or higher (i.e. for every gram of phosphorus burnt, four grams of sub-micron sized droplets are produced). Typical Indicative Yield Factors for a range of munition smokes are shown in Table 14-9 and highlight the effect of atmospheric moisture on the yield factor.

Table 14-9 Indicative Yield Factors

Munition	Composition	Indicative Yield Factor
Grenade Coloured Smoke, Training Smoke, Anti-Riot Smoke	Pyrotechnic Heater Composition + Volatile Material	0.5
Tube Launched HCE	ZnO/HCE	1.4 (60 %RH)
WP	White Phosphorus	2.3 (0 %RH) 16 (90 % RH)
Tube Launched RP	Red Phosphorus, $NaNO_3$, Mg, Binder	1.5 (0 %RH) 12 (90 %RH)

The mass extinction coefficient is a measure of how strongly a chemical species or substance absorbs or scatters light at a given wavelength per unit mass. Therefore, the higher the mass extinction coefficient, the more effective the material is as an attenuator. Figure 14-9 shows a typical mass extinction coefficient for a phosphorus smoke across a range of wavelengths.

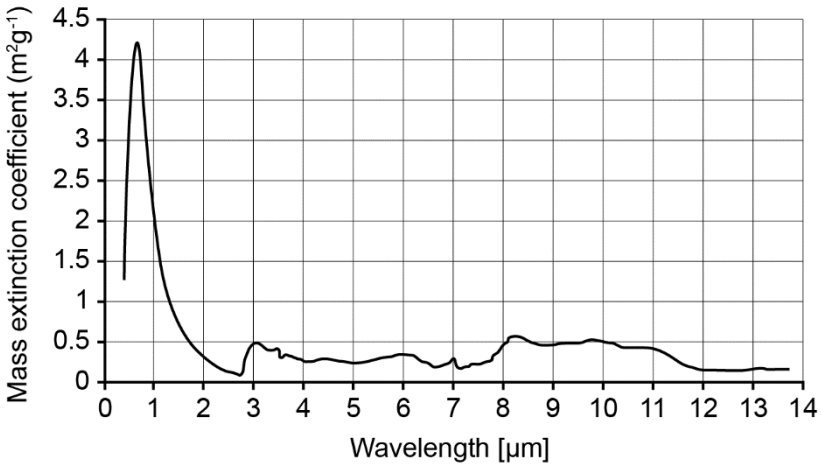


Figure 14-9 Mass extinction coefficient of a phosphorus smoke

The value of α peaks at ~0.6 µm and drops off in the far infrared region of the electromagnetic spectrum. Therefore, it is possible for high concentrations of phosphorus smoke to provide effective infrared screening.

There are two types of filling which can be used to give a phosphorus smoke. One is simply white phosphorus (WP) which spontaneously ignites on contact with air and is employed as a filling with a central high explosive burster charge to disperse burning phosphorus which continues to burn once on the ground. This method can be used in stores ranging from hand grenades through to mortars and large artillery shells.

The other phosphorus filling used consists of red phosphorus (RP). An example of a filling is composition PN841 consisting of red phosphorus and butyl rubber binder (95/5 % w/w). This composition is used in the Grenade Discharge Smoke Screening L84A4 used for vehicle screening. Examples of red phosphorus compositions and stores are detailed in Appendix A, Table A-9.

The use of red phosphorus is preferred on safety grounds since white phosphorus is relatively toxic compared to the red form. White phosphorus presently is not employed in UK Screening Grenades. However, it does have applications in UK mortar and artillery munitions. Red phosphorus is a versatile material which is used for many military applications. The chemical reactivity of red phosphorus can be altered depending on its intended application. Slow burning pellets are used to produce long duration smokes, it can be mixed with metal fuels and oxidants to accelerate its burning to produce rapidly formed dense smoke clouds, granular and thin films which burn rapidly to form a highly emissive infrared signature can be used.

The high mass extinction coefficient of a red phosphorus smoke cloud coupled with its high yield factor has resulted in it being used as the screening smoke for the complete range of smoke screening munitions (i.e. grenades, mortars and artillery shells).

Red phosphorus infrared decoys are used for the protection of slow moving military platforms, such as naval vessels, against modern heat seeking missiles.

An infrared emission profile for a red phosphorus/rubber composition is shown in Figure 14-10 and shows significant emission in the 8 – 12 µm waveband which is used by many IR surveillance and target acquisition devices.

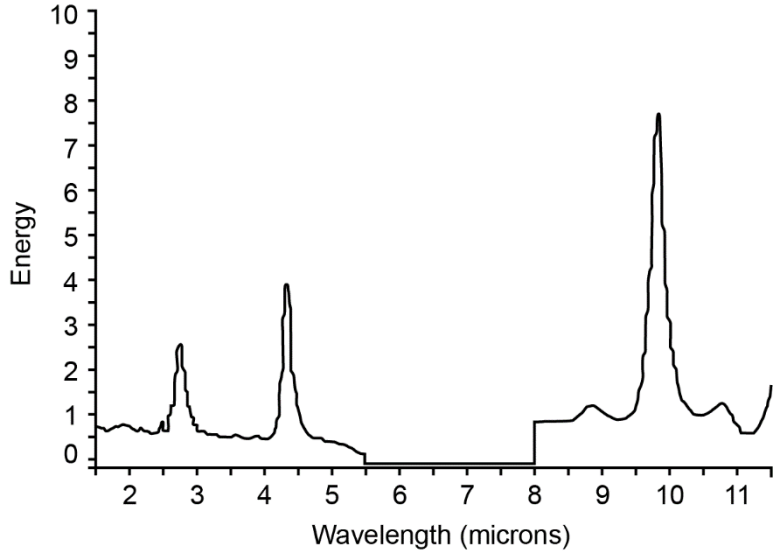


Figure 14-10 IR emission profile for a RP/Rubber composition

14.5.5.1 Phosphine outgassing and mitigation

A major issue associated with munitions containing red phosphorus is that during storage, red phosphorus can react with moisture and air, to form a mixture of corrosive phosphorus acids and the toxic gas phosphine, as detailed in Equation (14-15) below.

$$14P + 21H_2O + 11.275O_2 \rightarrow 5.2H_3PO_4 + 7.15H_3PO_4 + 0.65H_3PO_2 + PH_3 \quad \textbf{(14-15)}$$

This has raised serious concerns relating to the Health and Safety of personnel handling these munitions and resulted in the development of a suitable phosphine adsorbing material referred to as a “Phosphine Getter”. The phosphine getter consists of an activated carbon cloth impregnated with chemicals which react with phosphine to produce less benign reaction products. The getters are now being used successfully to mitigate phosphine evolution in both ammunition container assemblies housing munitions containing red phosphorus and in the main body of certain munitions.

14.5.6 Pyrotechnic Smokes

Pyrotechnic compositions used to create screening smoke are designed to produce hygroscopic metal salts essentially forming aqueous droplets of these salts. This is achieved by the use of halocarbons as a source of chlorine, acting as oxidant and a metal fuel. Zinc oxide is also present in these compositions and this takes part in some complex chemistry associated with the combustion

of these mixtures. Early compositions used zinc powder and carbon tetrachloride, however, for more stable fillings the fuel became calcium silicide ($CaSi_2$), and the oxidant, hexachloroethane (C_2Cl_6).

The main composition of this type developed in the UK was PN800, details of which are shown in Appendix A, Table A-10. Some of the reactions shown in the following equations, (14-16 to 14-20), are occurring when this composition is burning together with some minor reactions.

$$3CaSi_2 + C_2Cl_6 \rightarrow 3CaCl_2 + 2C + 6Si \quad \textbf{(14-16)}$$

$$CaSi_2 + ZnO \rightarrow CaO + Zn + 2Si \quad \textbf{(14-17)}$$

$$3Zn + C_2Cl_6 \rightarrow 3ZnCl_2 + 2C \quad \textbf{(14-18)}$$

$$C + ZnO \rightarrow Zn + CO \quad \textbf{(14-19)}$$

$$3ZnO + C_2Cl_6 \rightarrow 3ZnCl_2 + CO + CO_2 \quad \textbf{(14-20)}$$

Because this smoke is white, reaction (14-19) is important as this is the only way carbon can be removed. This reaction is significant above 1000 °C.

To increase storage stability, it is necessary to replace calcium silicide since it readily reacts with moisture to form hydrogen gas. The fuel of choice in aluminium powder and work in the United States of America has shown that the chemistry occurring with this mixture is driven by the Thermite reaction between aluminium and zinc oxide as shown in Equation (14-21).

$$2Al + 3ZnO \rightarrow Al_2O_3 + 3Zn \quad \textbf{(14-21)}$$

The reactions shown in Equations (14-18) and (14-19) then follow. It has been shown that a constant ratio of zinc oxide to hexachloroethane of 51/49 % w/w can be employed. The burn time for the composition is altered by changing aluminium content.

Some HCE smokes are used in large calibre artillery shells. However, due to the potential health hazards of lung damage associated with inhalation of HCE smokes, these types of composition are presently being phased out of British service. The intention being to replace the HCE smoke compositions with red phosphorus based smoke compositions.

14.5.7 Training Smokes

Training smokes are needed to reproduce the characteristics of tactical smokes without their toxicity problems. The UK standard training smoke (L83A1 and L83A2) used in training screening smoke grenades are based on cinnamic acid. US formulations are based on terephalic acid and these compositions are detailed in Appendix A, Table-11.

Kaolin, an inert material is used in UK compositions to moderate the heat of combustion and to act as a buffer to prevent the acid catalysed decomposition

of the potassium chlorate oxidant, present in the smoke composition, which can cause premature ignition of the composition. Sodium bicarbonate can be used as an alternative to kaolin.

Grenade Hand Smoke Screening Training L83A1, Figure 14-11, used as a replacement for white phosphorus, consists of two smoke pellets (lower and upper pellets). The lower pellet consists of a pressed pellet of composition CC265 whilst the upper pellet consists of a pellet of composition CC264. Both pellet compositions are based on cinnamic acid. Composition CC265 in the lower pellet burns at a faster rate than composition CC264 and this provides a rapid build-up of smoke on initiation.

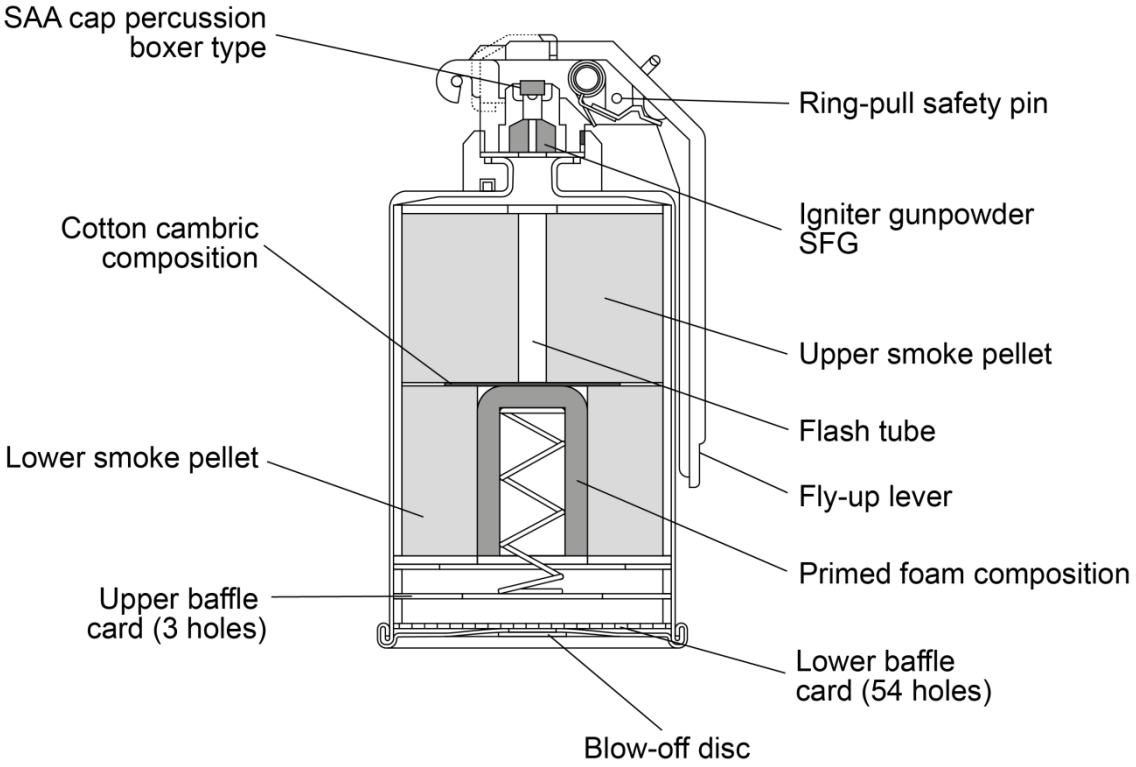


Figure 14-11 Grenade Hand Smoke Screening Training L83A1

The pyrotechnic smoke compositions used in both Generator Smoke 120/W6 Mk2 used by both the UK Royal Navy and the Royal Air Force for fire and ground defence training and Generator Smoke L4A1 used by UK land forces to produce a smoke screen in training are based on a composition consisting of Gum rosin, potassium chlorate and ammonium chloride. Examples of compositions and stores are detailed in Appendix A, Table A-12.

For comparison typical indicative mass extinction coefficients ($m^2 g^{-1}$) of phosphorus smoke, Zn/HCE smoke and training smokes containing cinnamic acid and terephthalic acid are given in

Table 14-10.

Table 14-10 Indicative Mass Extinction Coefficients

Smoke	α (visible)	Mid IR α (3-5 μm)	Far IR α (8-12 μm)
Phosphorus	4.6	0.3	<0.3
Zn/HCE	5.0	-	<0.1
Cinnamic Acid (UK)	4.8	-	<0.1
Terephthalic Acid (USA)	4.8	<0.1	<0.1

14.6 NOISE, FLASH and PYROTECHNIC WHISTLES

14.6.1 Noise and Flash

Noise in this context is produced by a pressure wave which can be achieved by confining a composition, even a slow burning one, in a container which bursts due to increased internal pressure or with a composition sufficiently fast burning to produce the pressure wave with no, or minimum confinement. The sound representation produced depends upon choice of composition, type of confinement and method of initiation.

Compositions producing various types of noise or sound outputs are used in battlefield simulator stores for training purposes such as ground burst simulator, booby traps, rifle fire simulators, etc.. Invariably the bang is accompanied by a flash and this can be advantageous particularly in stun grenades. The usual fuels used in noise and flash compositions are magnesium and aluminium which have high heats of reaction. Although aluminium is well protected by its oxide coat to the extent that it is relatively ineffective in a flare composition, it reacts violently when subjected to the temperatures of a flash and bang composition.

Burning pyrotechnic compositions including gunpowder are used in confinement. Gunpowder is used for a simple explosion simulator and also to represent small-arms strikes. Composition SR371C is the filling for the Gunfire Flash and Sound AFV Simulator.

The high energy noise and flash compositions, which burn very rapidly, are probably the most sensitive and most dangerous of the pyrotechnic mixtures. The Thunderflash device, which contained composition SR801B, caused many injuries in training and through misuse such that it has been removed from the inventory of Service pyrotechnics. Great care must be taken if noise/flash type pyrotechnics are used in confined spaces and underwater where the damage

potential is enhanced. Examples of noise and flash compositions are given in Appendix A, Table A-12.

Heavy gun-fire and mortar fire can be simulated by the use of ammonium nitrate based materials, some containing TNT and all initiated by detonator. Examples of simulator compositions initiated by a detonator are given in Appendix A, Table A-13.

14.6.2 Pyrotechnic Whistles

Certain pyrotechnic compositions, when pressed into candles, contained within a case, which on ignition burn cigarette fashion can produce an ear splitting whistle. These have been used as disorienting devices for example, riot control and for military training providing simulated effects of incoming artillery or bombs.

Compositions usually consist of aromatic hydrocarbons such as potassium benzoate, sodium salicylate, potassium 2,4-dinitrophenate or gallic acid as the fuel and a strong oxidant such as potassium perchlorate. The maximum frequency (critical frequency) obtained is dependent upon the composition. A mixture of potassium benzoate/potassium perchlorate (30/70 % w/w) has a critical frequency of around 500Hz. The potassium benzoate/potassium perchlorate whistle reaction is shown in Equation (14-22).

$$C_7H_6O_2K + KClO_4 \rightarrow 7CO_2 + 3H_2O + KCl \quad \textbf{(14-22)}$$

The whistling sound is produced when composition burns in a tube and is produced by a combination of oscillating burning of the composition plus sound reflecting up and down the length of the tube with the characteristic frequency varying with ingredients used, ratio and geometry. Burn rates are faster for mixtures emitting at high frequency with superior whistles obtained with finely ground ingredients. Whistle compositions are extremely sensitive and candles are prone to explode when burning.

14.7 OXYGEN GAS PRODUCTION

Gases are produced by all pyrotechnic compositions with the carbon dioxide produced from the combustion of organic fuels the most copious produced. However, its manufacture by this method is of little interest. The most important gas production by pyrotechnics is that of oxygen which can provide a safe supply for critical life support and revitalisation in submarines.

Most oxygen producing reactions rely on the thermal decomposition of chlorates or perchlorates as shown in Equation (14-23).

$$NaClO_3 \rightarrow NaCl + 1.5O_2 \quad \textbf{(14-23)}$$

The decomposition requires a significant amount of energy input to drive the chlorate decomposition with the source of the energy being the oxidation of iron powder which is formulated with the sodium chlorate. A typical oxygen producing composition consists of a mixture of sodium chlorate, powdered iron and barium peroxide. When the mixture is ignited the iron burns at around 600°C which supplies the heat required for the reaction. The sodium chlorate breaks down into sodium chloride and oxygen equation (14-23) with some of the oxygen combining with iron to form iron oxide. During the decomposition of chlorates and perchlorates chlorine gas often several hundreds of ppm is produced. Chlorine is highly toxic and even ppm levels must be removed to ensure that the oxygen is breathable. To remove any chlorine, barium peroxide is added as shown in Equation (14-24).

$$BaO_2 \rightarrow Cl_2 \rightarrow BaCl_2 + O_2 \qquad \textbf{(14-24)}$$

Sodium chlorate is often chosen as it has a very high oxygen storage capacity (i.e. 784 dm^3 oxygen/dm^3 which is similar to the volume/volume capacity for liquid oxygen (798 dm^3 oxygen dm^{-3}). A typical oxygen generator, based on sodium chlorate can be formulated to produce 3300 dm^3 of oxygen over a period of 40 to 60 minutes. A typical Self Contained Oxygen Generator (SCOG) is shown in Figure 14-12.

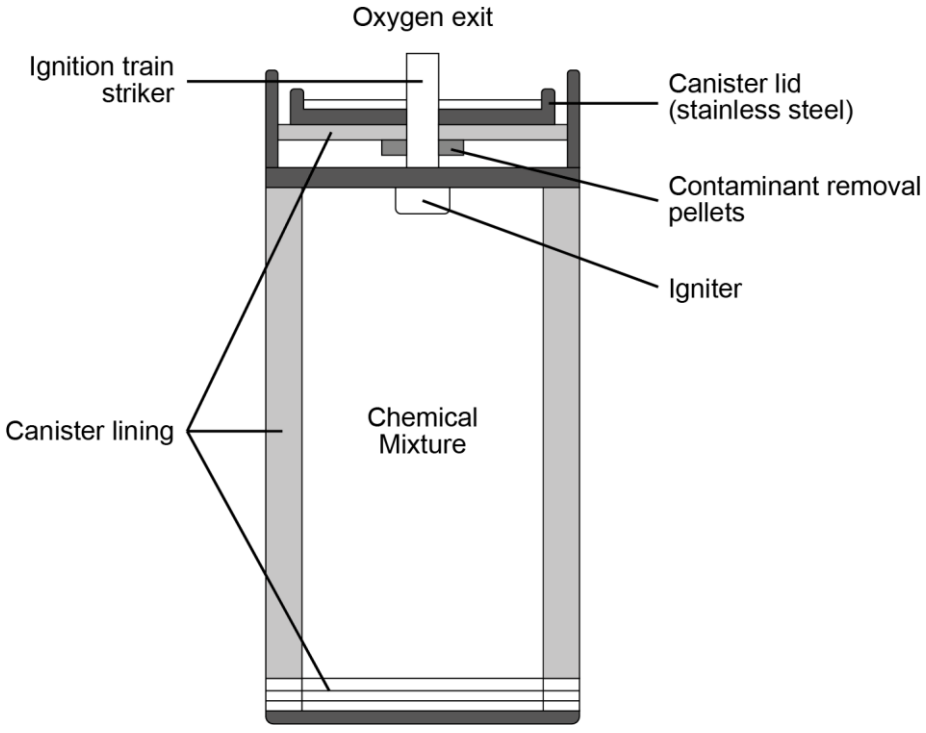


Figure 14-12 Typical self-contained oxygen generator

14.8 THERMAL BATTERIES

Many missile systems contain thermal batteries as energy sources. A typical battery consists of a stack of electrical cells each consisting of an anode and a cathode in the form of discs separated by a solid electrolyte and pyrotechnic heater composition (pellet).

When operated, an electrical current is applied to the battery to ignite a suitable igniter such as a fusehead or squib and an ignition strip which causes the pyrotechnic heater material to ignite and begin to heat. Heat produced from the pyrotechnic heater material causes the solid electrolyte to melt and become conductive. When the electrolyte melts current can flow and the battery discharges. Whilst the electrolyte remains in a solid state it is an electrical non-conductor hence, no current flows. In this state, the battery may remain without deterioration for decades.

The essential arrangement consists of an anode and cathode pair (typically lithium alloy and iron sulphide respectively), separated by the electrolyte (typically a eutectic of potassium chloride and lithium chloride). Ignition of the heater pellets can be achieved by the use of strips of heat paper (woven silica impregnated with fast burning zirconium and barium chromate) running the length of the battery. The pyrotechnic 'Heat Pellet' composition used, almost universally, is a fuel rich mixture of iron powder and potassium perchlorate. Because the reaction products are not electrically conducting, the preferred heat mixture contains a large excess of iron powder (i.e. 80 % in the mixture). This also has the benefit of moderating the reaction which is violent near stoichiometry. The burn rate achieved with a suitable mixture is around 100 mm s^{-1}. Heat paper is very readily ignited and burns around 200 mm s^{-1}.

The requirements placed on the pyrotechnic heat composition are somewhat severe. They must not deteriorate over decades; combustion products of the pyrotechnic reaction must form a good electrical conductor because they are part of the electrical circuit; pellets are required to be very thin to reduce battery weight. Their total heat output, rate of heat output and ignition time must be carefully controlled and the combustion should generate little gas to guarantee that the entire battery remains hermetically sealed. Compacted composition should not melt at any stage of the combustion because the cells must maintain their physical shape. The temperature should not be so high that other components in the battery are damaged and the pyrotechnic reaction should initiate and propagate very rapidly to minimise time taken to melt the electrolyte and activate current generation. Typical advantages and disadvantages of thermal batteries are summarised in Table 14-11.

14.9 SOLAS STORES

To meet the requirements of the “International Maritime Organisation (IMO) Convention for the Safety of Life at Sea (SOLAS) chapter III” and the “Maritime

and Coastguard Agency (MCA) Marine Guidance Note 280 (M) - Small Vessels in Commercial Use for Sport or Pleasure, Workboats and Pilot Boats" that require vessels and craft to carry distress pyrotechnics on-board a range of Distress sets are available. These sets are made up from a variety of stores to meet the relevant SOLAS/MCA regulation.

Warships are exempt from the SOLAS legislation, however to meet the Secretary of State requirements to produce outcomes that are at least as good as those required by UK legalisation they will carry the required SOLAS stores.

All SOLAS stores are commercial of the shelf items and are not required to undertake Safety and Suitability for Service Use testing. The stores are accepted in to service having passed the SOLAS testing requirements. Typical stores are detailed Appendix A, Table A-14.

Table 14-11 Thermal Battery Advantages and Disadvantages

Advantages	Disadvantages
Very long storage life (>20 years)	Short activated life
No maintenance requirements	High surface temperatures (>200 ^{o}C)
High reliability	Non-linear output voltage
Instantaneous activation	One-time use
High power output (0.1 – 2 KW)	
Rapid power availability (<1 sec^{-1} hour or more	
Able to withstand severe mechanical stresses of acceleration, shock, vibration and spin	
Wide operating temperature range (-54 ^{o}C - +74 ^{o}C)	
Safe operation	

14.10 REFERENCES

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Appendix A Pyrotechnic Compositions

Pyrotechnic composition designations

The following pyrotechnic composition designations are referred to in this chapter and in the Tables shown in Appendix A:

Original Compositions:

SR	Superintendent of Research Composition
SRE	Superintendent of Research Elastic Composition
PN	Porton Composition
RD	Research and Development Composition

Commercial Compositions:

NE	Nobel Energetics (Now Chemring Energetics UK)
CC	Chemring Composition
WI	Wallop Industries Composition

Note: Due to the commercial confidentiality of the commercial pyrotechnic compositions referred to in the Tables shown in Appendix A, composition ingredient mix ratios and percentages for formulations are not given.

Table A - 1 Priming and ignition compositions

Designation	Composition Material	% w/w	Use
SFG	Potassium nitrate Charcoal	70.0 30.0	Flash pick-up
SR252	Potassium nitrate Silicon Sulphurless mealed powder	40.0 40.0 20.0	General purpose priming
SR214	Potassium nitrate Lactose	60.0 40.0	Cool priming for coloured smokes etc.
SR370	Magnesium Barium peroxide Charcoal	11.0 87.7 1.3	Shell-tracer priming
SR867	Magnesium Acaroid resin Strontium peroxide Bitumen Zinc stearate	6.9 0.6 80.0 12.5 1.0	Dark ignition for small arms tracer rounds
SR371C	Magnesium (grade 3) Magnesium (grade 5) Acaroid resin Potassium nitrate	32.0 10.0 8.0 50.0	Solid propellant igniter

Table A - 2 Incendiary compositions

Designation	Composition Material	% w/w	Use
SR306	Aluminium (size 25) Aluminium (size 120) Hammerscale Barium nitrate Boric acid	10.0 10.0 40.0 35.0 5.0	Thermite for ignition of bulk aluminium, magnesium or their alloys
SRE794	Boron Potassium nitrate Thiokol S.101 Magnesium oxide Curing agent	20.0 55.0 22.2 0.3 0.5 2.0	Paper incendiary for document destruction
SR365	Magnesium-aluminium alloy (50/50) Barium nitrate	50.0 50.0	Incendiary bullets and cannon-shell
CC466	Thermite Composition (similar to SR306)	---	Initiation of explosive filling in target munitions or initiate combustible materials to assist in the bulk destruction of munitions

Table A - 3 Delay compositions

Designation	Composition Material	% w/w	Rate of burning (s in^{-1})	Use
Gunpowder	Potassium nitrate Charcoal Sulphur	75.0 15.0 10.0	2.5	Safety fuze
SR57	Boron Bismuth oxide	10.0 90.0	0.5	Airburst AP mine
SR67	Boron Silicon Potassium dichromate	10.0 20.0 70.0	0.9	Ejector seat delay
SR112	Potassium nitrate Tetranitrocarbazole	60.0 40.0	2.9	Grenade fuze
SR149A	Gunpowder Potassium nitrate Sulphur	55.2 33.3 11.5	---	Marine marker / Surface signal
SR227A	Potassium nitrate Charcoal Sulphur	72.0 21.0 7.0	---	Shell fuze
SR651	Potassium nitrate Barium nitrate Purpurin	52.0 18.0 30.0	7.1	Mortar fuze
RD1368	Boron Barium chromate	4.5 95.5	4.2	L25A5 fuze
RD1370	Titanium Lead chromate	50.0 50.0	0.2	---

Table A - 4 Illuminating compositions (White Light)

	DESIGNATION							
	SR547	**SR562**	**SR563**	**SR563A**	**SR576A**	**SRS80**	**SR343A**	**SR502**
Magnesium (% w/w) (Grade)	26(0)	49(0)	50(0)	50(4)	60(0)	60(4)	50(0)	35(4)
Lithographic Varnish (% w/w)	4	5	4	4	3	4	-	4
Oxidant	$NaNO_3$	$NaNO_3$	$NaNO_3$	$NaNO_3$	$NaNO_3$	$NaNO_3$	$Ba(NO_3)_2$	$NaNO_3$/ $Ba(NO_3)_2$
Oxidant (% w/w)	42	39	46	46	37	36	40	41 & 12
Calcium Oxalate (% w/w)	16	7	-	-	-	-	5	-
Other	PVC	-	-	-	-	-	Wax	Mannitol
Other (% w/w)	12	-	-	-	-	-	5	8
Rate of Burning (s in^{-1})	39	17.8	12.0	5.2	6.1	2.3	11.0	15.5
Specific Intensity (cd in^{-2}) (000s)	7.6	63	100	240	184	365	360	385

NOTE: Figure in parentheses after percentage of magnesium represents the grade of magnesium, ranging from coarse (0) to fine (5).

Table A - 5 Coloured signal compositions

Designation	Composition	% w/w	Rate of Burnining (s in-1)	Use
SR170A Red	Magnesium (4) Boiled linseed oil Potassium perchlorate Strontium oxalate	48 4 38 10	7.2	Cartridge Signal 1.5-inch Red (Obsolete)
SR700 Green	Magnesium (4) Boiled linseed oil Barium nitrate Potassium perchlorate PVC	42 6 17 27 8	13.0	Cartridge Signal 1.5-inch Green (Obsolete)
SR560 Yellow	Magnesium (3) Lithographic varnish Sodium nitrate Sodium oxalate	45 4 46 5	7.4	Cartridge Signal 1.5-inch Yellow (Obsolete)
SR405 Blue	Lactose Potassium perchlorate Basic copper carbonate Mercurous chloride	48 22 8 22	33.0	
CC325 Red	Magnesium (0 and 4) Boiled linseed oil Chlorinated rubber Strontium nitrate	---	---	Signal Kit Pyrotechnic 16 mm
CC326 Green	Magnesium (3 and 4) Boiled linseed oil Chlorinated rubber Barium nitrate	---	---	Signal Kit Pyrotechnic 16 mm
CC327 White	Magnesium (3) Boiled linseed oil Barium nitrate Strontium nitrate Chlorinated rubber	---	---	Signal Kit Pyrotechnic 16 mm

NOTE: Figure in parentheses after percentage of magnesium represents the grade of magnesium, ranging from coarse (0) to fine (5).

Table A - 6 Tracer priming compositions

Designation	Type	Composition	% w/w	Use
SR867	Dark Ignition	Magnesium Bitumen Strontium peroxide Acaroid resin Zinc stearate	6.3 11.0 81.0 0.5 1.2	Small arms ammunition (5.56 mm, 7.62 mm)
SR390B	Bright	Magnesium Strontium peroxide Strontium nitrate Boiled linseed oil Talc	28.6 50.4 4.8 11.4 4.8	Small arms ammunition Spotter tracer (9 mm)
SR399	Bright	Magnesium Barium peroxide Acaroid resin	12.0 86.0 2.0	Artillery (40 mm)
SR372ABS	Bright	Magnesium Strontium nitrate Beeswax Chlorinated rubber Shellac Magnesium carbonate Zinc stearate	40.0 45.0 4.8 5.0 5.0 5.0 0.3	Artillery (30 mm)

Table A - 7 Tracer, tracking flare and target flare compositions

Designation	Composition Material	% w/w	Use
SR390A	Magnesium (4) Polymerised linseed oil Strontium nitrate Strontium peroxide Talc	29.3 11.7 51.7 4.9 2.4	Small arms ammunition
Commercial Composition	Strontium peroxide Barium peroxide Calcium resinate Barium nitrate	---	IR/Dim Tracer
Commercial Composition	Boron Potassium perchlorate Sodium salicylate Iron or magnesium carbonate Calcium resinate	---	IR/Dim Tracer
SR568A	Magnesium (3) Lithographic varnish Sodium nitrate	55.0 4.0 41.0	Tracking flare
SR399	Magnesium (4) Acaroid resin Barium peroxide	12.0 2.0 86.0	High altitude tracking flare
SR699	Titanium (powder 8µm) Boiled linseed oil Strontium nitrate Chlorinated rubber	48.0 4.0 45.0 3.0	Low smoke tracking flare

NOTE: Figure in parentheses after percentage of magnesium represents the grade of magnesium, ranging from coarse (0) to fine (5).

Table A - 8 Signal smoke and smoke compositions

Designation	Smoke Colour	Composition Dyestuff	Use
CC204	Green	Dye Solvent Green 3A Dye Solvent Yellow 33	Grenade hand signal smoke L152A1
CC147	Red	Dye Disperse Red 9	Grenade hand signal smoke L154A1
CC146	Blue	Dye Disperse Blue 180	Grenade hand signal smoke L71A1
CC168	Yellow	Dye Solvent Yellow 33 Dye Solvent Orange 86	Grenade hand signal smoke L156A1
CC486	Orange	Dye Solvent Orange 86 Dye Disperse Red 9	Grenade hand signal smoke L153A1 Grenade hand arctic smoke L145A1
CC271	Purple	Dye Disperse Blue 180 Dye Disperse Red 9	Grenade hand signal smoke L158A1 Grenade hand arctic smoke L145A1
CC428	Turquoise	Dye Solvent Green 3A	Grenade hand signal smoke L158A1 Grenade hand arctic smoke L146A1
CC355	Orange	Dye Solvent Orange 86 Dye Solvent Orange 7 Dye Disperse Red 9	Signal distress day and night Mk4/Mk5
PN739	Yellow	Dye Solvent Yellow 33 Dye Disperse Orange 11	Candle smoke yellow Mk N7

Note: All compositions contain potassium chlorate, lactose, kaolin, zinc oxide

Table A - 8 Marine marker and smoke compositions

Designation	Material	% w/w	Use
SR414	Calcium silicide Magnesium powder Manganese dioxide Oiled red phosphorus	6 6 28 60	Candle Smoke White (Early Mks)
SR622B	Oiled red phosphorus Calcium sulphate Oxalic acid dihydrate	52.0 45.1 2.9	Marker Marine No.4 Mk11
WIC227	Amorphous red phosphorus (encapsulated) Manganese dioxide Calcium silicide Magnesium Acaroid resin	---	Float Smoke and Flame Mk5 Candle Smoke White Mk N6

Table A - 9 Phosphorus screening smoke compositions

Designation	Material	% w/w	Use
Commercial Composition (Pellets)	Red phosphorus (encapsulated) Potassium nitrate Magnesium Ferric oxide Binder	---	Grenade Discharge Visual and IR L131A1
Commercial Composition (Leaflets)	Red phosphorus (encapsulated) Potassium nitrate Binder	---	
Commercial Composition	Red phosphorus (encapsulated) Potassium nitrate Binder	---	Grenade Hand Smoke L84A3

Table A - 10 Pyrotechnic visual screening smoke composition

Designation	Material	% w/w	Use
PN800	Hexachloroethane Potassium nitrate Zinc oxide Calcium silicide	44 2 47-32 7-22	Shell

Table A - 11 Training smokes and smoke compositions

Designation	Material	% w/w	Use	Country
CC264 (Slow Burning)	Cinammic acid Potassium chlorate Lactose Kaolin	--	Grenade hand smoke screening training L83A1/L83A2	UK
CC265 (Fast burning)	Cinammic acid Potassium chlorate Lactose Kaolin	---		UK
UK Composition	Cinammic acid Potassium chlorate Lactose Kaolin	33 26 26 15	---	UK
USA Composition	Terephthalic acid Potassium chlorate Sucrose Magnesium carbonate Stearic acid PVA	56 23 14 3 3 1	---	USA

Table A - 12 Noise and flash compositions

Designation	Material	% w/w	Simulation
SR371C	Magnesium (Gd 3) Magnesium (Gd 5) Potassium nitrate Acaroid resin	32 10 50 8	Gunfire
Commercial Composition	Magnesium Potassium nitrate Strontium nitrate Iron oxide Sodium bicarbonate Silicic acid	---	Cartridge flash bang smoke
Commercial Composition	Potassium chlorate Charcoal Acaroid resin	---	Small arms fire
SR801B	Magnesium Potassium perchlorate Graphite	57 37 6	Explosion (bombs, shells etc.) Thunderflash

Table A - 13 Simulator compositions initiated by detonator

Designation	Material	% w/w	Simulation
NE 1243	Ammonium nitrate Charcoal Aluminium (paint fine) Cork dust TNT	91 3.5 2.75 2.75 -	81 mm mortar
NE1244	Ammonium nitrate Charcoal Aluminium (paint fine) Cork dust TNT	80 3 2.4 2.4 12.2	Heavy mortar
NE1245	Ammonium nitrate Charcoal Aluminium (paint fine) Cork dust TNT	73.6 2.8 7 2.2 14.4	120 mm BAT

Table A - 14 SOLAS stores

Item	Variant
Rocket Hand Fired Para Red Distress	Mk8A
Rocket Hand Fired Para White Distress	Mk8
Hand Flare Red Distress	Mk8
Hand Flare White	Mk8
Lifesmoke	Mk9
Marker Man Overboard	Mk9
Line Thrower L1A1	-
Signal Set Submarine	L1A2
Signal Set Diver Supervisor	L5A1

CHAPTER 15
PYROMECHANISMS

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15 PYROMECHANISMS

Author – A Bentley (Chemring Energetics Ltd)

15.1 AWARENESS SUMMARY

15.1.1 Definition of a Pyromechanism

The term “pyromechanism” is used to describe a mechanical device that is capable of releasing energy stored in a chemical composition and harnessing this energy to perform useful mechanical work or to create particular mechanical effects. The chemical compositions used are generally of the energetic material type and energy is released from these by arranging for the material to undergo a combustion process. Pyromechanisms therefore require an input energy, usually in the form of an electric current or by means of mechanical percussion, in order to initiate the sequence. The energy outputs achieved can be orders of magnitude higher than the input energy and therefore these devices are very useful for performing functions where high thrust and energy are required from a low mass in small, confined spaces. Outputs tend to be in the form of mechanical motion, either linear or rotary and the vast majority of pyromechanisms contain all the high pressure gases produced during the combustion of the energetic material. The output is therefore a controlled mechanical movement or a directed effect to perform a particular function. A pyromechanism can therefore be thought of as a transducer, a device to convert energy from one form to another. The big advantage is the very large amplification between input and output energy.

15.1.2 Background and History

The concept of pyromechanisms has been largely developed since World War 2 where explosive bolts were successfully used in the German V1 and V2 weapon systems. This basic technology was further developed post-war by the US and Russian space programmes. The Apollo programme for instance used over 500 pyromechanical devices per mission for a variety of release and deployment tasks on the Saturn range of launch vehicles. Since that time the technology has seen a significant increase in the number of applications particularly in the weapon system and space domains. Other industries too have adopted pyromechanical devices and systems and these are now commonplace in safety systems on board road and rail vehicles and commercial airliners.

15.1.3 Types and Uses

Pyromechanism products are now well established in a number of fields and have found usage in many different defence related systems performing a variety of functions. Their ability to provide a high energy output from a small energy input makes them particularly useful where space is confined and remote operation is required.

Pyromechanisms can either be of the detonating (high explosive) type or a deflagrating type where a more controlled output is achieved. This distinction is used as a top level means of categorising pyromechanisms. In a detonating device the resultant shock is used to provide a directed franging effect within a structure while in the deflagrating type the rapid release of gas is used to drive a mechanism.

Detonating pyromechanisms have found use where cutting or franging effects are required. A good example is the explosive bolt shown in Figure 15-1 where a detonator is used to fracture a weakened portion of the bolt. The bolt can then be used to perform a release function where two structures held together by the bolt can be remotely separated. Another example is that of the military aircraft canopy fracture system to assist emergency aircrew egress. Essentially, this uses a detonator and a miniature detonating cord arranged in a pattern on the underside of the canopy. As part of the ejection sequence the detonator is fired and shatters the canopy.

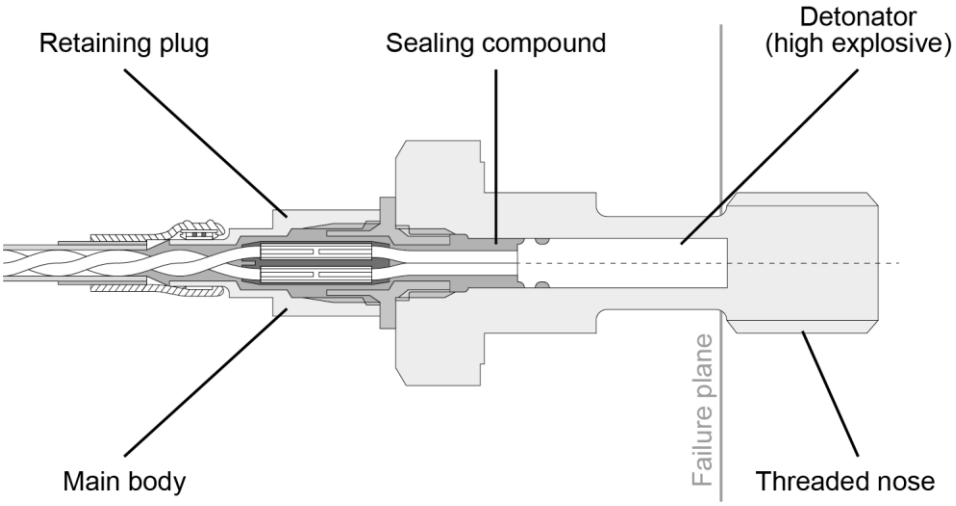


Figure 15-1 Cross-section of an exploding bolt (Courtesy of Chemring Energetics Ltd)

Deflagrating types are able to contain all the effects from burning the energetic material within the body of the pyromechanism and a whole range of mechanical functions have been derived from this such as piston protraction, piston retraction, cable cutting, separation and release. These functions are very useful in missile systems where power and space are limited and yet high force and energy outputs are required. Thus deflagrating pyromechanisms are used in missiles for launch motor separation, various detent applications, fin locking, wing unfolding and flight termination.

In nearly all examples of deflagrating pyromechanisms a confined propellant powder, usually black powder (see 4.2.1) or single base smokeless powder (see 12.2.2), is ignited and drives a piston. The forward movement can give mechanical thrust as in a protractor shown in Figure 15-2 or create the cutting action of a guillotine as shown in Figure 15-3.

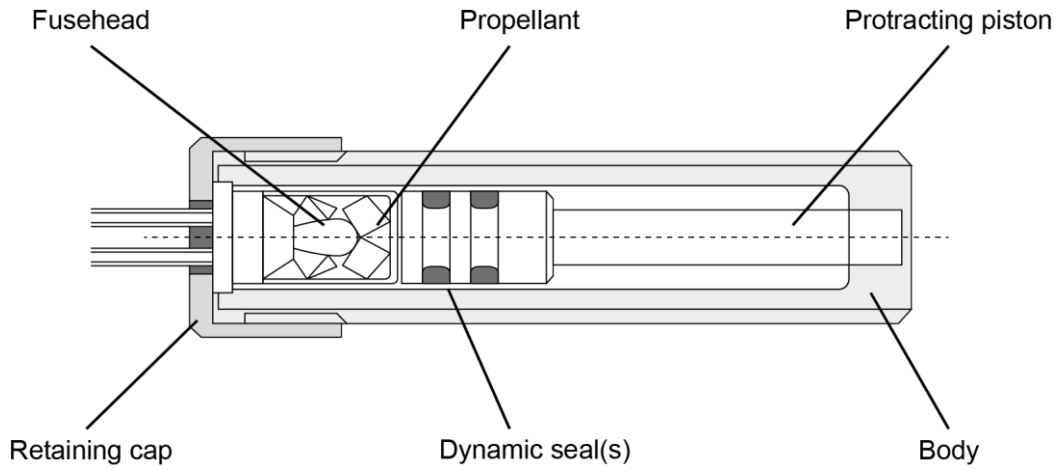


Figure 15-2 Cross-section of a typical protractor (Courtesy of Chemring Energetics Ltd)

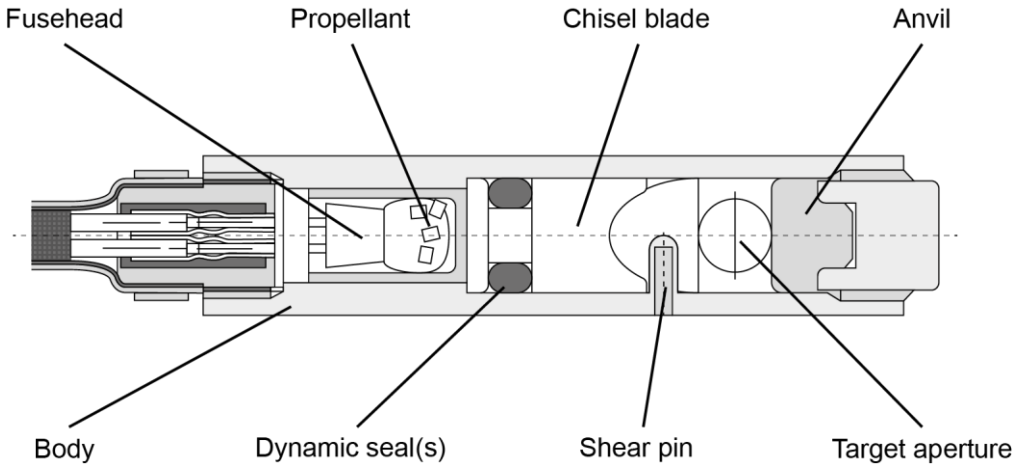


Figure 15-3 Cross-section of a pyromechanical cutter (Courtesy of Chemring Energetics Ltd)

A third major type of piston driven pyromechanism provides valves for controlling gas or liquid flow. They can be designed to either allow a flow to start or to stop. Figure 15-4 shows a valve where the flow line is closed and when fired the piston shears the barrier, which falls in to the trap below with the piston end closing off the hole produced in the pipe. In Figure 15-5 the flow line is open and when fired a blade cuts through the pipe forming a barrier to flow.

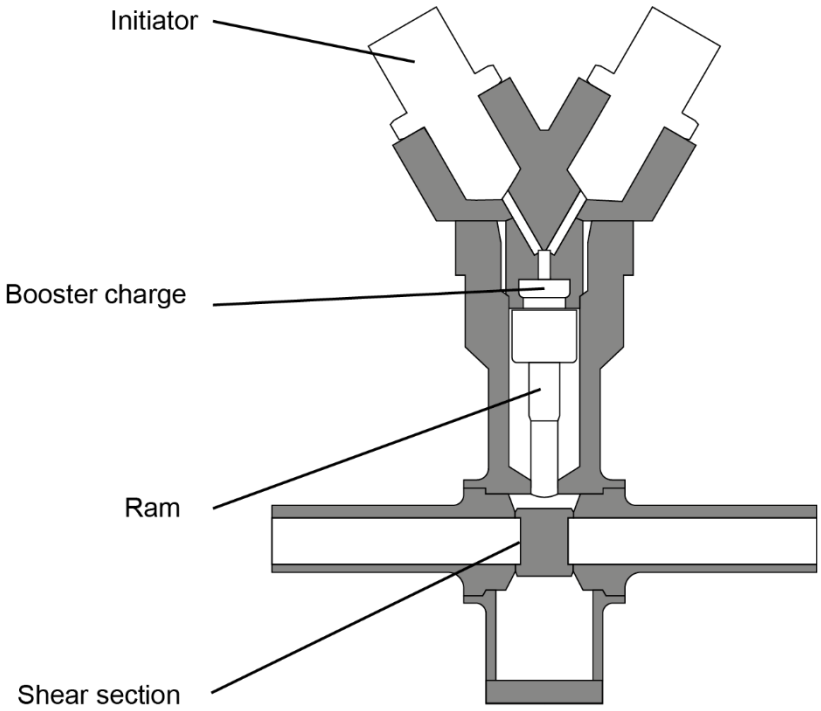


Figure 15-4 Cross-section of a normally closed valve

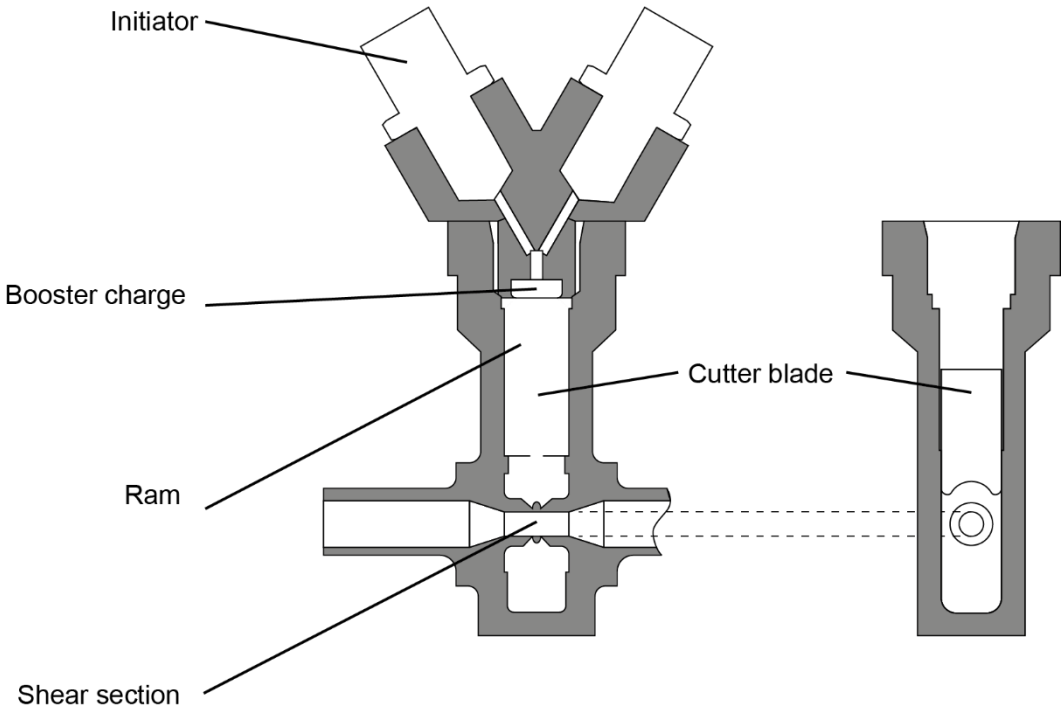


Figure 15-5 Cross-section of a normally open valve

15.1.4 Advantages and Drawbacks of Using Pyromechanisms

The very high energy density of the pyromechanism leads to relatively compact designs and this gives rise to a number of advantages over conventional (mechanical) stored energy systems. These advantages can be summarised as follows:

i. Pyromechanisms incorporate all the necessary energy for the task
ii. They are comparatively small and light and yet have considerable intrinsic energy and work potential
iii. The designs permit remote operation either manually or automatically
iv. The designs are robust and relatively unaffected by a range of environmental conditions
v. They can be hermetically sealed and in the main all the explosive effects can be contained within the device (for deflagrating types)
vi. Very little firing energy is required in return for the potentially large energy outputs from the system (this can be from electrical or mechanical input energy)
vii. Response time can be, and usually is, very rapid, within a few milliseconds
viii. Reliability of these devices is very high
ix. Pyromechanisms require no maintenance throughout their service life.

There are also some draw-backs in the use of pyromechanisms. The principal disadvantage is that they all tend to be single shot devices. In this respect they can only be used once and actions are therefore irreversible. Due to the fact that they contain chemicals and elastomeric seals they have a finite life. This can depend on the material selected but lifespans offered by modern pyromechanisms are generally in line with other lifed items used within weapon systems. Other disadvantages can relate to the type of ignition system used and electrically initiated pyromechanisms in particular may require suitable protection from electromagnetic radiation and electro-static effects.

15.1.5 Summary

Pyromechanisms offer simple and elegant solutions to some complex problems. They are ideal where a high energy output is required from a low level energy source in a relatively compact space. They can perform a number of tasks operating as single shot prime movers, providing either mechanical motion or franging effects. This makes them suitable for use in missiles, bombs, torpedoes, countermeasure systems and in aircrew egress systems to name but a few examples. Typical applications include release functions (e.g. bomb release), missile fin-locking and wing unfolding, launch motor separation, cable severance, flight termination, aircraft canopy break-up etc. This is just a small sample of possible uses for pyromechanisms and there are many other applications within space, automotive, aerospace and safety and security industries.

15.2 TYPES OF PYROMECHANISMS

Pyromechanisms may be divided into two broad categories; Detonating and Deflagrating devices.

15.2.1 Detonating Devices

This type of pyromechanism is initiated by a detonator and may or may not have a secondary charge. The main characteristic here is that the pyromechanism will produce some kind of disruptive effect on its surroundings but the effect is directed at performing a particular task. There may be some fragmentation or spatter associated with the functioning of the pyromechanism. This type of device is very likely to be included in UN Hazard Class 1 Explosives for transportation purposes because of the inherent hazards associated with it.

The pyromechanism uses the resultant shockwave to fracture surrounding materials. These can be metallic such as in explosive bolts where the detonative shock occurs along a weakened portion of the bolt to effect a separation. Other applications include devices to frange (disrupt/shatter) glass such as the covers on some ship launched missiles or acrylic screens such as in aircraft canopies. The essence of the design of a detonative pyromechanism is in the direction of the energy and the reduction of collateral damage. Effects should be kept to the local area and widespread, uncontrolled fragmentation would render the device unsuitable for the task in hand. The device does not use the shattering effect for the purposes of causing harm or random destruction.

Nearly all detonating pyromechanisms are initiated by a low voltage electrical signal that initiates a fusehead, which in turn ignites a primary explosive that burns to detonation (see 6.3.4.6).

15.2.2 Deflagrating Devices

These represent the more common type of pyromechanism and are probably preferred from an end user perspective due to the reduced hazards associated with this type of device. In the main, these pyromechanisms will contain all explosive effects and the only outputs are of a mechanical nature.

A deflagrating device can be considered in two parts. The first part contains the initiation system and the energetic material (generally a propelling charge). The second is a purely mechanical system which uses the energy produced from the energetic material to drive it. In this sense, pyromechanisms can either be fully integrated where the initiation system, energetic material and the mechanism are all housed in a single sealed unit, or can be split into their respective parts where the energetic part (the cartridge) is a separate item from the mechanical assembly. The latter comes under the description of either Cartridge Actuated Devices (CADS) or Propellant Actuated Devices (PADS). CADS/PADS tend to have a self-contained cartridge unit which can be screwed

into a pre-assembled mechanism. This type of system offers many advantages in that it enables the fitment of the energetic and therefore hazardous part immediately before use. It also offers the potential for modularity as different cartridge inputs and outputs can be selected and fitted in order to alter the characteristics of the mechanism. The concept of CADS/PADS leads to a range of gas generating squibs with different electrical firing characteristics and different gas yield in terms of the burn time and quantity of gas produced. This approach leads to thoughts of standardisation of cartridge fitment but the industry has yet to fully embrace this concept. NASA has probably come closest to achieving standardisation with the introduction of the NASA Standard Initiator (NSI). This is a qualified unit which can then be applied to a number of applications without further exhaustive testing. Associated mechanisms can be configured to receive one, two or even more cartridges which can assist overall system reliability. The downside here is that the overall pyromechanism tends to be rather bulky.

Integrated pyromechanisms on the other hand can be smaller for the same output and cheaper but offer reduced scope for alteration of input and output characteristics. There are, however, many examples of integrated pyromechanisms used within weapon systems and some of their mechanical functions are listed below:

i. Puncturing containers (to release liquids or pressurised gas)
ii. Pushing mechanical loads (e.g. opening valves)
iii. Locking a device to prevent rotary or linear motion
iv. Releasing a device to enable rotary or linear motion (using a retracting mechanism)
v. Operating a switch
vi. Cutting wires, cords, or small bolts

15.3 PYROMECHANICAL APPLICATIONS

Pyromechanisms have a wide range of uses in the defence industry and in particular can be found on aircraft, ships, missiles, bombs, torpedoes and countermeasure systems. Some example applications are given below:

15.3.1 Aircrew Egress

A number of pyromechanisms are used in fast jet aircrew egress systems where it is necessary to eject the crew through the canopy. Specifically designed ejection seats require a certain sequence of activities to be completed to enable safe ejection. Different types of pyromechanism are employed to achieve the required effects and these range from basic squibs (cartridges) for unlocking detents to complete release of the parachute once the seat is clear of the aircraft. To assist through-canopy ejection, a canopy break-up system is often employed. This takes the form of a miniature detonating cord (MDC) which is bonded on the underside of the aircraft canopy, which is constructed of either stretched or cast acrylic. The system is initiated by a detonator, often with mechanical initiation systems and this is activated by the first movement of the

seat. Transmission cord links the system to the MDC and conveys the detonation front to enable immediate break-up of the canopy. The MDC is arranged in a pattern which optimises the break-up ensuring no oversize fragments and a relatively free passage for the seat and its occupant. The explosive charge loading within the cord is sized to ensure sufficient cutting energy is imparted to the canopy and that the aircraft is not carrying excess energetic material in the vicinity of the aircrew. This is an example of a detonating pyromechanism where the system is designed to produce a shattering effect with minimal collateral damage as shown in Figure 15-6.



Figure 15-6 Miniature detonating cord (MDC) can be seen attached to the aircraft canopy (left) and completely fragments the canopy as part of the ejection sequence (right) (Courtesy of Chemring Energetics Ltd)

15.3.2 Missiles

Pyromechanical actuators, retention mechanisms, cutters, separation devices and weapon release cartridges all help to perform a range of critical “launch, fly, arm and operate” functions.

15.3.2.1 Weapon Release

Electrically initiated pyrotechnic cartridges (known as Cartridge, Ejector Release Units – CERU) are used to assist in providing a release and separation function from the aircraft. These cartridges produce a rapid supply of hot gas resulting from the burning of its propellant. The CERU uses the gas to drive pistons within the overall mechanism. The whole CERU plus the cartridge is considered to be a pyromechanism.

Missiles contained in a launch tubes may be “unlocked” as part of the launch sequence by electrically initiated retractors. The device shown in Figure 15-7 was designed for a shoulder launched anti-tank weapon. It has a retracting pin which operates a micro-switch for feedback once in the fully unlocked position.

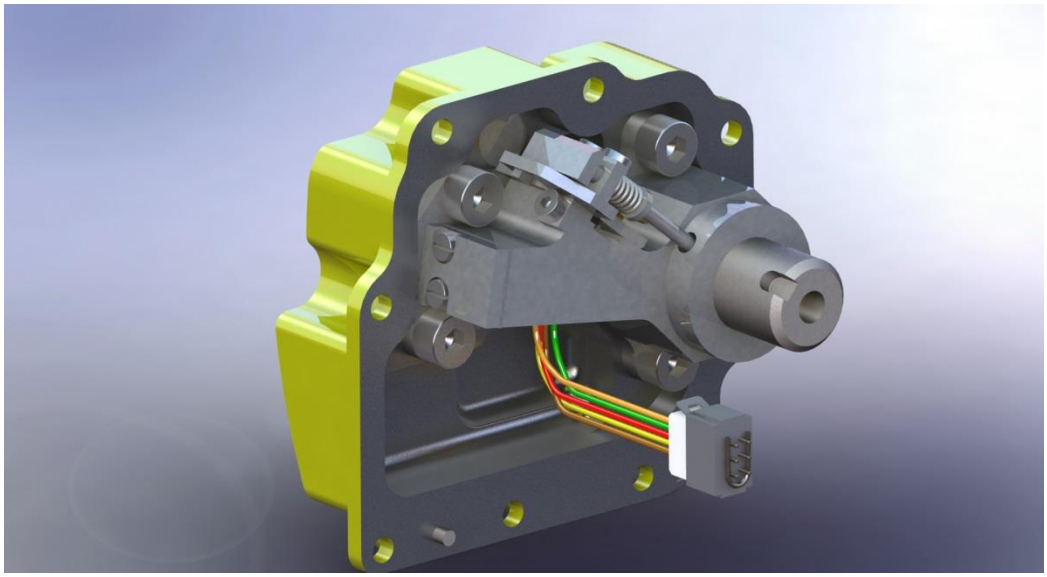


Figure 15-7 Retractable missile detent in shoulder-launched weapon (Courtesy of Chemring Energetics Ltd)

15.3.2.2 Fin Unlocking and Wing Unfolding

Integrated pyromechanisms are used to lock the control surfaces of a missile prior to deployment from an aircraft. On electrical command, the device unlocks the missile fins and allows autonomous control. Larger pyromechanisms can be used to unfold missile wings from the stowed position. Conventional pyromechanisms with fast burning propellants operate too quickly and may damage the wing on deployment. Therefore it is necessary to slow the operation down and sometimes fluid damping mechanisms are employed to give the wing a softer opening.

15.3.2.3 Booster Motor Release

Surface launched missiles that use solid booster motors to rapidly accelerate the missile during the launch phase require a means of releasing the motor after burn out. Pyromechanical release bolts or explosive bolts can be used to achieve this. Three or four units may be required to secure the motor and all can fire simultaneously to effect the release.

15.3.2.4 Missile Safe and Arm Units (SAU)

Although the latest complex weapons are tending towards the use of “in-line” warhead initiation, earlier systems used out-of-line SAU’s which required the use of pyromechanisms to enable alignment of the detonator with the booster. There are still a number of examples of this technology in service today. Here, pyromechanical protracting or retracting devices can be used to provide detents which when fired will initiate mechanical timing mechanisms.

15.3.2.5 Lug Retraction Devices

Upon actuation of a cartridge, a spring loaded rod extends to retract lugs into the missile body to reduce its radar cross section.

15.3.2.6 Valves

Pyromechanical valves are designed to be lightweight and reliable and these are critical to the liquid and gaseous fluid systems for complex missiles. Valves can be either designed in a normally open or normally closed configuration. Valves are typically associated with fuel flow and can be designed to isolate fuel during storage by sealing it within the fuel tank. Upon actuation the valve allows unrestricted fuel flow to the missile and in parallel, unrestricted flow of pressurised air back into the fuel tank. Conversely, a valve can be used to shut off the flow of fuel to act as a means of flight termination as described below.

15.3.2.7 Missile Flight Termination

There are a range of methods that can be used to terminate the flight of a missile and this may depend on the type of missile and its method of propulsion. Historically, shaped charge cutting cords have been utilised to completely sever the missile into two aerodynamically unstable parts. These tend to be rather complex requiring their own dedicated safety and arming units due to the presence of the detonators, booster and detonating cutting charge.

A simpler approach is employed on cruise missiles and the aim here is to terminate the fuel supply by either disrupting the fuel pump, cutting off the electrical power supply to it or to operate a valve to stop the fuel flow. Pyromechanical cutters or valves have been widely used to fulfil these tasks where their electrical means of initiation and compact and robust designs lend them to this application.

15.3.3 Countermeasure Systems

A number of applications have developed over the years using pyromechanisms in modern aircraft and ship countermeasure systems. These tend to be release type devices (bolts or nuts) or cable cutters. The unit shown in Figure 15-8 is from a towed electronic countermeasure used by fast military jets to defeat incoming missiles. It uses a dual ignition cable cutter for severance of the tow cable at the appropriate time. The dual ignition system enhances the reliability of the device to a very high level.

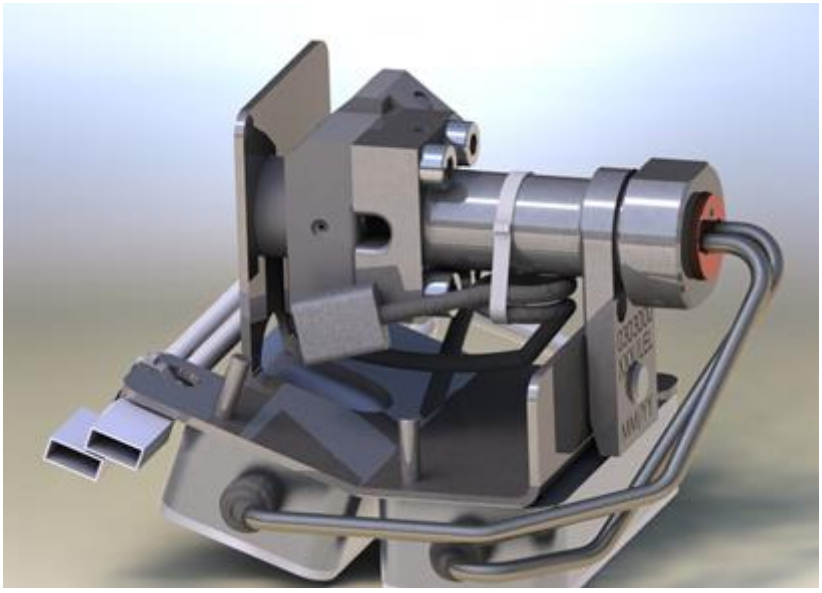


Figure 15-8 A pyromechanical cable cutter used on an aircraft decoy (Courtesy of Chemring Energetics Ltd)

The cable cutter in Figure 15-8 is protected by two electronic filters which are housed in the two boxes at the bottom of the image. These are connected to the cable cutter via the two sets of steel tubes. The design also includes a tellback feature to communicate that the cutter has operated and successfully cut the cable.

15.3.4 Other Applications

There are numerous other applications for pyromechanisms but one in particular worthy of mention is that used for gas bottle opening which has a specially configured piston. The piston penetrates the diaphragm in the top of the gas bottle and has a cut out section to allow the release of gas.

15.4 DESIGN AND CONSTRUCTION

There are many different types of pyromechanisms and it is not possible to cover all within a document of this nature. However, a selection of examples is considered below to illustrate the features of the common types and some aspects of the design of these are considered.

15.4.1 Design Overview

15.4.1.1 Overall architecture

Pyromechanisms, whether of the detonating or deflagrating type, have some common elements which assist in their overall environmental integrity, performance and reliability. First and foremost they have a means of initiation which can be either electrical or mechanical. There is usually a main charge, either propellant or high explosive material, a casing or housing that is usually

metallic, a means of sealing against environments incorporating glass to metal seals and the mechanism which is being driven.

15.4.1.2 Initiation

The vast majority of pyromechanisms are electrically initiated and use a range of low voltage type bridgewire igniters or detonators. There are a number of igniter products available with a variety of all-fire current levels and these can be incorporated into the pyromechanism. Selection of the igniter depends on a number of factors and one of the main drivers tends to be the availability of current from the firing circuit. Higher no-fire thresholds tend to be preferred for better protection from electro-magnetic effects. 1 Amp, 1 Watt, 5 Minute, No Fire igniters are effectively the industry standard and provide a high degree of protection to the pyromechanism and reduce the possibility of inadvertent initiation. These igniters require anything between 3 Amps and 5 Amps to be certain of firing. Lower threshold igniters can be used if there are limitations from the power supply but any device incorporating these is likely to require fully screened leads and possibly electronic filters to combat Radio Frequency/Electromagnetic Interference (RF/EMI) effects where induced currents can be created in the firing circuit. For most military applications, initiators should be characterised in accordance with STANAG 4560[(1)].

There are also mechanical means of initiating a pyromechanism and these use either percussion (see 6.2.2.4) or stab sensitive primers (see 6.2.2.3) or detonators. Percussion ignition systems tend to be more difficult to seal than electrically initiated pyromechanisms but they are not susceptible to RF/EMI. It is also more difficult to operate a percussion system remotely.

15.4.1.3 Energetic materials

Pyromechanisms make use of a range of energetic materials. The main charge is the driver behind the unit. Selection of the energetic material depends on the application and whether a disruptive or purely mechanical output is required.

Pyromechanisms intended for explosive cutting or break-up use a miniature detonating cord system incorporating PETN, HNS or RDX powders to achieve the desired effect. In aircraft canopy break-up systems, lead sheathed cord is currently used as this brings good flexibly and ability to bend around tight radii. Work is underway to identify suitable lead alternatives which will deliver similar handling and performance characteristics. This is primarily driven by EU REACH (see 1.3.2.4.6) regulations. Some disruptive pyromechanisms require only a detonator to perform the task and sometimes dished or conical ends are employed to enhance the performance using a Shaped Charge effect (see 8.1.3).

Deflagrating pyromechanisms usually require a fast burning charge. Single base NC small arms propellants (see 12.2.2) lend themselves well to this application. These materials are easy to initiate, are available in volume production and burn at the required rate to enable the pyromechanism to perform its duty. They are very efficient at producing hot gas which is used to

drive the mechanism. The NC incorporates a stabiliser (see 12.2.4.1) which assists in maintaining the propellant in a safe state and prolongs the life of such material. Single base NC is very tolerant of a wide range of temperatures and will meet the majority of weapon system requirements.

Black powder (gunpowder) is also very common as a main charge within pyromechanisms. Again this burns very rapidly (in the loose filled state), although it is not as efficient as NC for producing gas and it yields a lot of solids in the products of combustion. Black powder is a relatively stable material and is useful for pyromechanisms requiring good longevity.

15.4.1.4 Housings

Unless specifically designed to provide a disruptive effect, a key requirement for a pyromechanism is to contain its explosive event and channel the energy into a mechanical movement. This places great importance on the structure and in many cases requires the structure to cope with very high pressure levels. It is not uncommon for a pyromechanism to generate an internal pressure in the range of 200 – 500 MPa (2000 – 5000 bar). Material selection is therefore critical. The deciding factors may be a choice between size and mass. Very high strength steels can be employed to provide the thinnest wall section to cope with a particular pressure level. High strength stainless steels such as precipitation hardening steels (to BS 2S143/145) are good for their combined strength and corrosion resistance. Smaller, lower power pyromechanism housings can be manufactured in free machining brass and aluminium. These materials are good at containing lower pressure events and are cheaper to produce than their high strength steel counterparts. All materials used in contact with the energetic material must be tested for compatibility (see 20.10.3.1).

15.4.1.5 Sealing

For electrically initiated pyromechanisms, it is necessary to convey the electrical firing pulse to the igniter which is normally housed inside the pyromechanism body. In order to maintain a good hermetic seal, the igniters are often mounted on glass to metal seals (GTMS) and this allows the current to be conducted through the seal via pins which pass through the glass beads. These GTMS are capable of withstanding high pressure for short periods and have been proven over many years use within pyromechanisms.

Percussion initiated pyromechanisms are much more difficult to seal. Most of the conventional percussion primers (link to 6.2.2.4) are not capable of holding high pressure gas post function and therefore some means of back-up is required. This can result in elaborate striker mechanisms which use elastomeric O ring seals on the striker parts. The issue here is that the O rings absorb significant amounts of striker energy and compensation needs to be made in the energy source.

Pistons on protracting or retracting mechanisms use elastomeric O rings to prevent gas escape and keep all explosive effects within the housing. Ethylene propylene diene monomer (EPDM) rubber is a common material for the O ring

as it is compatible (see 20.10.3.1) with most energetic materials, tolerates high temperature for short durations and offers good longevity.

15.4.2 Electro-static Protection

Electrically initiated pyromechanisms are prone to inadvertent actuation through electro-static discharge (ESD). Build-up of static electricity can cause problems unless the pyromechanism has suitable protection designed in. Any discharge taking place within the device around the energetic material chamber is likely to cause ignition. A common failure mode is where discharge takes place between the electrical pins and the metallic body of the device. The design of the pyromechanism needs to take account of this and many pyromechanisms now offer some insulation between the internal walls of the device and the igniter using a suitably compatible plastic with high a di-electric strength.

A number of tests have been developed over the years to simulate various electro-static environments and these tests are used to determine the adequacy of the pyromechanism to cope with electro-static discharge. The most common test involves charging a 500 pF capacitor to 25 kV and then discharging this through either the pins to case or pin to pin with a 5000 Ohm or 500 Ohm resistor connected in series. This represents a worst case human discharge and is therefore appropriate for ensuring the device is safe to handle. Such tests are standardised and defined in common EED standards such as MIL-DTL-23659F(2) and STANAG 4560(3).

Other techniques to combat ESD include appropriately designed air gaps which encourage the discharge to take place outside of the energetic chamber. This technique works well but relies on there being no foreign matter entering the air gap.

15.4.3 Radio Frequency/Electro-magnetic Induction Protection

Another common issue with electrically initiated pyromechanisms relates to their behaviour in strong electromagnetic fields and in close proximity to radio transmitters. Such fields can generate sufficient electrical current in the firing circuits and if this is above the no-fire level of the igniter, the pyromechanism can fire inadvertently. As with other explosive systems there are means to combat this by including certain features in the design. Perhaps the most obvious is the selection of a high threshold igniter. The 1 Amp, 1 Watt, 5 Minute, No Fire types are particularly good at coping with RF/EMI environments but they require a reasonable level of firing energy from the circuit and this may not always be possible. Twisted pairs help reduce the chance of inductive pick-up but are not adequate on their own. Screening of the electrical leads is effective provided all joints and terminations maintain the screen through 360º. It may also be necessary to ensure the pyromechanism sits in a complete Faraday cage. Electronic Filters are also widely used in the design of the firing circuits. These tend to be of the capacitive low pass type which filters out unwanted high frequency signals. EMI suppression filters are also common and their fairly small and compact design does not add too greatly to the overall size and mass

of the pyromechanism. These filters can also assist with the electro-static discharge as most have built-in bleed resistors to earth.

15.4.4 Detonating Devices

15.4.4.1 Explosive bolts

The use of the explosive bolt has a long history, principally to facilitate the remote and rapid release or separation of one object from another. It relies on the principle of brisance to cause structural failure; brisance being defined as “the ability of an explosive to shatter the medium which contains it”. In this case, the explosion involves a detonation shock wave, which leads to failure along a predefined plane.

The principal advantage of the explosive bolt is its simplicity having no moving parts and as such it is a relatively low cost solution as a separation mechanism; however, there are several major disadvantages:-

- It utilises high explosive material
- On functioning, it releases hot gasses and combustion products at high pressure, together with fragmentation of the metal body.
- Its detonation may impart a significant shock to the structure to which it is attached.

In many cases, these will be highly undesirable characteristics.

15.4.5 Deflagrating Devices

15.4.5.1 Protractors

The protractor represents the simplest form of pyromechanism in use today. As its name suggests it is designed to protract with a pushing motion in relation to its body. When initiated, the rapid gas expansion resulting from the burning propellant forces a sealed piston forward with a calculated amount of energy. This energy can then be used to do work outside the device itself. In Figure 15-9 the igniter within the protractor can be seen to be protected by a plastic insulation sleeve. This prevents any possibility of electrical discharge between the walls of the device and the igniter pins and thus renders it safe from inadvertent firing to electro-static effects.

The whole structure has been designed to contain all the effects of the “explosive” event and therefore all wall thicknesses have been sized to contain the very high transient pressures. Equally, the base of the protractor is capable of arresting the piston which travels at high velocity until it impacts on the base at the end of its stroke. The piston is prevented from moving by a shear device. The illustration above shows a “septum” feature at the base of the unit which holds the piston in place until, on initiation, the internal gas pressure builds up to a point where the resultant force on the piston breaks the septum. Shear devices can be used to tune the protractor and this can alter its characteristics.

The design of the protractor includes an electrical igniter which is mounted on a glass to metal seal. The latter helps retain all the flame and gaseous effects. For small protractors the only explosive present may be the fusehead.

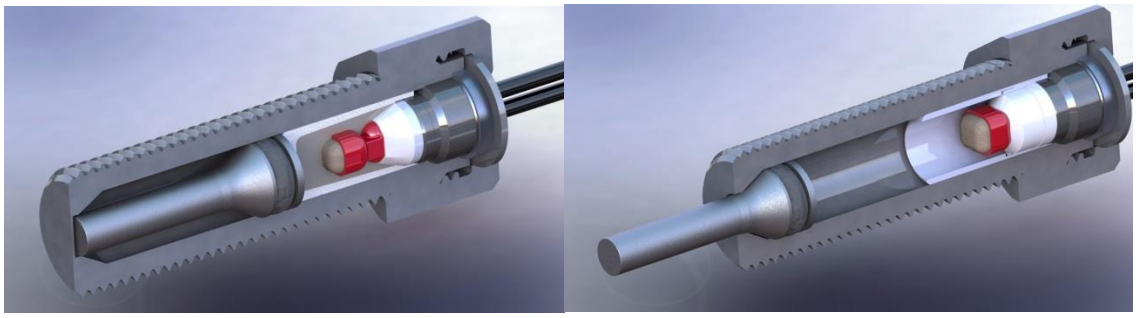


Figure 15-9 Protractor in the unfired (left) and fired (right) positions (Courtesy of Chemring Energetics Ltd)

The performance of protractors that use fast burning explosive powders and propellants have a characteristic thrust profile. The majority of burning takes place before the piston starts to move and therefore the highest thrust occurs at this point. Once the shear element has failed, the piston then accelerates rapidly driven by the expanding gas until it arrests on the base of the unit. Placing axial loads on the piston will change the overall characteristic as the energy in the gas is given up to moving the load. The lowest thrust will always occur at the end of the stroke.

It is very easy to measure the energy and thrust output from a protractor. Energy measurement systems utilise a known mass which is propelled vertically. The height the mass achieves is recorded and this is used to compute the energy output through a simple “mass x gravitational constant x height” calculation. Alternative energy measurement methods use a pendulum approach where a mass suspended on a pendulum arm undergoes an angular displacement when receiving energy from the protractor. The angular displacement is then converted to an energy value through a simple algorithm. Thrust can be measured by operating the protractor with a suitable load cell in the system.

There are many protractors on the market with various characteristics and these products tend to be defined by their stroke length, energy or thrust output and electrical firing characteristics. In some sectors there has been some standardisation regarding installation features and it therefore becomes possible to interchange protractors from different manufacturers.

15.4.5.2 Retractors

The retractor is designed to have a pulling motion in relation to its body. It achieves this based on gas pressure acting on the differential area between the piston shank and the piston head. Each part of the piston is sealed by an appropriate O ring. There are various designs of retractor in existence but the common types either have integrated energetics to maintain the slender profile of the device or they have a side-entry gas cartridge.



Figure 15-10 Retracting device with side entry gas cartridge (Courtesy of Chemring Energetics Ltd)

On firing, the gas pressure is directed to the void between the two O ring seals by means of ports, thereby causing the piston to retract inside the body. It can be seen from Figure 15-10 that the design of the retractor is necessarily more involved, generally resulting in a larger space envelope and higher cost than that of an equivalent protractor. For these reasons, its use is less frequent than the protractor; however, in some applications it does provide the most appropriate, reliable and cost effective solution to the needs of the designer. As with the protractor, the retractor has built in ESD protection.

Assessment of retractor performance is usually made by applying side loads to the piston and then operating it to determine whether the device is capable of fully retracting. Excess loads are applied to prove the margin in performance. The bulk of retractor applications involve operating against a side load so this is a representative means of testing. As with the protractor, the highest thrust takes place at the start of the stroke and decays once the gas expands and cools. Again, it is common for the piston within the retractor to be held in place by a shear device (commonly a shear pin). This can be used to tune the performance of the retractor during the design phase.

15.4.5.3 Cable cutters

In essence, the pyromechanical cutter is a protractor with a blade embodied in the piston nose, an end-of-stroke anvil to arrest it, and an aperture between, to locate the target.

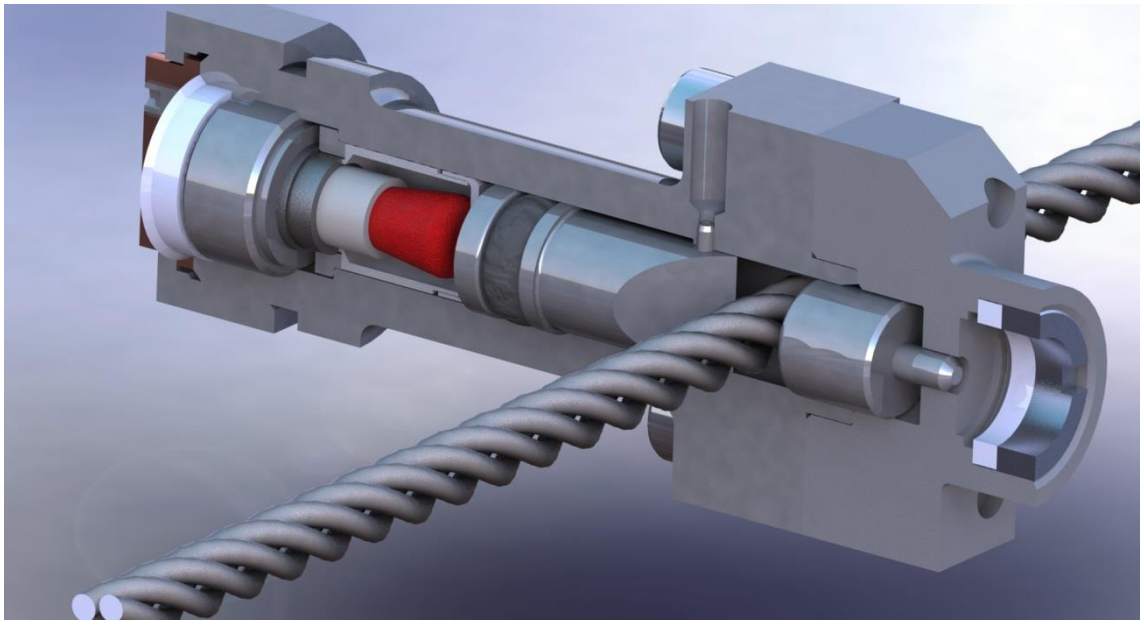


Figure 15-11 Pyromechanical cutter with target cable (Courtesy of Chemring Energetics Ltd)

The simplest form of cutter, illustrated in Figure 15-11, for cutting typically plain wire, cable or rope, employs a chisel blade, with a through-hole (target aperture) through which the target is threaded, normal to it and adjacent to the anvil. The cutting method here is similar to that of an axe where the target fails through a combination of shear and tensile failure; however, depending on size and geometric arrangement, the alternative of a circular blade which acts more like a pastry cutter may be used.

Cutter mechanisms also can be designed with side openings or removable anvils; thus allowing the cutter to be brought to the target (in situ). This eliminates the need for the cutter to be permanently fixed, and hence the need for "threading" the target. As such they can be used to cut many different types of targets from very thin cords and wires, to solid tool steel bars.

Figure 15-12 shows a large pyromechanical cutter which is capable of severing a 100 mm diameter steel armoured cable. The cable aperture is on the right hand side of the view. As can be imagined a high propellant load is required to cut the target and this gives rise to very high pressure inside the device. This has resulted in a finished product of 1.2 meters in length and a mass in excess of 150 kg due to the high strength casing. This particular cutter has spent several years on the sea bed and although there is high degree of surface corrosion, the components of the cutter remain pristine and fully operational. This demonstrates the potential robustness of a properly designed pyromechanism with adequate sealing.



Figure 15-12 Pyromechanical cable cutter designed for a deep sea environment (Courtesy of Chemring Energetics Ltd)

15.4.5.4 Release Bolts

The release bolt is another derivative of the protractor; in this case however, doing all the work inside the device with a very short stroke of the piston.

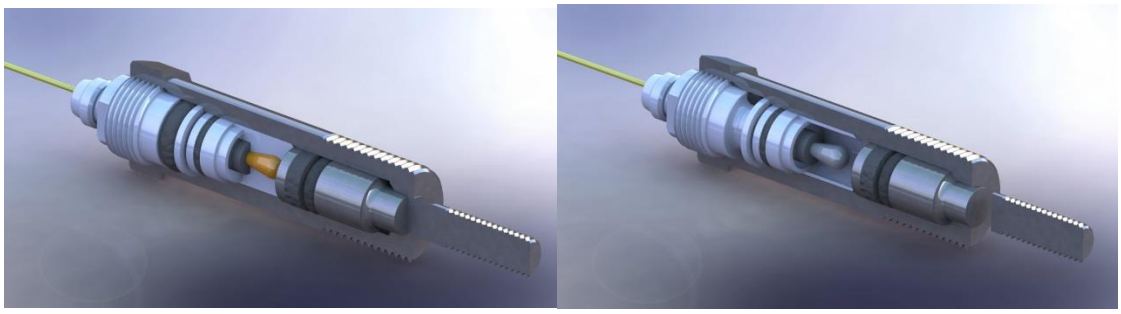


Figure 15-13 Release bolt in the unfired (left) and fired (right) positions (Courtesy of Chemring Energetics Ltd)

As can be seen in Figure 15-13, the piston (at rest) is mounted in a stall condition relative to the bolt shank, so that during the initial stage of gas generation the piston is restrained from moving forward. When the design pressure is reached, the piston is thrust forward a short distance to cause shear failure of the shank at the predefined circumferential shear plane; thereby allowing the threaded nose of the bolt to break away, whilst retaining the piston in the main body of the bolt.

Immediately, the advantages of this device over the explosive bolt are apparent:-

- It does not utilise high explosive material
- Upon functioning, the device separates into two parts only, with no fragmentation
- After functioning, it contains all products of combustion
- There is no detonation shock wave

Release nuts are also commonly used (in lieu of the release bolts). Both release bolts and release nuts can be designed with recoil-less features to reduce further the effects on the surrounding structure.

15.4.5.5 Pyromechanical valves

The pyromechanical valve comes into its own for handling fluids which require highly reliable sealing and isolation for long storage periods, where traditional valve techniques are inappropriate or inadequate. It is particularly useful when handling volatile, corrosive or hazardous fluids, which would quickly destroy conventional synthetic sealing materials. Typical applications would be fuel lines for rockets or torpedoes, where any leakage and/or evaporation cannot be tolerated.

Its principle of operation is not dissimilar to that of the release bolt, where an advancing piston is used to cause failure at a predetermined shear plane (two in this case) as shown in Figure 15-14. In this application however, the piston has a much longer stroke, so that after shearing the blind ends, it continues to end of stroke, where it presents an aperture to the flow-line thus permitting fluid flow.

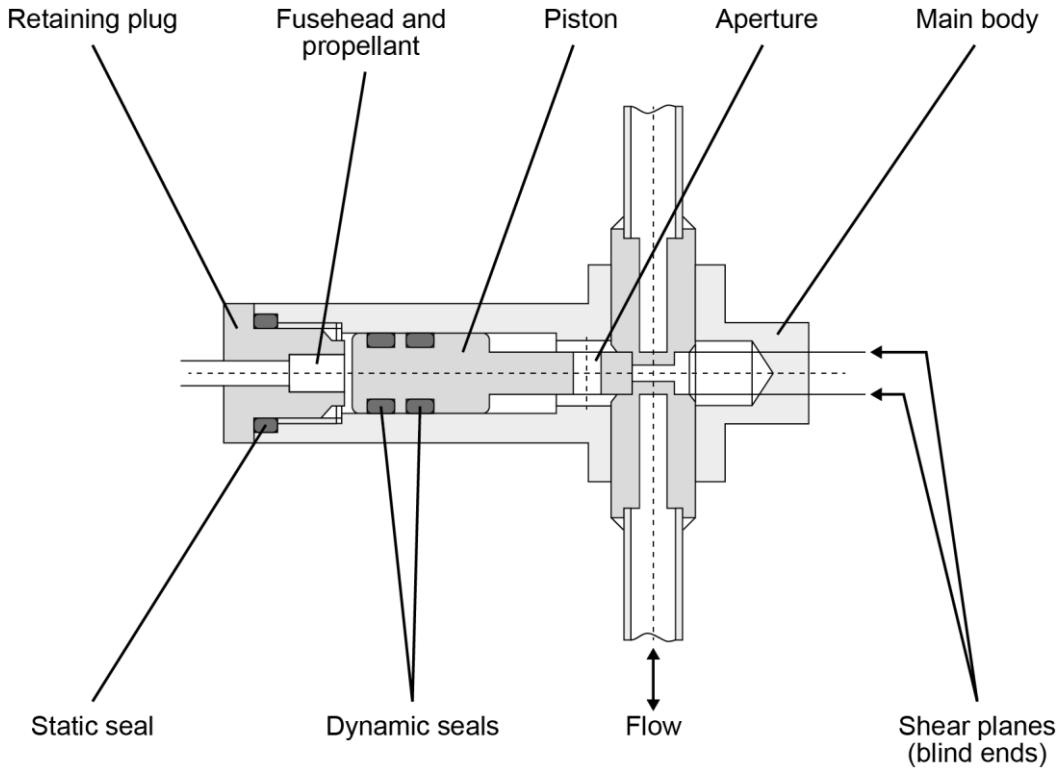


Figure 15-14 A typical pyromechanical valve layout (Courtesy of Chemring Energetics Ltd)

The valves can be configured in different ways to provide either normally open (NO) or normally closed (NC) options. In some instances it is possible to have

dual function valves that change state from closed to open and then closed again. These, however, result in fairly complex, bulky and expensive valves.

15.4.5.6 Damped pyromechanisms

The majority of pyromechanisms that use a fast burning propellant tend to have a very fast function time. As such, the event can be over within 10 or 20 milliseconds. The speed at which they operate can impart much shock into the surrounding structure and such fast operation may not be suitable for some applications. To combat this, there are techniques to slow down the operation cycle. One such technique employs a damping fluid.

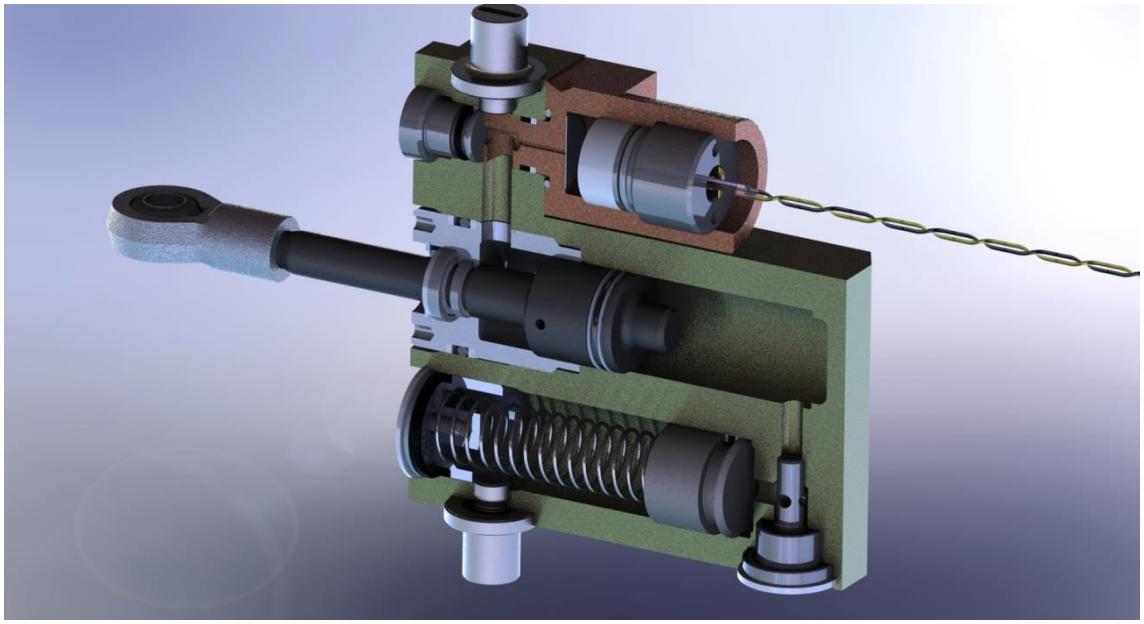


Figure 15-15 A damped pyromechanical retracting device (Courtesy of Chemring Energetics Ltd)

Figure 15-15 shows the layout of a damped pyromechanical retracting device. This particular unit has a gas generating cartridge at the top of the picture which contains a single base, rapid burning NC propellant. On activation, the high pressure gas is directed to the main cylinder via a port and this acts on a sealed piston. On the other side of the piston is a damping fluid which is held in situ behind a diaphragm that covers a small orifice. When the pressure imparted to the fluid reaches a certain level, the diaphragm is ruptured and the fluid flows through the orifice and into a second chamber. The orifice controls the mass flow rate of the fluid and this provides a damping action on the piston. The fluid then collects in the second chamber and drives the second piston down the bore of the empty chamber. This action provides a more controlled displacement vs. time profile and results in operating time in the hundreds of milliseconds rather than tens of milliseconds. The pulling motion of the retractor is therefore suitable for applications such as cruise missile wing unfolding where wing inertial loads may cause problems under a fast acting actuator. Selection of the damping fluid is crucial in a damped pyromechanism. It is important the material is stable over a wide temperature range.

15.4.6 Design Considerations

15.4.6.1 Performance

As pyromechanisms generate considerable energy in relation to their size, it is important when developing a new device, that apart from the obvious need to ensure it meets all aspects of the operational requirements, there is not too much unwanted energy produced that might put unnecessary stress on adjacent components. It is therefore important to fully understand the relevant parts of the system which interface with the pyromechanism. The external loads placed on a pyromechanism can considerably influence its performance and the design needs to be able to cope with the extreme pressures of a stall condition.

Modern day pyromechanical design makes good use of computational techniques and this can be underpinned with real test firing data. To enable the most accurate performance simulation, the particular propellant that is to be used in the pyromechanism must be characterised, that is to say that its burning rate/pressure/time performance must be fully understood and expressed mathematically. The resultant model is then improved and refined with the feedback of test firing results and the comparison of the actuals with the predictions. This approach reduces the amount of iterative testing required during development and results in a more precisely engineered product with a shorter and more effective non-recurring element of the development programme, prior to commitment to manufacture, and has clear benefits in terms of cost and programme time scale.

Peak pressures developed within a deflagrating pyromechanism typically lie between 200 and 500 MPa (2000 – 5000 bar). In normal operation the peak pressure is only a transient, nevertheless it should not be forgotten that to qualify as a non-explosive device the pyromechanism needs to contain the developed pressure for an extended period of time.

Response times have been stated as being short; generally in the order of 10 - 20 milliseconds from the time of application of the firing pulse to the mechanical action being complete. By way of illustration, Figure 15-16 below shows the recorded pressure/time curve from the actual firing of a large pyromechanical cutter where the vertical axis shows the internally generated pressure (bar), and the horizontal axis the elapsed time (milliseconds).

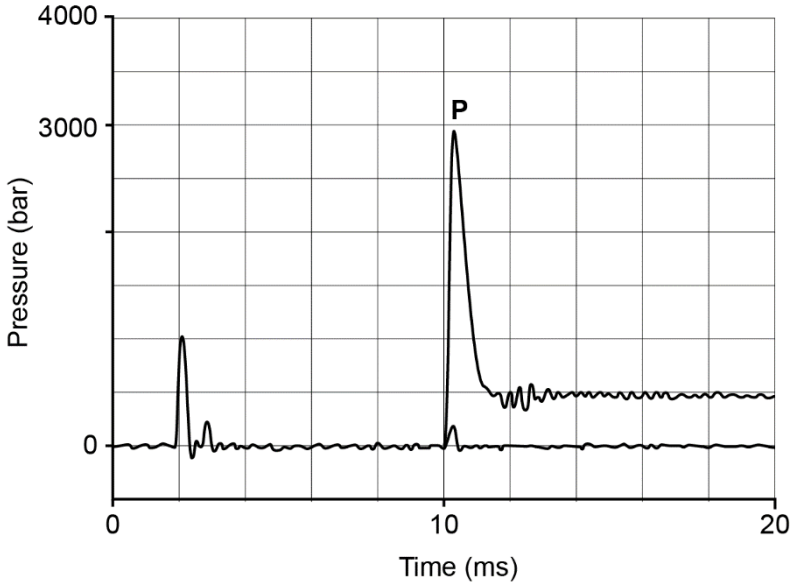


Figure 15-16 Typical pressure v time curve of a large pyromechanical cutter

The peak value “P” at nominally 10.5 ms indicates the maximum internal pressure inside the device and it can be seen that there is a delay of only 8 ms from the firing pulse (at 2 ms) to the start of pressure rise. This is the time it takes for the electrical energy applied to the igniter to cause the pyrotechnic composition to inflame and start the combustion of the propellant. Once the propellant has started to burn, the pressure/burning rate escalation effect (see 7.2.3.2) produces a near vertical pressure rise up to 300 MPa (3000 bar). Allowing for the accuracy of the recording instrumentation, the pressure rise clearly takes less than a millisecond. Peak pressure soon decays once the piston/cutter blade moves, increasing the internal volume, and the heat, generated during combustion, is dissipated through the metalwork of the body. Again, this occurs in a timeframe of less than 10 ms.

The velocity of the blade reaches a peak of approximately 90 m s^{-1}, and the whole cutting operation takes place in 10 ms. This can be put into perspective when it is realised that a blink of the human eye takes approximately 45 ms.

15.4.6.2 Environments

As most pyromechanisms are of sealed construction, they will not generally be adversely affected by their environment, whether underwater, in air, or in outer space. They are of rugged construction and generally unaffected by the extremes of shock and vibration levels to which military weapon systems are typically subjected. However, before embarking on the design of a pyromechanism, the environment in which it will perform must be fully understood, particularly with respect to the temperature in service. Pyromechanisms generally cope well with a temperature range of -54 °C to +85 °C provided there are only short duration excursions to the higher limit.

Very high levels of shock can cause problems to a pyromechanism unless it has appropriate features built into the design and the general rule here is to make sure that none of the internal components are unsupported.

As stated earlier, electromagnetic environments will have an effect on the pyromechanism and it is important to establish the details of this as it may require special measures to be taken with the design of the pyromechanism such as provision of filter boxes and screened twisted pairs to protect the circuits.

15.4.6.3 Reliability

As a “single shot” device it is very important, particularly in safety related applications, that the pyromechanism operates when it is required to do so and does not inadvertently operate when in stand-by mode. The reliability of pyromechanisms is therefore crucial. There are a number of methods of assessing the reliability of a pyromechanism and the most common method is by testing although this is not the most cost effective. Testing a large quantity of pyromechanisms will enable the statistical assessment of reliability. For example, if 298 one shot devices are tested without failure this equates to a reliability of 0.99 with 95 % confidence.

Budget and time constraints often preclude testing as a means of establishing reliability, particularly where very high levels of reliability need to be proven. Other methods that can be used are by “parts count” where published failure rates are assigned to the components of the pyromechanism. A base rate failure is then computed and this may be modified with environmental factors to take account of the lifecycle profile of the device.

Pyromechanisms have a good track record for reliability and it is not uncommon to see reliability levels of 0.998 or better depending on the type of pyromechanism, the life and the environment.

15.4.6.4 Life

The main enemy of modern explosives from the point of view of longevity is temperature. As all explosives decompose at a rate directly related to the temperature to which they are exposed, the life of any pyromechanism becomes a function of the type of explosive material that it contains and its environment, in terms of maximum level of, and fluctuations in, temperature. Consequently a pyromechanism which is subjected to high temperatures for prolonged periods will not exhibit as long a life as it would if kept reasonably cool, say at about 20 °C.

As a precursor to a comprehensive in-service real time surveillance programme it is possible to calculate the expected life of pyromechanisms containing single base propellants by maintaining them at an elevated temperature for a given length of time and then measuring the performance in a standard rig. This performance is then compared with the pre-trial performance to provide a measure of any deterioration.

The relationship between the temperature of storage and the total life can be estimated by application of equation ((15-1).

$$P_1 = P_2 . A^{(T_2 - T_1)/10} \quad \textbf{(15-1)}$$

Equation (15-1) with an Arrhenius factor A, which is specific to each explosive and usually in the range of 2 to 3, shows that equal degradation is produced in an explosive stored either for a period P_1 at temperature T_1, or for a period P_2at a temperature T_2.

Although the above equation has limitations, it is valuable for initial estimates. The accuracy of an accelerated ageing programme starts to become compromised if prediction periods (P_1) greater than 10 years are used. Under these circumstances a combination of real time storage and accelerated ageing may be used to good effect. To make the best use of this technique a 'stockpile to target' sequence for the weapon system is required which predicts what fraction of its total life it will spend in any given environmental condition.

Many pyromechanisms are capable of achieving a life of ten or more years depending on the environments and the pyrotechnic materials selected. Unless refurbishment is an option for some of the larger pyromechanisms (see below), time expired pyromechanisms must be disposed of and replaced.

15.4.6.5 Safety

Safety of pyromechanisms is paramount. The majority of pyromechanisms are designed to contain very high pressure events. It is therefore vital that adequate safety factors are provided in the design to ensure sound integrity of the device. All hazards associated with the pyromechanism must be fully understood and this can be achieved by conducting an appropriate hazard analysis. Construction of a product safety case to accompany each design is now mandatory and in general these are compiled in accordance with Def Stan 00-56[(4)].

15.4.6.6 Refurbishment

Pyromechanisms, are by nature, 'one shot' devices; however, under the right circumstances, refurbishment can be an option. The factor that controls this is mainly the cost of refurbishment compared with the cost of a new item. Even if a device is recoverable after use, its refurbishment will not necessarily be economically viable unless the device is sufficiently large enough to justify it. If refurbishment is a requirement, then the designer must be made aware of this at the very earliest stage in the design process, as it is necessary to incorporate this feature into the baseline product; retrofitting not being a practical option.

15.5 CLASSIFICATION FOR TRANSPORTATION AND STORAGE

It may seem a contradiction to even consider that an item containing explosive material could be legally classified as a "non-explosive" article. However

provided that specific criteria are fully satisfied, it is certainly true as far as the UK authorities are concerned.

The criteria are:-

- The total net explosive content must not exceed 100 mg
- There must be no emission of hot gas or explosive effects outside the device during or after functioning
- Initiation must be electrical, not mechanical
- If a cutter: the target aperture must be no greater than 5 mm
- Any external mechanical motion must not exceed 20 mm

Classification as “non-explosive”, and therefore exemption from the terms of ER 2014(5) and associated legislation on the transport of explosives(6), simplifies and makes cheaper the storage, transport and handling of the devices for both supplier and user.

Any newly developed pyromechanism must be tested during its development phase to demonstrate the maintenance of its structural integrity at the extremes of its performance envelope. It will be evaluated in a representative stall condition, where the piston is prevented from moving when fired; thereby subjecting it to the maximum possible internal pressure to confirm that it will not rupture or explode under this extreme condition. Additionally the device is tested with no load on the piston, so as to achieve maximum velocity by the end of stroke, at which point it must be arrested within the structure, and demonstrate that it will not be ejected from the mechanism.

There are a number of protractors, retractors and cable cutters that have achieved an exemption from Dangerous Goods Class 1 Explosives. However, any detonating (disruptive) pyromechanical system is likely to carry an explosive hazard classification of 1.4S at best.

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CHAPTER 17
DETECTION AND ANALYSIS OF EXPLOSIVES

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17 DETECTION AND ANALYSIS OF EXPLOSIVES

Author – P P Gill (Cranfield University)

17.1 AWARENESS SUMMARY

Detection and analysis are important at all stages in the life-cycle of an energetic material, from manufacture through storage to deployment, the actual technique employed for a particular activity being dependent upon the type of information required.

Some common applications are:

a. Detection of hidden explosives as part of security procedures
b. Analysis of explosives as part of quality control procedures during the manufacture and filling of explosive munitions
c. Identification of explosives of unknown composition. This includes examination of post explosion residues, foreign ammunition and recovered terrorist devices
d. Critical examination of materials and stores in support of accident or defect investigations
e. Examination of materials after periods of service or after undergoing trial programmes, for example during trials and in support of in-service surveillance programmes

Information at the simplest level is provided by detection techniques. These are able to establish whether or not a substance is present. Some are also capable of distinguishing between types of compound but, in general, detection techniques provide no detailed chemical information. It should be noted, however, that while the information obtained from detection techniques is simple the technique itself might be extremely complex. Thus detection techniques range from colour, or 'spot', tests to the combined x-ray and neutron activation devices used for explosives detection at airports.

The number of techniques available for the detection and analysis of energetic materials is vast and this chapter does not seek to give a comprehensive description of each of them. What it does attempt to do is provide a broad introduction to the major techniques, their applications and advantages, at a level that does not assume a detailed technical knowledge.

17.1.1 Instrumental Techniques for detection and analysis

Instrumental techniques are normally used for the detection of concealed explosives in, for example, airports and public buildings. The main requirements of an instrumental explosives detector in these circumstances are therefore:

i. Sensitivity
ii. High success rate
iii. Low false alarms
iv. Rapid Response
vi. High reliability
vii. Non-intrusive
viii. Non hazardous
ix. Multiple parameter

v. Simplicity in use

x. Low cost

Instrumented detection techniques can be further subdivided into techniques for vapour detection and bulk detection.

17.1.1.1 Vapour Detection Techniques

Vapour detection techniques, commonly called Explosive Trace Detection (EDS) systems are designed to detect very small quantities of explosives often in the vapour phase or from material (cotton) swabs. The two leading technologies, Ion Mobility Spectroscopy (IMS) and Mass Spectroscopy (MS), both detect explosives in the vapour phase. In the border security applications the samples are either taken directly from the air near to a suspected contaminated area or the explosive is concentrated onto a fabric swab, which is then vaporised into a gas stream for analysis. When in the gas phase both techniques ionise the molecules and then detect the ions generated. IMS determines the time taken for an ionised molecule to reach the detector, enabling detection of the explosive by calibrating the detection (drift) time against known standards. The MS uses a magnetic field to separate the ions into their separate mass to charge ratios, enabling identification by determination of their molecular mass. Whilst MS is the more accurate and elegant analytical tool, IMS is the market leader for Explosive Trace Detection systems because it is easy of miniaturise, simple to use and has low cost.

17.1.1.2 Bulk Detection Techniques

Bulk detection techniques, commonly called Explosive Detection Systems (EDS) are design to detect large quantities of explosives sealed within containers. To obtain information from within the sealed container it is normal to use the short wavelength parts of the electromagnetic spectrum that can penetrate through solid objects, such as X-rays. Conventional transmission X-ray devices have been used for many years to detect for explosives. However, simple X-ray techniques cannot easily distinguish between a block of plastic explosive and a paperback book of similar size. Effective bulk detectors therefore require a more discriminating method for distinguishing explosives.

Dual energy X-ray systems are able to discern between materials based on the atomic numbers of atoms that make up the material (z-numbers) but have great difficulty discerning density. X-ray scattering, either back towards the X-ray source (back scatter) or passed forward through the object (forward scatter) has been proposed as an effect way of luggage inspection. A scattered image will give information about z-numbers and the density of the object, meaning plastic explosives can now be distinguished from common plastics and clothing. A major problem is the position of the object relative to the X-ray source and the detector has a strong influence on the scattered signal and this can cause errors in interpreting the data.

X-ray technology continues to be the preferred method of explosive screening because it is safe to humans and luggage, and is relatively cheap to buy and

operate. However it is by no means the best option and suffers from high false alarm rates. Duel Energy X-ray instruments and X-ray Scattering will significantly reduce the false alarm rates, but at a greatly increased cost and complexity.

17.1.2 Chemical Analysis Techniques

Chemical analysis techniques for energetic materials are capable of providing detailed qualitative and quantitative information. Thus analysis can establish both the identity and the concentration of a component in an energetic material.

While traditional "wet" chemical methods of analysis are still useful for some energetic materials the vast majority of analyses are these days carried out using instrumental techniques. One area where chemical methods remain appropriate is the analysis of simple inorganic materials in, for example, pyrotechnics. However new instrumental techniques such as ion chromatography are now beginning to replace the traditional chemical methods for these determinations.

The two most widely used types of instrumental technique employed in the analysis of energetic materials are spectroscopy and chromatography. They complement one another to a large extent since spectroscopic techniques are most useful for qualitative analysis while chromatography is used mainly for quantitative analysis. The two techniques are often linked to provide a particularly powerful analytical device.

Chromatography encompasses a range of related analytical techniques, each of which involves the separation of a mixture of components by exploiting differences in the equilibrium distribution of the components between a mobile and a stationary phase. As well as separating complex mixtures into components parts to allow for identification by a spectroscopy technique it can be used in its own right to identify materials, based on comparing the equilibrium distribution of the explosive in the mobile and station phase compared to a known standard.

Infrared Spectroscopy (IR) and Mass Spectroscopy (MS) are two key spectroscopic techniques. If the explosive is a pure form IR is an important technique that is very quick, cheap, and easy to perform. It will quickly identify the number and types of chemical bonds within a covalent molecule. However if the explosive is ionic this technique will not be able to identify the explosive. In addition since most energetic materials are mixtures, the IR data will be very difficult to interpret because the data for each component will overlap.

Reference has already been made to the use of detectors based on mass spectrometry (MS). However, MS is also widely used analytical technique and as such can provide one of the most powerful methods for characterizing an unknown material. Mass spectrometric detectors are now used routinely in Gas Chromatography (GC) and Liquid Chromatography (LC) separations as they offer high sensitivity and an ability to provide compound identification.

17.2 DETECTION OF EXPLOSIVES

17.2.1 Explosive Trace Detection (ETD) - Vapour Detection

Vapour detectors rely on the fact that every substance has a characteristic vapour pressure, defined as the pressure exerted by the vapour of the substance when it is in equilibrium with its solid or liquid phase. Many organic compounds have high vapour pressures while inorganic salts such as ammonium nitrate have negligibly low vapour pressures. The vapour pressure of a substance increases with temperature and in general the smaller the molecule the higher the vapour pressure at any given temperature. Liquid explosives will have significant vapour pressures at ambient temperature and solid explosive less so.

Table 17-1 Vapour Pressure of Some Explosives (20 °C)

Compound	Vapour pressure (mm Hg)	Concentration of vapour (g cm^{-3})
NG	5.8×10^{-4}	7.7×10^{-9}
EGDN	4.2×10^{-2}	3.8×10^{-7}
HMX	9.5×10^{-16}	1.7×10^{-20}
RDX	2.1×10^{-7}	2.7×10^{-12}
PETN	1.8×10^{-6}	3.3×10^{-11}
TNT	2.5×10^{-6}	3.4×10^{-11}

A number of common explosives substances have high enough vapour pressures to generate a detectable concentration of vapour in air. Some typical figures are shown in **Table 17-1**. It can be seen that the nitrate esters nitroglycerine (NG) and ethyleneglycol dinitrate (EGDN) are likely to be most readily detected using a vapour detector and explosives containing RDX or PETN, often found in plastic explosives, not susceptible to vapour detection. TNT at first sight would seem to be in the same category as RDX and PETN; however, minor impurities such as dinitrotoluene (DNT) have a much higher vapour pressure than TNT and can be detected by this method. Apart from the vapour pressure of the explosive substance, the performance of the detector is also affected by the background against which the detector has to operate and by the packaging in which the explosive is concealed.

17.2.1.1 Animals

There are two types of olfactory sensors, natural and artificial. Dogs are commonly used to detect explosives, but the time and cost of training animals, the lack of quantitative information and their lack of flexibility means alternatives are being developed. Several different types of electronic noses are currently under development, but there needs to be an improvement in their specificity, reliability and portability before they will be suitable for fieldwork.

Dogs have a highly developed sense of smell and this has been exploited for the detection of explosives since World War II. Today the use of sniffer dogs to detect volatile explosive vapours is still widespread. They are fast, directional and able to be deployed in real time over large areas. Other animals have also been investigated for the detection of explosive vapour.

17.2.1.2 Electronic Noses

Artificial olfactory sensors ‘electronic noses’ usually consist of an array of chemical sensors that interact with an explosive vapour in different ways. Each sensor will give a different response depending upon the nature and concentration of the vapour present and combining this with a pattern recognition system will allow the identification of the explosive vapour. The chemical sensor can be electronic, piezoelectric or optical and could be either organic or inorganic.

17.2.1.3 Chemical

Detection techniques for energetic materials can be subdivided into a number of types. The simple type is that which involves a chemical reaction between the energetic material (or a component of it) and a prepared reagent. This may occur in solution, as in the case of a soluble solid energetic material, or in a detector tube in the case of an explosive vapour. Such detector tubes, which are packed with the prepared reagent, are commercially available.

There is a wide range of chemical reactions that are suitable for energetic materials detection. Most of these yield a coloured product and are known as colour or 'spot' tests when they are applied to small quantities of an energetic material in solution. For example di- and tri-nitroaromatic compounds develop characteristic red colours with 30 % v/v potassium hydroxide solution. This reaction and, numerous variations on it, is widely used for the detection of nitroaromatic high explosives such as TNT.

Nitrate esters and nitramines can also be detected using spot tests. One of the most frequently used employs the Griess reaction in which the nitrate ester or nitramine is first hydrolysed in alkaline solution to the nitrite ion (NO_2^-). This then forms a highly coloured azo compound in the presence of an aromatic amine and a suitable coupling reagent, as shown in Figure 17-1.

Another common spot test for nitrate esters and nitroaromatics uses diphenylamine. In this case, the reagent is a 1 % (v/v) solution of diphenylamine in sulphuric acid that reacts with nitrate esters and nitramines to give a deep blue colour. This reaction is also frequently used to develop component spots in the thin layer chromatography of high explosives.

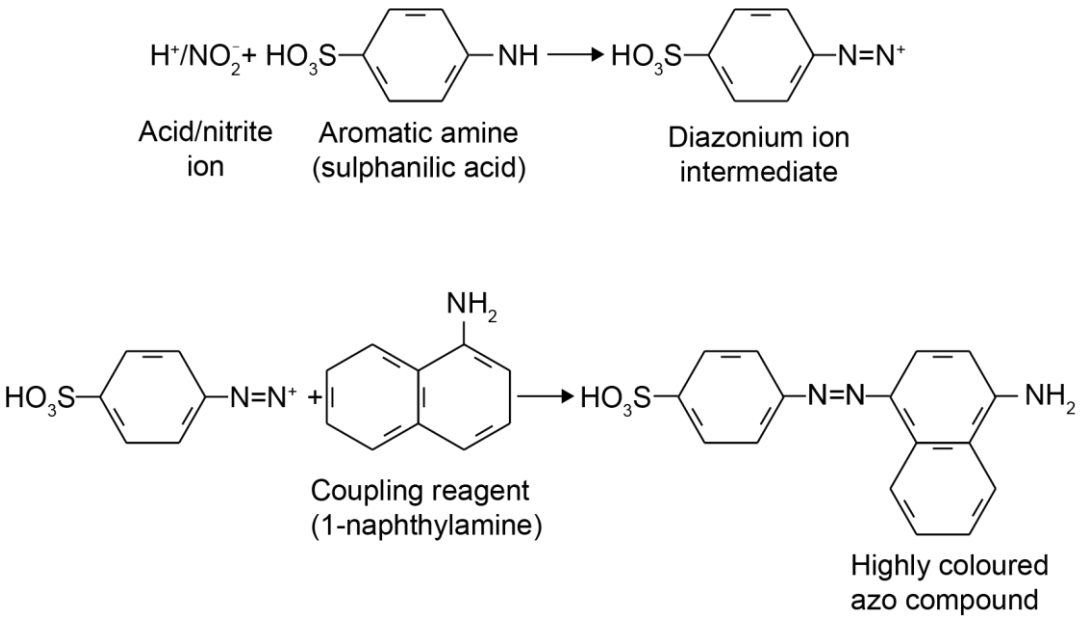


Figure 17-1 Reaction of nitrite ion to produce a highly coloured compound

Spot tests are particularly useful in identifying inorganic ions such as those found in pyrotechnics. For example, spot tests are available (Table 17-2) for most of the common anions such as nitrate (NO_3^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) and the common metal ions such as potassium (K^+) and sodium (Na^+).

Table 17-2 Selected Spot Tests for Some Ions Found in Energetic Materials

Ion	Reagent/Conditions	Ion indicated by
Na^+	Zinc uranyl acetate in acetic acid solution	Yellow precipitate
K^+	Sodium tetraphenylboron in water (2 %)	White precipitate
NO_3^-	Conc. sulphuric acid droplet on a ferrous sulphate crystal in a pool of test solution	Brown ring around crystal
ClO_3^-	Manganese (II) sulphate in strong phosphoric acid solution, warmed	Violet colouration

Vapour detection is normally carried out using a commercially available detector tube designed for a particular compound or class of compounds. The tube is used with the same manufacturer's sampling pump. A certain amount of air containing the vapour is thereby pulled across the reagent in the tube and a colour change occurs, the extent of which gives an indication of the vapour concentration.

An example of a chemical reaction that is used in vapour detector tubes is the hydrolysis of ethylene glycol dinitrate (EGDN), a common explosive ingredient with the reaction scheme shown in Figure 17-2.

$$(CH_2ONO_2)_2 + H_2SO_4 \rightarrow HNO_3$$

$$HNO_3 + \text{aromatic amine} \rightarrow \text{Yellow/orange reaction product}$$

Figure 17-2 Hydrolysis of EGDN and reaction to give coloured reaction product

The EGDN detector tube containing the aromatic amine can detect 0.25 ppm of the vapour through the observed colour change.

17.2.1.4 Electrochemical

Electrochemical sensors can be categorised into potentiometric (measurement of potential difference/voltage); amperometric (measurement of current) and conductimetric (measurement of conductivity) type devices according to the transduction approach adopted. These types of sensor are fast, inexpensive with high sensitivity and a viable option for miniaturisation. Electrochemical detection techniques can respond to substances that can undergo chemical oxidation or reduction (redox); the electrical output results from a flow in electrons or ions caused by the chemical reaction that takes place at the surface of the electrode. Due to this, the redox properties of nitroaromatic explosive substances ideally lend themselves to electrochemical detection. The detection of peroxide-based explosives by other techniques is more challenging due to the fact they do not fluoresce, have minimal UV absorption and a lack of nitro groups, all necessary parameters upon which traditional detection techniques are based. Electrochemical sensors in this context offer an opportunity to detect peroxide-based explosives that would otherwise prove problematic.

17.2.1.5 Immunochemical

Immunochemical sensors exploit characteristics of the antibody–antigen reaction in such a manner that produces a device that can be highly specific to its target molecule. This feature and the fact that it is possible to produce antibodies for a specific purpose make this an expanding field of research into explosives detection.

17.2.1.6 Luminescence

Luminescence-based sensors for detecting explosive compounds may be described as utilising either direct or indirect detection methods. Direct detection techniques utilises any fluorescence which the sample may emit itself or through inducement with a chemical reaction. Indirect detection involves the evidence of explosives being present through their effect on a fluorescent material such as, for example, via quenching where the fluorescence is reduced by the explosive.

17.2.1.7 Nanotechnology

Nanotechnology has become a rapidly expanding area of research over recent years as techniques and knowledge have developed. Materials often possess unique characteristics when in a nanoscale form as compared to bulk materials

and as such, the incorporation into existing techniques is an active area of research to enhance sensitivity and selectivity. For example, the benefits of using such materials as carbon nanotubes are that they display enhanced detection sensitivity compared to sensors incorporating other carbon platforms (possibly due to increased surface area), they have electrocatalytic effects, are mechanically strong and flexible and have excellent electrical and thermal conductivity. Nanoparticle systems have also been used such as metal nanoparticles, again they can lead to enhanced sensitivities especially in electrochemical systems due to increased surface areas, catalytic effects and improving electrical conductivity. Metal nanoparticles can also have beneficial effects in optical sensors due to increased surface areas and a number of optical effects such as surface enhanced Raman spectroscopy.

17.2.1.8 Molecularly imprinted polymers

Molecularly imprinted polymers (MIPs) are generated through both covalent and non-covalent interactions of functional monomers with the molecule of interest or its analogues, acting as a template. MIPs allow the formation of molecules with recognition sites specific for a target analyte producing a substance specific coating that may then be incorporated onto a sensing platform. MIPs are stable and robust which accounts for the interest in researching possible uses for them as sensing materials.

17.2.1.9 Quartz crystal microbalance

The quartz crystal microbalance utilises the resonance frequency change due to changes in mass upon the crystal surface as a means to detect the presence of a substance of interest. This technique is further enhanced through coating the surface with various compounds that help provide specificity to the system.

17.2.1.10 Electron capture detectors

One of the most widely used instrumental vapour detectors is the electron capture detector. In this device electrons are produced from a radioactive β-emitter (usually nickel-63), which forms the cathode of an ionization chamber. An inert carrier gas (nitrogen or argon) is contained within the chamber and the electrons collide with the carrier gas molecules and thereby lose much of their energy, becoming in the process 'thermal' electrons. These thermal electrons then migrate to the anode under a fixed voltage, thus producing a constant (baseline) current between the electrodes. When an electron-capturing gas or vapour is introduced into the ionisation chamber it causes a decrease in the baseline current due to the interaction of the thermal electrons with the electron-capturing molecules. The extent of the decrease in current is an indication of the concentration of the electron-capturing molecules present.

An electron capture detector is very sensitive towards compounds with a high affinity for electrons. These include compounds containing highly electronegative groups such as -F and $-NO_2$. Although electron capture detectors are, therefore, by no means specific for explosives, they respond well to explosive compounds that contain the nitro group.

Electron capture detectors have a fast response and a limiting sensitivity of about 1 x 10^{-3} g for an electron- capturing compound. Their major drawback as detectors for explosive vapours is their lack of specificity. A number of methods have been used to improve this. The most successful is to install a separating column upstream of the detector so that the components in a mixture of vapours are separated before they reach the detector. The detector then becomes part of an analytical device incorporating gas chromatography and electron capture detection. This technique, which is the basis of a number of commercial devices, is discussed more fully in a later section.

17.2.1.11 Ion mobility spectrometers (IMS)

Another type of instrumental vapour detector for explosives is the ion mobility detector. In this device air is drawn through the detector continuously by means of a small fan. Electrons are produced inside the detector chamber by a high voltage (typically 3 kV) discharge. Some of these electrons are captured by molecules of the explosive forming negative ions which, in turn, pick up water molecules from the air to produce large 'ion clusters'. The ion-laden air is then passed through an ion mobility electrode grid that is optimised to allow only the passage of ions in a certain mass range corresponding to explosive compounds. A further electrode then collects the ions allowed through the grid and the resulting current is processed and fed to a signal device.

17.2.1.12 Mass spectrometry (MS)

Mass spectrometry (MS) has been extensively used as the basis of detectors for explosive vapours. In the majority of such devices the sample molecules are bombarded by electrons that are emitted from a hot rhenium or tungsten filament and accelerated to an energy of 70 eV. The electrons cause fragmentation of the sample molecules and generate positive ions from the fragments. The ion fragments are then filtered according to their mass/charge ratio while being accelerated through a magnetic field. They are detected using an electron multiplier and the fragmentation pattern (mass spectrum) is characteristic of the original sample molecule. Complex mixtures of vapours may not be readily analysed using mass spectrometry because of overlapping spectra, but if separation is carried out beforehand, for example using a gas chromatography (GC) column, then the technique (GC-MS) becomes a useful analytical tool.

17.2.2 Explosive Detection Systems (Bulk Detection)

Vapour detectors have an obvious disadvantage in that they are suitable only for those components in an energetic material, which have an appreciable vapour pressure. Bulk detectors are therefore necessary, particularly in the context of the growing demand for the detection of all types of concealed explosives.

17.2.3 Conventional Transmission X-ray

X-ray devices have been used for the bulk detection of explosives for many years at airport baggage checks. Conventional X-ray screen systems measure the attenuated X-ray energy after it has passed through a scanned object. A standard airport hand-baggage scanner has a fan shaped or scanning X-ray beam whose absorption is measured by a line of detectors, and a high quality image is derived from the degree of absorption is produced. Simple X-ray techniques, however, cannot easily distinguish between a block of plastic explosive and, for example, a paperback book of similar size. Effective bulk detectors therefore require a more discriminating method for distinguishing explosives.

17.2.4 Dual-energy X-ray

At higher energy levels (over 100 kV) the energy absorbed by an object depends primarily on the density of the material. The higher the density, the more energy is absorbed by the object and the darker the image. Metals would appear very dark in the transmission image, however an explosive behind a denser material remains difficult to detect. At lower energies (approximately 80 kV) the absorption depends mainly on the effective atomic number as well as the thickness of the material.

A system that uses two X-ray energy levels is called a dual energy system. Heavy metals will appear dark in both views, but areas of light elements are darker in the lower energy view. Comparing both views means light elements such as carbon, nitrogen and oxygen can be detected. Using a dual energy method can give density and thickness information about the sample; the challenge is that the actual density of objects is poorly known for real luggage items and theory only generates an estimate of atomic number.

Dual energy X-ray systems are now widely used in airports and organic materials (low z) can theoretically be distinguished from inorganic materials and metals (high z), where z denotes the atomic number of an atom. However, X-ray intensities are not only related to its material composition but also its position, orientation and thickness. So unless they are combined with volume imaging (e.g. CT or stereoscopic imaging), they only provided an indication of the atomic number of the object. Even when used with volume imaging, the sensitivity and specificity are low and only allows materials to be characterized broadly as inorganic or organic.

17.2.5 Scatter Imaging

Image data from an object that is collected from scattered X-ray energy back towards the X-ray source (back scatter) or passed forward through the object (forward scatter) has been proposed as an effect way of luggage inspection. Dual energy X-ray systems are able to discern between materials based on the atomic numbers of atoms that make up the material (z-numbers) but have difficulty discerning density. A scattered image will give information about the z-

numbers and the density of the object, meaning plastic explosives can now be distinguished from common plastics and clothing.

The backscatter signal depends on the competition between photoelectric absorption and Compton scattering. The photoelectric cross-section increases with the atomic number of the object, while the Compton cross-section is relatively independent of the atomic number. So the backscattering signal favours low atomic elements of high density, such as plastic explosives and provides a direct measurement of the density of elements with low atomic number.

Image scatter can be characterised as coherent (elastic) or incoherent (inelastic or Compton) scattering. Forward scatter in the region of 3-10° contains predominately coherently scattered photons and at large angles the scattered beam is dominated by incoherent scattered photons. Measurement of both of these is useful. Coherent scatter leads to diffraction effects whose intensity gives information on atomic number and physical density. Incoherent scatter intensity is dependent on density and hence both of these can be combined to isolate atomic number information.

This technology has been used successfully on cars and trucks (cargo) where explosives can be present in large quantities, but airport luggage has presented a more difficult problem due to the smaller quantities involved. A major problem is the position of the object relative to the X-ray source and the detector has a strong influence on the scattered signal and this can cause errors in interpreting the data.

X-ray technology continues to be the preferred method of explosive screening because it is safe to humans and luggage, cheap to buy and operate, and is well understood. However it is by no means the best option and suffers from relatively high false alarm rates.

17.2.6 Terahertz

Terahertz radiation also known as submillimeter radiation and T-waves lies in the far infrared region from 0.1 to 10 THz. In this range waves can penetrate through many non-polar dielectric materials, such as wood or leather, and the low photon energies are at a level one million times less than that of X-ray photons. Most explosives and explosive related compounds have spectral fingerprints within this range and, as many apparatus operate within the range 0.1–2.0 THz, this highlights THz radiation as a prospective sensor and imaging agent for the detection of concealed explosive substances.

Terahertz radiation can penetrate fabrics and plastics, so it can be used in surveillance, such as security screening, to uncover concealed weapons on a person, remotely. This is of particular interest because many materials of interest have unique spectral "fingerprints" in the terahertz range. This offers the possibility to combine spectral identification with imaging.

17.3 CHEMICAL ANALYSIS

The chemical analysis of energetic materials seeks to provide more information than simple detection and, unlike detection, generally requires some sample preparation. The principal aims of analysis are to identify the components of an energetic material (qualitative analysis) and to establish how much of each is present (quantitative analysis).

While traditional "wet" chemical methods of analysis are still useful for some energetic materials the vast majority of analyses are these days carried out using instrumental techniques. One area where chemical methods remain appropriate is the analysis of simple inorganic materials in, for example, pyrotechnics. However new instrumental techniques such as ion chromatography are now beginning to replace the traditional chemical methods for these determinations.

The two most widely used types of instrumental technique employed in the analysis of energetic materials are spectroscopy and chromatography. They complement one another to a large extent since spectroscopic techniques are most useful for qualitative analysis while chromatography is used mainly for quantitative analysis. The two techniques are often linked to provide a particularly powerful analytical device.

17.3.1 Spectroscopy

Spectroscopic techniques of analysis depend upon the absorption of electromagnetic radiation by matter leading to excitation of energy levels (nuclear, electronic, vibrational, etc.) within atoms and molecules. A technique is characterised by the region of the electromagnetic spectrum used in its application since this determines the nature of the excitation.

In a typical investigation the prepared sample is irradiated by scanning through consecutive wavelengths over the chosen region of the electromagnetic spectrum. Energy is absorbed at certain wavelengths and this gives rise to a characteristic absorption spectrum. The spectrum may help to identify an unknown compound or, less frequently, it may be used, by calibration of a suitable absorption band, for quantitative analysis.

17.3.1.1 Infrared (IR) and RAMAN spectroscopy

Infrared spectroscopy is one of the most widely used spectroscopic techniques in energetic materials analysis. When a molecule absorbs energy in the infrared region of the electromagnetic spectrum excitation of its vibrational energy levels occurs. Particular groups of atoms can therefore be identified from their characteristic absorption frequencies. For example the infrared spectrum of TNT contains various absorption bands at wavelengths (or frequencies) characteristic of the nitro ($-NO_2$) group. Similar bands are found in the infrared spectra of all molecules containing this group but the precise

position depends upon the molecular environment of the NO_2 group. The overall infrared spectrum of a molecule provides a "fingerprint" of that molecule.

Infrared spectroscopy is particularly useful for the identification of inorganic oxidisers in pyrotechnics. These are relatively simple molecules (e.g. KNO_3, $NaClO_3$) and have uncomplicated and characteristic infrared spectra.

Infrared spectrometers are relatively inexpensive items of equipment, the basic components being an infrared source, a sample compartment and a detector for sensing the infrared radiation not absorbed by the sample. Spectra are easy to obtain and the technique is widely applicable across the range of energetic materials. Fourier transform infrared (FTIR) spectrometers, in which the whole of the infrared spectrum impinges on the sample at the same time rather than wavelength-by-wavelength, are able to generate spectra in fractions of a second.

Modern IR spectrometers are the standard way of obtaining the reflected spectra of energetic materials (or separated components thereof). Either discrete spectra of specific sample sites or mapping to provide multiple spectra from an even larger area, offering data about the spatial location of the components in a multicomponent sample as well as the component spectra.

Mapping data obtained from attenuated total reflectance (ATR) objectives also can provide similar data as acquired using transmission or reflection methods, but without the sample preparation required for transmission or reflection experiments, eliminating the requirement to grind the sample to a fine powder and press in a KBr disc or mix with a mulling agent (usually Nujol, a viscous hydrocarbon mixture).

Raman spectroscopy, which like IR spectroscopy depends upon the excitation of vibrational modes in a molecule, is of growing importance in explosives analysis. The technique is useful because it is non-destructive, potentially very sensitive and can identify molecules *in situ*, without any sample preparation or pre-treatment.

Raman spectroscopy involves the scattering of light by molecules. Most light that hits a sample is transmitted or reflected but some is scattered elastically (Rayleigh scattering, where no net energy is absorbed or emitted), and an even smaller amount is absorbed and then scattered inelastically (with energy being absorbed or emitted). This inelastic scattering is Raman scattering. Only about 1 photon in 10^9 is Raman scattered and so an intense light source (e.g. a laser) and complicated optics are required to study the effect.

Although they both relate to changes within vibrational energy levels, IR and Raman methods do not produce identical vibrational spectra. The selection rule for Raman activity is that the polarizability of the molecule must change (compare IR which requires a change in dipole moment). This means that IR produces stronger bands from vibrations of polar bonds while for Raman the stronger bands arise from non-polar bonds. Raman spectroscopy has the advantage over IR in that specialized sample preparation is not required. It can

be used to investigate samples in situ (e.g. drugs still in a plastic bag) and for process monitoring by the use of optical fibres.

17.3.1.2 Ultraviolet-Visible (UV-Vis) spectroscopy

Excitation of electrons within molecules is caused by the absorption of ultraviolet or visible radiation by matter. The absorption bands in the spectrum of a compound are, as in infrared spectroscopy, characteristic of particular groups of atoms. However the technique of UV-Vis. spectroscopy does not distinguish clearly between molecules and groups of atoms and it is generally not as useful as infrared spectroscopy for the qualitative analysis of energetic materials.

UV-Vis absorption bands are very intense and therefore the technique is useful for quantitative work and for the trace analysis of pure compounds or the separated components of a mixture. Spectra are normally recorded in solution in a non-absorbing solvent. UV-Vis. spectrometers are commonly used as detection devices for high performance liquid chromatography (HPLC).

17.3.1.3 Nuclear Magnetic Resonance (NMR) spectroscopy

In the technique of NMR spectroscopy the sample is dissolved in a suitable solvent and held in a glass tube between the poles of a powerful magnet. It is then irradiated with energy in the radio frequency region of the electromagnetic spectrum. Depending upon the energy (or frequency) of the impinging radiation, transitions occur between spin states of certain nuclei in the sample (those of the element to which the spectrometer has been "tuned") at frequencies that are characteristic of the chemical environment of the nuclei.

Thus if a particular nucleus, say C-13, is present in a compound in six different environments then, in general, the C-13 NMR spectrum of that compound will contain six absorption peaks. In practice the spectrum may be more complex than this as a result of nuclear - nuclear interactions.

Nuclei that are amenable to study by NMR spectroscopy include H-1, C-13, F-19 and P-31. However it is a technique that requires expensive instrumentation and a skilled and knowledgeable operator. It is used mainly for determining the molecular structure of new compounds but it is also useful for the identification of unknown organic components in, for example, an energetic material. Because of its great expense NMR is not normally used for the routine analysis of explosives.

17.3.1.4 Laser induced breakdown spectroscopy (LIBS)

Laser-induced breakdown spectroscopy (LIBS) uses a high intensity laser to vaporise a sample creating a plasma plume. The subsequently emitted light from this plasma enables the characterisation of the sample. LIBS, as a detection technique, holds many advantages, especially in the field of explosives detection, such as: no need for sample preparation, the ability for real time results, apparatus that may be ruggedised and miniaturised for field

work, a sensitive technique requiring only a small sample and the capacity for stand-off detection approach.

17.3.1.5 X-ray fluorescence (XRF) spectroscopy

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis. In principle, the lightest element that can be analysed is beryllium (Z = 4), but due to instrumental limitations and low X-ray yields for the light elements, it is often difficult to quantify elements lighter than sodium (Z = 11), unless background corrections and very comprehensive inter-element corrections are made. The technique is usually combined with optical microscopy enabling the mapping of elements on or just below the surface of the sample.

17.3.1.6 Mass spectrometry

Reference has already been made to the use of detectors based on mass spectrometry (MS). However, MS is also widely used analytical technique and as such can provide one of the most powerful methods for characterizing an unknown material. Mass spectrometric detectors are now used routinely in GC and HPLC separations as they offer high sensitivity and an ability to provide compound identification.

In a mass spectrometer the molecules of the sample, which may be a directly-injected pure compound or a separated component from a GC or HPLC column, are firstly ionized, usually by a source of energetic particles. This normally leads to the formation of a ‘molecular ion’ from which the molar mass of the compound (M) may be determined as shown in Equation (17-1).

$$M + \text{energy} \rightarrow M^{+\cdot} + e^{-} \qquad \textbf{(17-1)}$$

In some modes of MS the high energies used also cause bond cleavage and hence fragmentation of the molecular ion ($M^{+\cdot}$). These fragment ions, together with the molecular ion, are then separated in a magnetic field by virtue of their different mass/charge ratio with most ions being singly charged. It is this pattern of separated ions, which constitutes the mass spectrum and which, through a library search or by interpretation, can help to identify an unknown compound.

High-energy electrons are a common means of bringing about sample ionization in mass spectrometers. This technique is known as electron (impact) ionisation (EI) mass spectrometry. At the energies normally employed it leads to considerable fragmentation and hence much structural information but does not always yield a molecular ion. This is particularly the case with compounds of low thermal stability such as explosives. Chemical ionisation (CI) provides an alternative means of generating ions from gas phase species. In this case ionized molecules of a simple gas e.g. methane, ammonia are made to react

with the sample to cause ionization by proton transfer. CI is a ‘soft’ ionization method and gives a clearly defined molecular ion or pseudo-molecular ion such as MH^+ but provides less structural information than EI.

Ions can also be generated from species in solution. These might be compounds dissolved in the mobile phase of an HPLC system. In Electrospray Ionisation (ESI) the solvent is evaporated from charged droplets to produce molecular ions that are then passed into the mass analyser. ESI is a ‘soft’ ionisation technique and produces mainly molecular ions.

In recent years there have been major developments in desorption ionisation (DI) methods, where ions are formed at surfaces. Two important sampling and ionisation methods have emerged, Desorption Electrospray Ionisation (DESI) and Direct Analysis in Real Time (DART). In DESI the ions are formed by directing a solvent spray at trace species on a surface while in DART a jet of ionised gas is used. Both techniques are ‘soft ‘ionisation methods.

17.3.2 Chromatography

Chromatography encompasses a range of related analytical techniques, each of which involves the separation of a mixture of components by exploiting differences in the equilibrium distribution of the components between a mobile and a stationary phase. The International Union of Pure and Applied Chemistry (IUPAC) have defined chromatography as: “A physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (the stationary phase) while the other (the mobile phase) moves in a definite direction. The stationary phase may be a solid, or a liquid supported on a solid, or a gel. The stationary phase may be packed in a column, spread as a layer, or distributed as a film, etc.; in these definitions ‘chromatographic bed’ is used as a general term to denote any of the different forms in which the stationary phase may be used. The mobile phase may be gaseous or liquid”.

The word chromatography (‘colour writing’) was coined by the Russian scientist Mikhail Tsvet (1906) and arises from the original use of the technique to separate coloured pigments (Greek chroma = colour). From these beginnings it developed slowly until the work of Synge and Martin (1941) laid the foundations of modern gas chromatography. Modern (high pressure) liquid chromatography was a later development and is generally reckoned to start with the publication of work by Huber and Hulsman (1967). Today chromatographic techniques play a major part in the chemical analysis of a wide range of materials, including pharmaceuticals, biochemicals, foods, petroleum products, dye-stuffs, environmental pollutants, pesticides, fertilizers, explosives and various other materials of forensic interest.

The essence of modern chromatography is very simple. A sample of the mixture to be analysed is introduced into a stream of mobile phase (a gas or a liquid) that flows over a stationary phase (a solid or a liquid coated on to a solid, usually contained within a tube or “column”). The sample molecules are

distributed between the phases so that they each spend some time in the mobile phase and some time in the stationary phase. This is illustrated in Figure 17-3. All molecules are in dynamic equilibrium between the two phases. Certain molecules (those chemically dissimilar to the stationary phase molecules) spend relatively less time in the stationary phase and are therefore swept forward rapidly by the mobile phase. Others (those more chemically similar to the stationary phase molecules) spend relatively more time in the stationary phase and move forward more slowly.

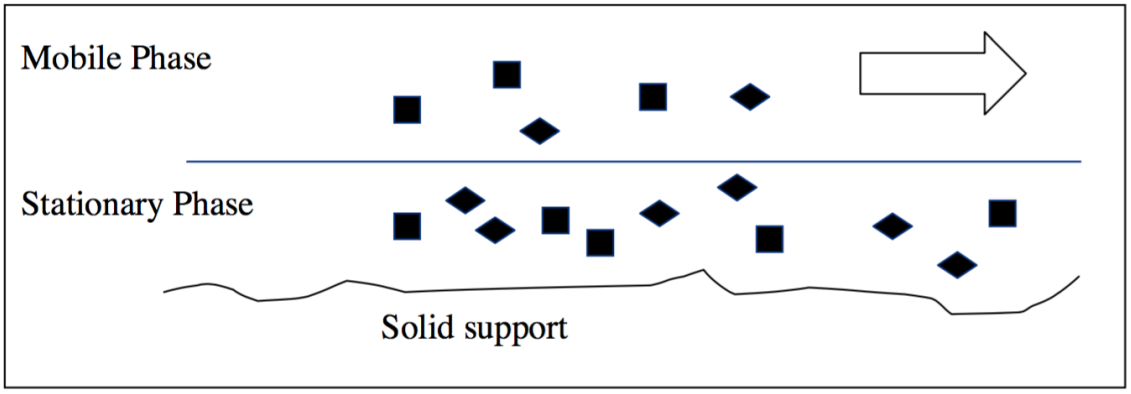


Figure 17-3. Distribution of different molecules between phases in chromatography

After the successful separation of the various components of a mixture into bands on the chromatographic column each band, as it emerges, is detected by a suitable device that responds to some property of the molecules present (e.g. ultraviolet absorption, thermal conductivity, refractive index, ion current following ionization etc.). The responses are then fed into a recorder to produce a series of peaks called a chromatogram (Figure 17-4).

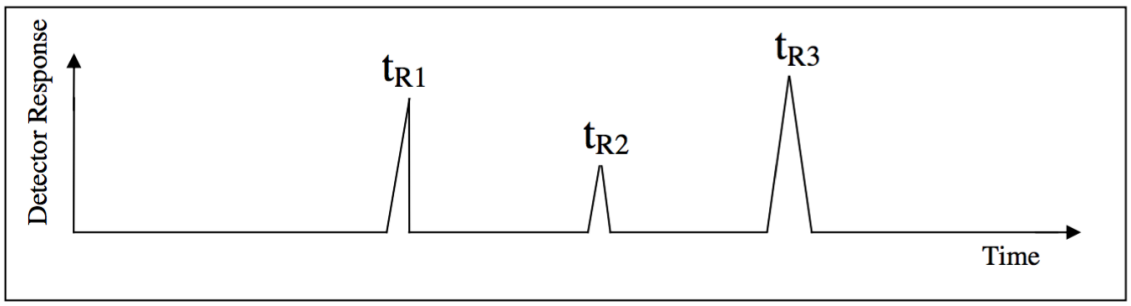


Figure 17-4. A simple chromatogram

Different kinds of molecule present in the mixture are therefore separated into bands as a result of differences in their distribution between the two phases. The time taken for a particular band to progress through the column (from injection to detection) is called the retention time, t_R. It is dependent on a large number of factors such as column temperature, mobile phase flow-rate, stationary phase composition and column length. Retention time is not in itself a reliable means of identifying separated components although a number of indices have been devised for use with some types of compound.

The basic components of a modern column chromatograph are a source of mobile phase (liquid or gas), a sample injection device, the column (usually contained within a temperature controlled oven), a detector and a recorder plus data handling facilities within a PC (or data station). An HPLC also incorporates a pump between the mobile phase reservoir and the injector to pump the mobile phase through the system.

The most general classification of chromatographic techniques is in terms of the mobile phase so the two major divisions are gas chromatography and liquid chromatography. For most separations gas chromatography is used with helium or nitrogen as the mobile phase (carrier) gas in conjunction with a liquid stationary phase coated (or chemically bonded) on to a suitable solid support. This particular subdivision of gas chromatography depends upon partition as the distribution mechanism and is sometimes called gas-liquid chromatography.

Other distribution mechanisms used in gas and liquid chromatography are illustrated in Figure 17-5. Adsorption is used in gas chromatography for the separation of permanent gases.

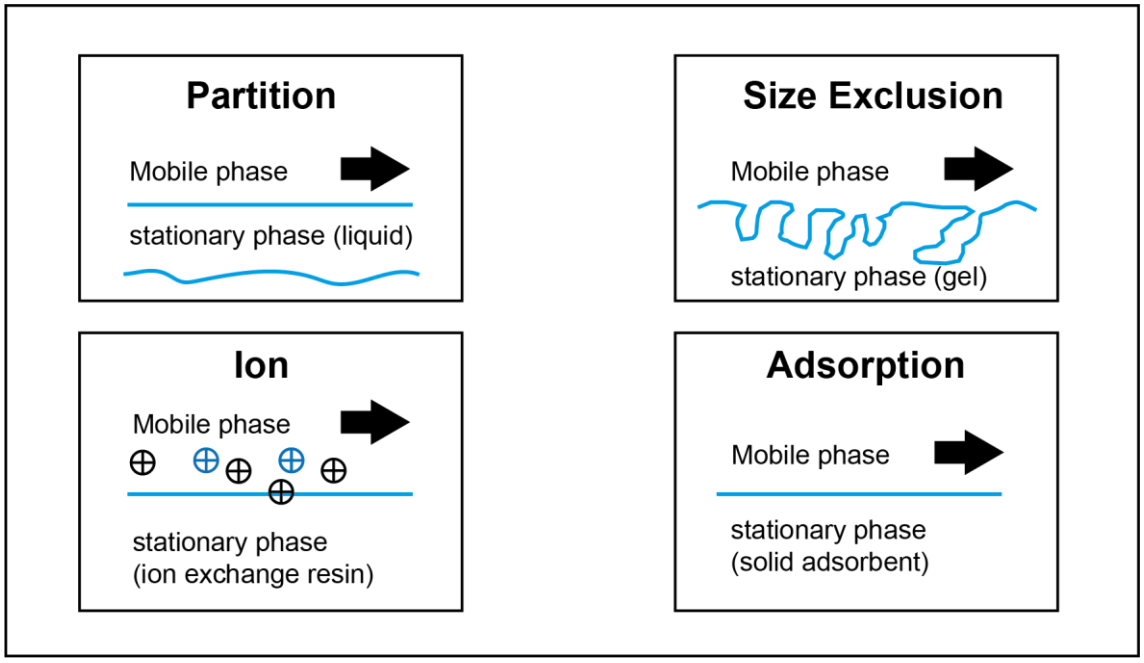


Figure 17-5. Chromatography distribution mechanisms

Liquid chromatography can be operated in a number of formats. These include thin layer chromatography (TLC) in which the stationary phase is alumina or silica coated onto a glass plate, conventional (gravity flow) column chromatography in which the liquid mobile phase passes down a vertical glass column packed with silica or alumina and high performance liquid chromatography (HPLC) in which the mobile phase is pumped under high pressure through a stainless steel column packed with stationary phase. HPLC is the most widely used of the liquid chromatography formats but TLC is often employed for the preliminary qualitative analysis of simple mixtures. TLC and conventional column chromatography both rely on adsorption as the distribution

mechanism but in the case of HPLC partition is more important. For the separation of typical organic mixtures two extreme modes are possible. When the stationary phase coating is polar (e.g. an alcohol) and the mobile phase is a non-polar liquid (e.g. hexane) it is called normal phase HPLC. The reverse situation, when the stationary phase coating is non-polar (e.g. a hydrocarbon) and the mobile phase is polar (e.g. methanol and water), is called reverse phase HPLC. The latter mode is much more widely used. Two important specialist HPLC techniques are Ion Chromatography (IC) in which ion-exchange resins are used for the separation of mixtures of cations or anions and Size Exclusion Chromatography (SEC) that uses the pores in a gel to separate polymer molecules according to their size.

Chromatography is particularly useful for the quantitative analysis of organic components in an energetic material of known composition. Such analyses may be carried out by an external or internal standard method. In the latter case the chromatography detector response of the component of interest is calibrated against that of an internal standard, which is then added to the energetic material sample solution at a known concentration. A plot of simple detector response against time is called a chromatogram.

It is not possible to use chromatography to carry out qualitative analysis on an unknown compound using the simple response detectors normally employed. However using a device such as a mass spectrometer or a Fourier Transform Infrared (FTIR) spectrometer as a detector for GC turns the technique into a very powerful analytical tool, which can be used for both qualitative and quantitative work.

17.3.2.1 Thin layer chromatography

Thin layer chromatography (TLC) is a simple form of liquid chromatography in which the stationary phase is coated on to a glass plate, which is then held vertically in a beaker containing a small amount of mobile phase, enough to cover the bottom few inches of the plate. A spot of the sample solution is then placed on the plate just above the liquid level. As the liquid moves up the stationary phase on the plate the components in the sample become separated. The separated spots are "developed" using a chemical spray that produces a colour by reacting with each component or by irradiating with UV light.

TLC is simple to carry out and requires no complex instrumentation. It is particularly suitable for the preliminary qualitative analysis of explosive mixtures (e.g. RDX/TNT) and for distinguishing between single-base and double-base propellants (see 12.2.2).

17.3.2.2 Gas chromatography (GC)

GC is the chromatographic method used for the analysis of gases and volatile compounds. The hardware is simpler than for HPLC and it is generally easier to operate successfully. However, since it is often necessary to use GC column temperatures in excess of 250 °C in order to get the analytes (the compounds that are being analysed) into the vapour phase and achieve effective

separation, its drawbacks are obvious. In general GC is suitable only for samples that are volatile below about 350 °C and are not thermally degraded.

Following the separation of a mixture of organic compounds by GC the compounds, when they emerge from the column, are detected either by a simple 'response' detector, which responds to some property of the compound but is unable to identify it or by a 'smart' detector, which is usually able to identify the compound. The most widely used response detector is the flame ionisation detector (FID), which responds to all molecules containing C-H bonds and is fairly sensitive. The response arises from the generation of an ion current when molecules from the compound being detected are passed into a hydrogen/air flame and break down to give ions such as CHO^+. A modified form of the FID called the alkali flame ionisation detector (AFID) is particularly sensitive to nitrogen or phosphorus compounds. It can be "tuned" to either type and can detect them in the presence of non-N or non-P containing compounds. The AFID is often called a Nitrogen Phosphorous detector (NPD).

Another specific GC detector is the Thermal Energy Analyser (TEA). This responds to compounds, which on pyrolysis, release nitric oxide (NO) or a closely related species such as NO_2, which can be readily converted into NO. Detection is by means of the chemiluminescence produced by the reaction of NO with ozone (O_3). Since NO or NO_2 are products of the pyrolysis of many energetic materials the potential usefulness of the TEA can be appreciated. It offers sensitivity similar to that of an ECD but has much greater selectivity for particular types of compound. TEAs are considerably more expensive than other detectors and are not at present (2017) widely used.

Other response detectors used in GC include the thermal conductivity detector (TCD) which is used mainly for permanent gases and is considerably less sensitive than an FID, and the electron capture detector (ECD) which is very sensitive but responds only to molecules containing the most electronegative groups (e.g. –F, $-NO_2$). However, it is becoming easier and more common to interface spectrometers to gas chromatographs as 'smart' detectors, leading to techniques such as GC-MS and GC-FTIR. The advantage of these is that the separated components can then be positively identified in most cases rather than simply detected. Response detectors such as the FID, TCD and ECD are therefore becoming less widely used since a mass spectrometer can do everything and more that a response detector can do. Although a mass spectrometer detector is more expensive than a simple response detector the greater power of the MS generally outweighs the extra expense.

In recent times the separation of organic vapours is carried out using mainly wall coated open tubular (WCOT) or 'capillary' columns. These are very narrow bore columns made of fused silica in which the stationary phase is chemically bonded onto the inside wall of the column. Porous layer open tubular (PLOT) columns contain adsorbent particles on the column wall and are suitable for the separation of permanent gases. Injection on to such columns, with their very low capacities, is normally carried out via a so called 'split-splitless' injector

where much of the injected liquid is diverted to waste and only a small proportion enters the column.

The principal disadvantage of GC in relation to energetic materials analysis is the fact that, in order to shorten separation times, it is necessary to heat the column at a constant temperature ("isothermal") or at a steadily increasing temperature ("temperature programming"). This clearly presents problems for the separation of thermally labile compounds such as molecular explosives, which decompose below 250 °C, a typical maximum column temperature. Most GC injector systems also involve raising the temperature of the injected sample to about 250 °C and this further limits the usefulness of GC for explosives analysis. However such materials can often be successfully analysed by GC using short open-tubular columns and cold on-column injection devices. It is nevertheless more common to use HPLC for separations of explosive mixtures.

GC, which is generally more reliable and easier to operate than HPLC is particularly useful for the quantitative analysis of the volatile organic components in a nitrocellulose (NC) based propellant, such as the stabiliser, where an FID and a flash vaporising injector are perfectly adequate.

17.3.2.3 High performance liquid chromatography

The most widely used form of HPLC for the separation of organic materials is reverse-phase HPLC. In this mode the liquid stationary phase is a non-polar material (commonly octadecyl silane, containing $–C_{18}H_{37}$ groups) and is chemically bonded onto tiny particles (3-10 µm diameter) of a silica support, which are then packed into a stainless steel column. The mobile phase used with a typical reverse-phase column is a polar solvent mixture such as water/methanol or water/acetonitrile flowing at about 1-2 $cm^3\ min^{-1}$. In order to speed up separations the mobile phase composition can be changed during a run. This is termed gradient elution and may be seen as analogous to temperature programming in GC. In isocratic elution the composition of the mobile phase remains fixed throughout the run. Since reverse-phase HPLC is carried out at, or just above, ambient temperatures in order to improve temperature control of the column it is suitable for the separation of thermally sensitive and non-volatile compounds that cannot be analysed by GC. Injection in HPLC is carried out using a loop injector, the sample initially being held in the loop (10 – 100 µl) and then flushed on to the column by diverting the mobile phase through the loop.

The most common response detectors used in reverse phase HPLC systems are UV detectors, which depend upon the ability of the detected molecules to absorb ultraviolet radiation, often at a fixed wavelength of 254 nm. Other detectors have been used, but the presence of the liquid mobile phase always create problems and there is no sensitive HPLC response detector as effective as the FID in GC. Variable wavelength UV detectors are capable of being operated at wavelengths as low as 190 nm where weakly absorbing molecules are more likely to be detected, but they are then particularly susceptible to interference from strongly absorbing impurities in the mobile phase solvents. As

in GC there is an increase in the use of MS detectors. These are much more effective than UV detectors in providing a positive identification for a compound as UV spectra are considerably less characteristic than mass spectra. It is less straightforward to interface an MS to an HPLC than to a GC but the efficiency of interfaces such as electrospray ionization is increasing and LC-MS is now a routine technique.

17.3.2.4 Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) is a type of HPLC used for the separation of polymers. Here the stationary phase is a gel that contains pores of various sizes through which the polymer molecules permeate as they are carried by the mobile phase, hence the former name of gel permeation chromatography. The different sized molecules are retained to different extents and become separated. SEC is used in energetic materials research principally for separating nitrocellulose (NC) molecules covering a range of molecular weights. A molecular weight distribution can then be obtained for an NC sample. A UV detector is not suitable for SEC and instead a refractive index detector is used which responds to differences in refractive index between pure mobile phase and the mobile phase containing a sample.

17.3.2.5 Ion chromatography (IC)

Another type of HPLC used in the energetic materials field is ion chromatography (IC). In this technique the stationary phase within the chromatography separating column is an ion-exchange resin that has a different affinity for each anion, or cation, in the sample. In the case of anion separations the mobile phase is an aqueous alkali, most commonly a mixture of carbonate and bicarbonate, while for cation separations dilute mineral acids can be used.

IC normally makes use of conductometric detection techniques but in order to detect the separated ions in a sample it is necessary to ensure that the background conductivity of the mobile phase as it passes through the detector is low, otherwise that of the sample will be swamped. In most IC separations this is achieved by fitting a so-called "suppressor column" between the separating column and the detector. This contains an ion-exchange resin, which interacts with the ions in the mobile phase. For anion separations the reaction is typically that shown in Equation (17-2).

$$\text{Resin-H}^+ + \text{M}^+ + \text{HCO}_3^- \rightarrow \text{Resin-M}^+ + \text{H}_2\text{CO}_3 \qquad \textbf{(17-2)}$$

The background conductivity due to the bicarbonate (M^+ is a metal counter-ion) is thereby reduced to a level at which the sample ions may be detected.

Ion Chromatography is particularly useful for the determination of inorganic ions in pyrotechnics and home-made explosives containing metal nitrates, chlorates or other metal/oxidiser salts and has replaced many of the "wet" chemical methods that have traditionally been used for the analysis of these materials. IC offers greater sensitivity and faster sample throughput.

17.3.3 Thermal Methods

When an energetic material is heated slowly at a constant rate of temperature increase it invariably undergoes a number of detectable changes before it decomposes or ignites. The study of these changes is the basis of a range of analysis techniques known as thermal methods, which can help to identify and characterise energetic materials.

Changes in weight, which occur when a material is heated, are studied by thermogravimetric analysis (TGA). The weight changes are measured on a few milligrams of material and are compared to an inert reference, usually alumina, which is heated at exactly the same rate. The weight changes may be due, for example, to a loss of water of crystallisation or to the breakdown and gasification of a ligand attached to a metal ion.

Changes that result in the release (exotherm) or absorption (endotherm) of heat at a particular temperature, e.g. melting, phase change, decomposition, etc., are recorded in differential thermal analysis (DTA) as shown in Figure 17-6. The melting point of TNT can be seen at 81 °C, that RDX has an endotherm on melting at 204 °C immediately before decomposing exothermically. HMX has a phase change endotherm around 200 °C and melts at 276 °C immediately before decomposing exothermically. As in TGA, the sample is compared to an inert reference. The technique is particularly useful for the study of pyrotechnic compositions since the melting points and crystalline phase changes for many of the ionic oxidisers are very characteristic.

In differential scanning calorimetry (DSC) the sample and reference are maintained at the same temperature as the two are separately heated. The difference in required power between the two heaters is recorded as a function of temperature and this gives a quantitative measure of changes occurring in the sample.

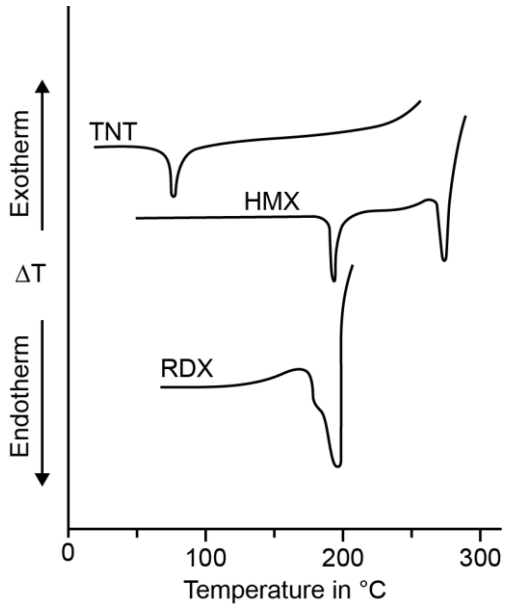


Figure 17-6 Differential thermal analysis of HMX, RDX and TNT

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CHAPTER 18
TOXICITY OF EXPLOSIVES

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18 TOXICITY OF EXPLOSIVES

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18.1 AWARENESS SUMMARY

18.1.1 Introduction

Propellants, high explosives and pyrotechnics are chemicals and as such will exhibit toxic properties, that is, the ability to poison people. Those who use, manage or even more importantly test ammunition must be aware of the potential toxic hazards of the explosive content but also of the products of detonation and burning. This purpose of this chapter is to provide a basic understanding to assist in identifying toxic hazards when working with ammunition and explosive materials including a detailed toxicology of individual chemical components.

18.1.2 The Toxic Risk

18.1.2.1 Exposure to toxic chemicals

The toxic risk from any chemical will be a function, among other things, of the amount that enters the body by one of the three main routes:

1. **Ingestion** – passing into the stomach, usually in food or drink. This should be easily controlled; however, poor hygiene after handling explosive materials can inadvertently contaminate something that is handled while eating.
2. **Inhalation** – passing into the lungs either as gas/vapour, droplets or dusts. This route is the most difficult to protect as people breath in anything that is in the air unless respiratory protection is used.
3. **Skin Contact** – solids and more particularly liquids on the skin are often capable of being absorbed in to the body. This route is often ignored as a potential hazard.

Other routes of entry such as through cuts or grazes are less likely; however, contamination of the eyes by chemicals is a serious hazard. The risk of transfer to the eyes or to the mouth via contaminated hands or gloves must be remembered.

During much of the lifetime of a munition there is minimal potential for exposure to the explosive content and thus there is no toxic risk. However, there are times when explosive may exude during storage and then present a toxic hazard. The greatest risk of exposure is during manufacture when explosive materials are handled or filled in to the ammunition. There is also an increased risk of exposure during disposal or dismantling for surveillance or servicing. Products formed from explosion or burning of explosives are often highly toxic.

18.1.2.2 Exposure limits

The most likely entry route for chemicals in the workplace is by inhalation and the potential for a chemical in the air to enter the body will depend on two factors, the concentration present and how long it is breathed in. For example if a person is exposed to a certain concentration for, say, one hour and a second person is exposed to a concentration half of the first but for two hours they will have the same amount of chemical enter their systems. To provide safety guidelines for safe workplace concentrations of chemicals in the air the Health and Safety Executive publish Workplace Exposure Limits (WEL) as an acceptable level in the workplace.

A WEL can be for a Short Term Exposure Limit (STEL), usually for 15 minutes exposure, or a Long Term Exposure Limit (LTEL) of 8 hours. The STEL value is usually greater than the LTEL but may have additional controls relating to overall exposure during the working day. The LTEL means that a worker can be exposed to that concentration for 8 hours a day, 5 days a week during the working year. These limits are expressed in part per million (ppm) or mg m^{-3}. The LTEL may be quoted as a Threshold Limit Value (TLV) based on the American Conference of Governmental Industrial Hygienists. The workplace is anywhere people are working, in this instance, with explosives or ammunition and will include explosive storage, ranges, magazines, etc. as well as places where explosives and ammunition are manufactured. The HSE publish guidance in EH40[(1)] which lists workplace exposure limits of many chemical substances although the data for explosives is limited. The forward to the printed 2005 edition explains that many substances had been removed from earlier editions because the HSE had doubts that the limit was soundly-based. The absence of a substance from EH40 does not mean that it is safe.

18.1.2.3 Additional toxicity data

Anyone supplied with an article has the right to demand a Safety Data Sheet (SDS) for the chemicals contained therein. Safety Data Sheets contain doses or amounts required to produce acute lethal poisoning effects by all three main routes of entry. It may also cover skin and eye irritation, some chronic effects, warnings about potential cancer causing chemicals and other hazards such as danger to the unborn child or potential to cause reproductive defects. They can also repeat data from EH40 or the equivalents from other jurisdictions, usually the USA.

Acute toxicity is the adverse effects of a substance that result either from a single exposure or from multiple exposures in a short period of time, usually less than 24 hours. To be described as acute toxicity, the adverse effects should occur within 14 days of the administration of the substance. Chronic toxicity is the adverse health effects from repeated exposures, often at low levels, to a substance over a longer time period of months or years. The ability of some substances to cause cancer can also be considered as a chronic effect. Certain chemicals can cause cancer with a single exposure but are very rare.

There is a classification system for the toxicity of chemicals by what are called Hazard or H Statements, which are based on well-defined test methods and place the materials into bands of toxicity depending on the test results. There are also rules for defining the classification of mixtures. Annex A to this chapter contains the main H Statements and outlines the boundaries between them.

These H statements are based on LD_{50} values and this represents the quantity of a chemical, usually expressed as mg of chemical per kg of body weight, that would cause lethality to 50 % of a large group of people exposed to that dose of the chemical. However, individuals may exhibit hypersensitivity to certain chemicals and therefore LD_{50} values should be treated with extreme caution as a basis for a COSHH risk assessment when a large number of people are potentially exposed. Potentially an individual may die from exposure to well below the LD_{50} dose. The Control of Substances Hazardous to Health (COSHH) Regulations(2) require that a risk assessment be made of the potential harm that might come from any exposure to chemicals.

18.1.3 Explosive Chemicals with Significant Toxicity

Error! Reference source not found. provides a list of explosives and explosion products that have a significant toxic risk and where they are found. Explosive materials not included are still to be considered as toxic and included in any COSHH assessment.

Table 18-1 Explosives or Explosion Products with Significant Toxicity

Explosive	Route of entry	Where found	Major effect
Nitroglycerine	Inhalation (vapour) or skin contact	Gun propellants, double base rocket propellants, gelatine dynamites	Severe headache and lowers blood pressure
Ethyleneglycol dinitrate	Inhalation (vapour) or skin contact	Taggant in plastic explosives	Severe headache and lowers blood pressure
Propyleneglycol dinitrate	Inhalation (vapour) or skin	OTTO fuel	Severe headache and lowers blood pressure
Trinitrotoluene	Inhalation (dust) or skin contact	High explosive formulations	Cyanosis, liver and kidney damage
Tetryl	Inhalation (dust) or skin contact	Booster charges in warheads, only found in legacy ammunition	Severe dermatitis in some individuals, liver and kidney damage if inhaled
Lead	Inhalation (dust)	Indoor small arms ranges	Anaemia and central nervous system
Carbon monoxide	Inhalation (gas)	Detonation in confined areas	Headache, dizziness and then lack of oxygen in the blood

18.2 TOXICITY OF EXPLOSIVE SUBSTANCES AND EXPLOSION PRODUCTS

18.2.1 Classification of Toxic Hazards

Those who manage ammunition or undertake work with explosive materials must be aware of their obligations and rights under REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals)[3] and CLP (Classification, Labelling and Packaging)[4]. In June 2015 all previous Classification and Labelling requirements that fell under CHIP (Chemical Hazard Labelling and Packaging) were replaced by these two documents which implement the Globally Harmonised System (GHS) of Classification and Labelling of Substances within the European Union. Both REACH and CLP are enforced in UK law through Statutory Instruments (REACH in 2008 and CLP in 2015). The MOD can grant specific exemptions to REACH (May 2014) but state that their "internal standards will be at least as good as those in the regulations where reasonably practicable".

There is a derogation from labelling explosives, as referred to in section 2.1 of Annex I of the CLP ("placed on the market with a view to obtaining an explosive or pyrotechnic effect") with anything other than their classification as explosive. There is no derogation from classifying the chemicals or having a classification for the chemicals. Anyone supplied with an article containing an explosive has the right to ask for a Safety Data Sheet (SDS) for the chemicals contained therein.

MOD should not have to classify the toxic hazards of an explosive unless the MOD actually produces them as novel chemicals. MOD should hold the SDS containing the classification for all explosives found in their ammunition stockpile. Prior to June 2015 some legacy MSDS (Material Safety Data Sheets) were acceptable but those who hold these will need to update them with SDS.

18.2.2 Toxicity of Explosive Chemicals Found in Propellants

18.2.2.1 Nitroglycerine (glycerol trinitrate)

Nitroglycerine (NG) is an extremely common constituent of many commercial explosives such as gelatine dynamites and of both certain gun (see 12.2.2) and rocket propellants (see 13.3.2). It is a liquid at most normal temperatures having a Melting Point of 13.2 °C[5]. NG is absorbed through the lungs and also through the skin. Nitroglycerine is a potent smooth-muscle relaxant and has been used as a vasodilator to widen blood vessels in the treatment of angina pectoris for over 100 years. Most of the SDS produced for NG are for its use as a medicine, where it can be found at the 1 to 2 % level diluted with other materials.

Because of this vasodilatory effect the early symptoms of exposure are a lowering of blood pressure leading to headache, dizziness, weakness and

nausea. The ‘nitro headache' common in nitroglycerine and cordite production works[6] is due to the cerebral vasodilation effect of NG. Because of this it is best to keep the sufferer in a standing position as this limits the blood supply to the brain[5]. At high doses NG causes methaemoglobinaemia, a condition described in section 18.3.1, where the blood has reduced capability to carry oxygen. NG has reasonable high volatility and sufficient vapour can exist to produce symptoms in enclosed spaces. For example, the distinctive smell will be noticeable in closed unvented propellant storehouses.

The US threshold limit value (TLV) for NG is 0.05 ppm (0.50 mg m^{-3}) and exposure at this level can cause slight headaches. Although NG is not quoted in EH40, when it was included in 2002 it had a WEL (section 18.1.2.2) value of 0.2 ppm (2 mg m^{-3}) and its short term exposure limit (STEL) was the same value. Exposure to this level has been shown to produce marked headaches in 50 % of those exposed within 3 minutes[5]. The saturated vapour pressure (SVP) of NG is such that a standing concentration of 0.65 ppm will occur in enclosed spaces at 25 °C.

The LD_{50} (oral) for rats is 105 mg kg^{-1}[7]. A daily dose of 10 mg is safe and effective as a medicine[5] but 9100 mg (taken with wine by mistake) has caused a fatality[5]. Alcohol is known to potentiate the symptoms. NG is classified as H300 (Acute Toxicity 2), H310 (Acute Toxicity 1) and H330 (Acute Toxicity 2)[7].

The mechanism of toxicity of NG is complex. It is known that there is a marked build-up of tolerance to NG with increasing exposure[8]. For more information see section 18.3.1.3.

18.2.2.2 Nitrocellulose (NC)

Nitrocellulose is a large polymer which is both water and lipid insoluble which cannot be absorbed into the body. Animals fed on diets containing up to 30 % NC for long periods developed no symptoms of poisoning[9]. NC has an LD_{50} greater than 5000 mg kg^{-1}.

18.2.2.3 Nitroguanidine (Picrite)

There is no evidence that nitroguanidine presents a toxic hazard to man under normal conditions. Animal studies confirm that this compound has exceptionally low toxicity both for acute and chronic poisoning. The LD_{50} for rats (oral) is 4640 mg kg^{-1} and mice fed nitroguanidine at 1000 mg g^{-1} day^{-1} for 90 days exhibited no ill effects[10].

18.2.2.4 Propylene glycol dinitrate (PGDN)

Propylene glycol dinitrate is a major constituent (76 %) of OTTO Fuel II and is responsible for virtually all the toxic problems associated with exposure to this torpedo propellant used either as a monopropellant, or as a bi-propellant with hydroxyl ammonium perchlorate (HAP).

Animals exposed to PGDN vapours exhibit lethargy, prostration, anoxia and methaemoglobinaemia (section 18.3.1), with reduced response to external stimuli and at high doses, death. There is no reliable inhalation exposure data for PGDN; a rabbit continuously exposed to 35 ppm (265 mg m^{-3}) died on the fourth day of exposure and one in nine monkeys exposed to the same level died after 9 days[11]. Chronic exposure to high concentrations of PGDN vapour induced fatty changes in the livers of guinea pigs, dogs and monkeys. Monkeys exposed to concentrations of PGDN in the range of 0.3 to 4.2 ppm, 23 hours per day for 125 days, suffered no apparent physical effects; neither was there evidence from behavioural tests of any discernible effect that could be ascribed to PGDN exposure.

PGDN is a potential health hazard to man by inhalation, ingestion or by absorption through the skin. Most of the symptoms produced by exposure to this compound are typical of the nitrate esters. Ingestion of liquid OTTO Fuel can cause gastrointestinal disorders as well as the usual systemic effects. Both the liquid and the vapour are known to cause mild eye irritation. The vapour pressure of PGDN is small (0.07 torr at 22 °C[12]) compared to water (20 torr) at the same temperature, but not negligible and inhalation is the major health hazard posed by OTTO Fuel. The acute systemic effects of mild OTTO exposure are nasal congestion, headache, nausea, eye irritation, lowering of blood pressure, dizziness and laboured breathing. The most common acute symptom is the well-known ‘nitro headache', which can be very severe and last for several hours after exposure. In common with NG, repeated exposure leads to a tolerance of the minor symptoms. Most of the effects of OTTO Fuel on individuals can be attributed to the cardiovascular action of PGDN. The National Institute of Occupational Safety and Health sets the TLV at 0.05 ppm[12]. Dizziness and a marked impairment in balance can be induced by concentration levels of 2 to 3 times the Occupational Exposure Limit. The saturated vapour pressure could create a concentration of 100 ppm in an enclosed unventilated space.

A comprehensive study of 87 workers chronically exposed to OTTO Fuel in their working environment, some for as long as 11 years, revealed a history of minor acute PGDN toxic symptoms but no serious chronic physical or neuro-physiological ill effects. No human deaths or other major toxic accidents due to PGDN have been reported. It seems likely that under normal working conditions, with good ventilation, peak PGDN concentrations are usually far below the Occupational Exposure Limit. The U.S. Department of Health and Human Services published a comprehensive study of the toxicological profile for OTTO Fuel II and its components in 1995[13].

18.2.2.5 Triethylene glycol dinitrate (TEGDN)

TEGDN is an energetic plasticiser for explosives and propellants. Studies with animals indicate that TEGDN is 2-5 times less lethal than propylene glycol dinitrate (PGDN) when administered orally or subcutaneously. ‘In vitro’ studies have shown that TEGDN interfered with nerve/muscle communication, which

could explain why TEGDN dosed animals tremored violently and convulse while those exposed to PGDN were lethargic and did not exhibit convulsions[14].

18.2.2.6 Ammonium Perchlorate

Ammonium perchlorate found in composite propellants is not classified as toxic under CLP. Ammonium perchlorate has a quoted LD_{50} (rat) of 4200 mg kg^{-1} but may can cause serious eye irritation. It can, however, cause chronic thyroid problems if ingested in drinking water, from which it is very difficult to remove, as it interferes with iodide take up by the thyroid gland. The Environmental Protection Agency in the USA has set a limit of 15 mg L^{-1} of drinking water at which there are not expected to be any adverse non-carcinogenic effects during a lifetime of exposure.

18.2.3 Toxicity of Explosive Chemicals Found in High Explosives

18.2.3.1 Trinitrotoluene (TNT) and related compounds

Typical symptoms of acute TNT exposure are paleness of face, grey lips, stomach ache, constipation, flatulence and possible jaundice. Changes in the blood, with a decrease in haemoglobin and the appearance of abnormal red blood cells are among the first signs to be present. Distinct poisoning has been observed in individuals exposed to an atmosphere containing TNT dust at a concentration of 3 mg m^{-3}. TNT dust has been known to cause irritation of the digestive tract on ingestion and also skin rashes and dermatitis. EH40[1] contains a workplace exposure limit of 0.5 mg m^{-3} for TNT. This would be as the dust as the Saturated Vapour Pressure only produced 0.08 mg m^{-3} at 25° C.

Inhalation of TNT dust, ingestion or absorption through the skin can cause cyanosis, liver and kidney damage and even death. In the first 8 months of World War I 17,000 cases of TNT poisoning with 475 fatalities occurred in the United States of America[15]. In the United Kingdom some 106 deaths were attributed to the toxic effects of TNT during the whole of World War I. In contrast there were very few cases of poisoning reported in Germany during WW1. Many of these early casualties may have been caused by impurities in the TNT and by very poor industrial hygiene practices. There were only 22 fatalities in the United States of America during World War II caused by TNT intoxication.

There is a record of acute toxic jaundice caused by TNT and autopsy revealed atrophy of the liver[16]. Skin adsorption is supposed to be enhanced by the skin being oily or sweaty. Skin symptoms are a reddening of the skin[17], it stains the skin of the hands a light yellow and discolours the hair to a reddish blond[18].

Metabolism of TNT in the human produces many products including a dinitrohydroxylamine derivative that is a potent producer of methaemoglobin. After serious or prolonged exposure, cyanosis caused by methaemoglobinaemia (see 18.3.1), kidney disorders and liver damage causing severe jaundice will occur. TNT also destroys the bone marrow tissue causing aplastic anaemia. Death is usually due to severe jaundice, anaemia or toxic hepatitis. An LD_{50} between 795 to 1320 mg kg^{-1} has been quoted[19] as have

similar values from other studies[5]. A manufacturer has classified TNT as H331, H311 and H301 but without references[20], which suggests that a more poisonous oral LD_{50} may have been reported. It also gives a TLV from the US of 0.1 mg m^{-3}.

Dinitrotoluene (DNT) is of interest as an impurity in TNT and as components of effluent from TNT production plants. While a mixture of isomers is produced, the main component is usually the 2,4-dinitro compound which is classified H301, H311 and H331. It is also H341 (suspected of causing genetic defects) and H350 (may cause cancer)[21]. The dinitrotoluenes are lipid-soluble and can be absorbed through the skin or by ingestion. Symptoms of poisoning include pallor, headache, giddiness, cyanosis and tremors. LD_{50} of 2,4-dinitrotoluene for rats is 270 mg kg^{-1} to 650 mg kg^{-1}[22]. The other isomers have an LD_{50} value in the same range. Chronic exposure of animals to DNT produced evidence of methaemoglobinaemia, central nervous system effects and liver damage. There is clear evidence from animal studies that the 2,4 isomer is carcinogenic. In the Ames test all DNT isomers are mutagenic. In general nitrotoluenes are reputed to be less toxic than nitrobenzenes, possibly because of the ease of metabolism within the body of the nitrobenzenes to the slightly toxic nitrobenzoic acids.

18.2.3.2 Nitrobenzenes

Nitrobenzene has been widely used as a semi-energetic fuel in improvised explosive mixtures. Both mono and the dinitrobenzenes can be produced during TNT manufacture particularly when using impure toluene.

Nitrobenzene can be readily absorbed into the body by inhalation of vapour or by absorption through the skin. As might be expected of an aromatic nitro compound, nitrobenzene will oxidise haemoglobin to methaemoglobin. It is also toxic to the liver and the nervous system. Exposure to vapour at a concentration greater than 5 mg m^{-3} is considered dangerous. Symptoms of nitrobenzene exposure include nausea, headache, dizziness, stomach upset and characteristic cyanosis. After severe acute exposure these symptoms will be intensified and heart palpitations, cramps, disturbance of vision and loss of consciousness may also occur. Chronic intoxication may lead to anaemia and liver damage.

It is likely that most of the casualties and fatalities caused during the early days of TNT manufacture were due to the presence of m-dinitrobenzene (DNB) as an impurity in the product. DNB is not very volatile but is readily absorbed percutaneously. An LD_{50} for 1,3 dinitrobenzene of 59 mg kg^{-1} has been quoted[23]. During World War I, there were many cases of up to 50 % of exposed factory or munition workers becoming poisoned by nitrobenzene exhibiting cyanosis and headaches[24]. Individuals exposed to DNB can develop methaemoglobinaemia, liver damage, convulsions and cerebral paralysis. After mild exposure, victims may completely recover in a few weeks but more serious cases may need 2 months or more to fully recover. In a few acute cases symptoms appear rapidly and death can occur in a few hours. Cases have been reported in which the onset of symptoms is much delayed, in some cases up to

several months after exposure has ceased. Dinitrobenzenes are classified as H300 (Acute Toxicity 2), H310 (Acute Toxicity 1) and H330 (Acute Toxicity 2).

18.2.3.3 Cyclotrimethylenetrinitramine (RDX)

RDX has a high melting point and at ambient temperatures has a low vapour pressure. Inhalation of RDX vapour therefore would not be expected to pose problems under normal circumstances. In spite of the low lipid solubility of RDX there have been some suggestions of dermal absorption. Inhalation of dust or ingestion will be the main routes of entry of RDX into the body.

The pharmacology of RDX is different to that of other previously mentioned organic nitro compounds and involves gastrointestinal, renal and central nervous system effects, the latter effect being the most prominent. The acute oral LD_{50} in rats is about 100 mg kg^{-1}. One modern SDS records RDX as Acute Toxicity 3; H301 and Skin Irritant 2; H315[25]. An older SDS records the chemical as “toxic” by all three routes of entry (R23/24/25). As there is evidence that inhaling the dust is dangerous H330 or H331 should always be considered when there is a chance of dust being produced.

Exposure to RDX dust can cause sudden loss of consciousness with convulsions, typically followed by a coma of several hours duration[26]. When RDX is handled in a moist state and dusting suppressed, or when workroom ventilation is improved, RDX intoxication does not occur. Five cases of convulsions occurred among 26 workers engaged in pelletising RDX in 1962 in the United States of America[27]. Typically the onset of symptoms occurs after a delay of several hours and may be preceded by preliminary signs of headache, nausea, vomiting or hyperirritability.

Cases have been reported of troops chewing plastic explosive containing RDX, the object being to produce a 'high' similar to the effects of alcohol and suffering severe RDX intoxication. Some military victims of RDX poisoning had used a similar RDX containing plastic explosive as a fuel for a cooking fire and either inhaled the toxic fumes or introduced particles of the material into their food[5].

The symptoms of RDX intoxication are quite severe, however, few deaths have occurred and survivors appear to recover completely over a period which can vary from days to several months in the case of long exposures. The US Department of Health and Human Services published a comprehensive review of toxicological studies on RDX in 2012[28].

18.2.3.4 Cyclotetramethylenetetranitramine (HMX)

The toxic symptoms of HMX are reported as being similar to those induced by RDX but HMX is regarded as being somewhat less toxic. The US Department of Health and Human Services published a comprehensive review of toxicological studies on HMX in 1997 in which they noted very few studies relating to effects on humans[29]. Some animal studies were reported in rats suggesting that acute LD_{50} for HMX is around 6000 mg kg^{-1} in rats for oral ingestion and about half this value in mice. This seems to be related to the low solubility of HMX

compared to RDX. At the Human and Environmental Toxicology of Explosives and related Compounds Meeting 2012 (Amsterdam), LD_{50} (rat) values were reported for RDX and HMX as 100 mg kg^{-1} and 6000 mg kg^{-1} respectively[19]. Their water solubilities were 50 mg L^{-1} for RDX and only 6 mg L^{-1}. HMX has been classified as Acute Toxicity 4; H302 and Acute Toxicity 3; H311, an 8 hr Time Weighted Average (LTEL) of 5mg m^{-3} and an oral LD_{50} of 1670mg kg^{-1}[30].

18.2.3.5 Pentaerythritoltetranitrate (PETN)

The toxic action of PETN is the same as other nitrate esters such as nitroglycerine. It has been used in medicine as a long lasting vasodilator in the treatment of angina. However the vapour pressure of PETN is negligible being 1.2×10^{-8} torr at 25 °C [31] leading to a saturated vapour concentration of 5×10^{-4} mg m^{-3} at 25 °C so inhalation of vapour will not occur at ambient temperatures. It also has a low solubility and even breathing small amounts of PETN dust has been reported as causing little effect[32], 0.25 g being required to produce irritation of the lungs. PETN is absorbed only slowly from the gastrointestinal tract, with a 64 mg oral dose in man produced no ill effects[5]. There is little, if any, absorption through the skin. The toxicity of PETN is certainly much less than that of NG. Some cases of dermatitis have been attributed to contact with PETN in ordnance facilities, but short term tests on a limited number of volunteers did not support this[5].

18.2.3.6 Trinitrophenylmethylnitramine (Tetryl)

The hazard from tetryl is due to the dust being inhaled, or coming into contact with the skin. The main symptom of tetryl is the development of a skin irritation after repeated handling but there is also a hazard from dust which will turn skin yellow and cause sensitisation dermatitis. In one processing plant where over 5000 people worked in a series of buildings 23 % suffered from the symptoms of tetryl illness of which 75 % developed definite tetryl dermatitis. The illness was not confined to those in direct contact with tetryl, 20 % of the operatives working in the same building but who did not handle tetryl developed the illness[5].

At low concentrations the dust irritates the upper respiratory tract. Breathing an atmosphere containing 1.5 mg m^{-3} of tetryl will cause symptoms to appear 2-3 weeks after exposure. Other symptoms of tetryl poisoning are insomnia, loss of appetite and giddiness. Chronic exposure can result in nitro induced anaemia and liver or kidney damage.

18.2.3.7 Hexanitrostilbene (HNS)

HNS is classified as R20/22 under the old toxicity classification system, harmful by inhalation and if swallowed. The studies on which this classification is based have not been found and the noted ingestion dose of >4000 mg kg^{-1} would not lead to it being classified under either the old or new system. One SDS notes that it has not been recorded as a carcinogen but may be a weak mutagen. Another SDS notes that pregnant women should not work with HNS.

18.2.3.8 Triaminotrinitrobenzene (TATB)

TATB is classified as R20/21/22 under the old toxicity classification system. LD_{50} for oral ingestion is quoted in one SDS as >5000 mg kg^{-1} which would not lead to this classification but there is evidence to irritation of the respiratory tract at the 5 mg m^{-3} level.

18.2.3.9 Ethylene glycol dinitrate (EGDN)

Ethylene glycol dinitrate is usually used in Dynamites mixed with nitroglycerine (NG) to lower the freezing point of the latter and thus avoid the dangers associated with low temperature applications. It is also used as a taggant in some explosives as it is more volatile than NG and thus is easier to detect as a vapour.

Ethylene glycol dinitrate produces the symptoms and tolerances typical of organic nitrates. It can be absorbed by inhalation or percutaneously. Headaches occur in non-habituated humans within 3 minutes at 2 mg m^{-3}. Chronic exposure can cause very low blood pressure and slowing of the heart rate known as bradycardia. Protracted inhalation of large quantities of vapour can give rise to fatal acute circulatory or cardiac failure after a prolonged latency period of 24-48 hours. Between 1927 and 1952 49 fatalities were recorded with a fatal heart attack occurring during the weekend or on a Monday morning[(5)]. Consumption of alcohol makes humans particularly susceptible to EGDN[(33)]. Since EGDN is 160 times as volatile as nitroglycerine[(31)], most vapour exposure casualties are caused by the EGDN when used together with NG. Good exhaust ventilation at the workplace with fresh air devices at head height are reported as being adequate to prevent problems due to inhalation of EGDN vapours.

18.2.3.10 New explosives

There are a number of new explosives that are being considered for next generation explosive formulations both propellants and high explosives. There is limited information on their toxic properties.

DNAN, 2,4-dinitroanisole, is classified as H302 harmful if swallowed and H341 suspected of causing genetic defects. However, the SDS from one manufacturer is careful to say that the acute and chronic toxicity of this substance is not fully known.

FOX12, guanylureadinitamide (GUDN), does not have any classification for toxicity and the SDS notes that LD_{50} (rat) is >2000 mg kg^{-1} for both oral and skin absorption.

HNF, hydrazonium nitroformate, is classified as toxic by ingestion with a quoted LD_{50} (rat) of 128 mg kg^{-1}. As a hydrazine salt it has, by analogy, a suspected carcinogenicity effect.

FOX7, 1,1-Diamino-2,2 Dinitroethene, has a SDS that quotes a very wide LD_{50} (rat) of between 200 and 2000 mg kg^{-1} without specifying a route of entry.

18.2.4 Toxicity of Chemicals Found in Initiating Substances

Many of the primary explosives used as initiators in the munitions industry are salts (e.g. styphnates or azides) of silver, lead or mercury. Most heavy metals are highly cumulative poisons and toxic doses can be acquired over a period of several years of exposure. There is much published information on these compounds including some concise toxicology(34).

18.2.4.1 Mercury

Mercury fulminate, the first common detonating primary explosive, is highly toxic as are most mercury salts. Cases of mercury poisoning are well documented amongst workers engaged in the first stages of production of this compound. Mercury metal itself is sufficiently volatile to produce a vapour hazard even though the vapour pressure at room temperature is low. Absorption can be through the skin, resulting from careless handling of the liquid metal or by breathing in vapour. Serious acute poisoning by elemental mercury or its salts, particularly the water soluble mercury salts which are much more toxic than the insoluble compounds, is not very common. Chronic human mercurialism is however very well documented. Toxic doses can be gradually built up in the body over a long period of exposure to the vapour.

Mercury vapour primarily attacks the brain, however, the kidney is the critical organ of injury following exposure to mercury salts. Characteristic symptoms of mercury poisoning include excitability, irascibility, fatigue, depression and tremor. In the environment, metallic or elemental mercury is converted to organomercury compounds which can be concentrated in the natural food chains and are potent and highly cumulative nervous system and kidney poisons. Methyl mercury produces teratogenic effects. In the notorious Minamata (Japan) poisoning episode inorganic mercury from an industrial process was discharged into seawater where micro-organisms converted it into methyl mercury. This was concentrated in plankton which in turn were eaten by shellfish and small fish which were eaten by large fish and eventually by humans leading to 765 deaths and over 2000 cases of non-fatal mercury poisoning(34).

18.2.4.2 Lead

Apart from specialist applications virtually all initiators for detonating explosive trains contain lead azide. Also, the majority of initiators for igniferous systems will contain lead styphnate, for example the percussion caps in small arms ammunition. In an era of improving environmental control the presence of lead in initiators is of increasing concern.

Lead is a highly cumulative poison and its chronic toxicity effects in man are well known(35). Dust and fumes of the metal as well as soluble lead salts are

poisonous. Lead poisoning produces many complex symptoms. Red blood cells are attacked producing anaemia. The nervous system is particularly sensitive to accumulation of lead; convulsions, delirium and other brain symptoms can be observed. The effects among industrial workers of chronic lead exposure leading to kidney and renal failure have been well documented. High concentrations of atmospheric lead dust have been found in indoor firing ranges and several cases of mild lead poisoning among shooting instructors have been reported; the lead dust originated both from the bullet cartridge primer and also from partial vaporisation of the bullet itself, both on firing and on fragmentation when impacting a hard target.

18.2.4.3 Silver

Silver azide finds use in specialised detonators. Chronic severe industrial exposure to silver fumes or dusts results in a condition known as argyria, which is a permanent light blue/grey pigmentation of the skin and eyes. The lethal acute dose for man is very high. However, silver nitrate solutions and dusts are both toxic and, even at very low concentrations are irritant to the skin and eyes. Taken orally silver nitrate ($AgNO_3$) can cause violent abdominal pain, vomiting and even death; the oral LD_{5O} in the mouse is estimated to be 50 mg kg^{-1}. This difference between the toxicity of the metallic element and its salts has been recognised by the American Conference of Governmental Industrial Hygienists (ACGIH) which has set the Threshold Limit Value (TLV) at 0.1 mg m^{-3} for metal dust and fumes, and a factor of 10 lower at 0.01 mg m^{-3} for soluble airborne silver compounds.

18.2.4.4 Azides

Exposure to azide is only likely in the manufacturing process of lead or silver azide through contact with the precursor sodium azide. On initiation the azide will convert to nitrogen gas. Most toxicological data in the literature about azides relates to hydrazoic acid or its sodium salt. Inorganic azides are well known poisons. Sodium azide (NaN_3) is about as toxic as sodium cyanide and, like cyanide, is a strong inhibitor of the vital metabolic enzyme cytochrome oxidase; it also binds strongly to haemoglobin and blocks oxygen transport from the blood. Hydrazoic acid, which is formed from aqueous solutions of azide salts by hydrolysis, is a volatile, highly toxic gas with an intolerable pungent odour. Sodium azide is classified as H300 and H310[36]. Fatal doses can occur at 10 mg kg^{-1} body weight.

In man the acute effects of exposure to hydrazoic acid vapour are eye irritation, headache, a fall in blood pressure, dizziness and collapse. The effects are due to the conversion of iron to iron oxide so that it can no longer fulfil its functions of the transport of oxygen as haemoglobin. No deaths have been reported for workers engaged in the manufacture of lead azide, but mild acute symptoms of hydrazoic acid poisoning are common. Long term exposure of animals to azide vapours has been reported to cause permanent damage to the nervous system but no such chronic effects have been reported in humans.

18.2.5 Toxicity of Chemicals Found in or Associated With Pyrotechnics

18.2.5.1 Screening Smoke

18.2.5.1.1 White phosphorus

White Phosphorus (WP) was commonly used as the main filling in screening smoke munitions but now has limited UK service use. It is found in legacy and foreign ammunition. WP is one of the most highly toxic inorganic substances known. It can be absorbed through the skin, the respiratory system and also by ingestion. Severe symptoms have been reported in man following a single dose of 15 mg. The human LD_{50} may be as low as 1 mg kg^{-1}. Skin contact with white phosphorus results in very painful burns which can penetrate deep into flesh. The US Department of Health and Human Services produced a Toxicological Profile for white phosphorus and the smoke that it emits in 1997(37).

The chronic effects of phosphorus poisoning among industrial workers is well known. Often the symptoms take several years to appear. The classic effect is on bone and the 'phossy jaw', a jaw bone necrosis, was an occupational disease among those involved in the match and firework industries until the use of white phosphorus was abandoned. The substance is classified as H300 Cat 1 (oral).

18.2.5.1.2 Red Phosphorus

Red phosphorus is much less toxic than the white variety. It is formed from white phosphorus by careful anaerobic heating and is a polymeric chain form rather than P_4 pyramids. This changes "toxicokinetics" so that the red form is relatively non-toxic but beware of contamination by white phosphorous. It is also chemically less reactive. White Phosphorus is H300 Cat 1 (Oral) whereas Red Phosphorus is not classified as toxic.

18.2.5.1.3 Phosphine

Phosphine gas, PH_3, can be liberated from both red and white phosphorus in storage if moisture contamination occurs. It has a STEL is 0.3 ppm and causes kidney and usual phosphorous skeletal effects. As an inhalable vapour its absorption by the body can be rapid and it has been used in suicides by ingesting a phosphide rat poison which forms phosphine in the stomach. The LC_{50} (rat) for 1 hr exposure is 22 ppm. LC_{50} is the concentration of a chemical in air, usually expressed as ppm or mg m^{-3}, that would cause lethality to 50 % of a large group of people exposed to that dose of the chemical. It is important to note that an LC value must relate to a given time of exposure. Emsley(38) has provided further information on phosphorus and phosphine toxicity and the toxicology is presented in section 18.3.3.

18.2.5.1.4 Hexachloroethane

Hexachloroethane (HCE) is found in HCE/zinc oxide/aluminium smoke compositions. It is a toxic chemical with a distinctive odour and most countries apply a TWA (8 hr) of 1 ppm. There is still limited use of HCE compositions in UK Service but will certainly be found in legacy munitions.

18.2.5.1.5 Products of Combustion

When phosphorus burns in air phosphorus pentoxide is produced, which in the presence of atmospheric moisture hydrolyses to phosphoric acid (H_3PO_4) or poly- phosphoric acids such as pyrophosphoric acid ($H_4P_2O_7$) and triphosphoric acid ($H_5P_3O_{10}$)[39]. The American Office of the Army Surgeon General of the USA published recommendations regarding permissible levels to which soldiers should be exposed. The emergency 15 minute concentration was 40 mg m^{-3} with longer exposures having lower limits. They also published data for hexachloroethane smoke, where the main toxic product is zinc chloride, as 10 mg m^{-3} of $ZnCl_2$.

Signalling smoke, both white and coloured, consists of solid particles in air. These have to be of a certain size to remain suspended for useful periods of time, a size that puts them in the class of respirable dusts. EH40[1] offers an almost universal upper limit of 10 mg m^{-3} for the 8 hr exposure limit to inhalable dust and 4 mg m^{-3} for respirable dust unless the limit is lower on other grounds. Signalling smokes will be denser than this to be effective.

The smoke itself is formed by evaporating a dye with a cool burning pyrotechnic. However it is inevitable that a small proportion of the organic materials in the smoke will be pyrolysed into unpredictable by-products. The compositions may also contain calcium oxalate which is harmful. In the past some of the dyes used were highly carcinogenic but modern compositions contain much safer materials. Most are anthraquinone based dyes and have an LD_{50} of about 5000 mg kg^{-1}[40]. Cinnamic acid, frequently used to give a white smoke, is classified as a skin and respiratory irritant[41]. The riot control agent CS (2-chlorobenzalmalononitrile) in pellet form is relatively non-toxic. Like signalling smokes it is pyrotechnically evaporated from a canister forming a particulate cloud known as ‘tear gas’ causing intense irritation of eyes, nose, mouth and throat mucous membranes causing profuse coughing, disorientation, and difficulty breathing, partially incapacitating the subject. It has an LC_{50} estimated as over 50,000 mg m^{-3} for a one minute exposure but it is intensely irritating at 1 mg m^{-3}.

18.2.5.2 Other pyrotechnics

All pyrotechnics except the phosphorus smokes are fuel-oxidiser mixtures with a wide range of potential ingredients. The toxicity of each ingredient must be considered separately and then all effects combined for the full toxicity classification. The additivity rules for classification are such that it is unlikely that any part of a pyrotechnic mixture will be present in such a small amount that it can be disregarded. It is not the intention to produce a comprehensive guide to the toxicity of such a large number of compounds.

In reality, the toxic hazards associated with pyrotechnic compositions are largely the concern of manufacturers that handle the chemicals. Once filled in to a munition the toxic hazard is no longer present unless the contents leak from the munition body. Nearly all of the ingredients are either crystalline solids or metal powders and so, even if the composition is exposed, there will not be a vapour hazard and then only skin contact must be avoided.

18.2.5.3 Pyrotechnic oxidisers

Inorganic nitrates, such as those of barium, potassium, sodium and strontium are used as oxidisers in pyrotechnic compositions. Inorganic nitrates do not produce methaemoglobinaemia symptoms in adults. The barium, sodium and strontium salts are classified as H302, harmful if swallowed. Potassium nitrate and ammonium nitrate are not classified as toxic, though the latter may cause skin and eye irritation and is found in a number of improvised explosive mixtures (see 16.3).

Other oxidisers include chlorates and perchlorates found in both pyrotechnic and improvised explosive mixtures. Potassium perchlorate and potassium chlorate are both H302 with the chlorate also being H332. In some formulations, particularly delays, uncommon oxidisers such as chromates or dichromates can be found which are H330 (Category 2 by inhalation), H301 (Category 3 if swallowed) and H312 (Category 4 in contact with skin). Permanganates may be found in some compositions and has an LD_{50} oral of 750 mg kg^{-1} for potassium permanganate and classified as H302, harmful if swallowed.

18.2.5.4 Pyrotechnic fuels and other ingredients.

Fuels can include non-toxic organic materials such as lactose sugar; metals including aluminium, magnesium, and zirconium; non-metals and metaloids including charcoal, boron and silicon and other materials such as antimony sulphide. Burn rate moderators such as calcium oxalate may be present and other processing aids could also be found. The major toxic hazard from these chemicals is accidental ingestion.

18.2.5.5 Pyrotechnic combustion products

Pyrotechnic compositions are often complex mixtures and when they burn can reach temperatures well in excess of 2000 °C. In most cases standard chemistry will predict the majority of the products, however, due to the complexity of the mixtures there may be a large number of minor products that are difficult to predict. Attempts have been made to quantify the products from some pyrotechnics, however, it is certain that many have not been studied. On functioning all pyrotechnics will create airborne products and so care should be taken to avoid inhaling them.

18.2.6 Combustion Products of High Explosives and Propellants

Any combustion or explosion in a confined space may reduce the oxygen content of the atmosphere to a level too low to support respiration. The oxygen

content in the workplace atmosphere should never be allowed to fall below 18 % by volume at atmospheric pressure, where the normal level is 20.8 %, though this level would be survivable.

Apart from the danger of asphyxiation, the burning of propellants or detonation of high explosives will always result in the production of toxic gaseous combustion products. The most important of these are the oxides of nitrogen (NO and NO_2) and of carbon (CO and CO_2). Some nitrate esters will also produce small amounts of hydrogen cyanide if an excess of oxygen is not available during combustion. Adequate ventilation is thus essential in order to maintain an environmentally acceptable atmosphere.

18.2.6.1 Carbon Dioxide

Carbon dioxide is not an asphyxiant at low levels but it is mildly narcotic at a concentration level of 3 % and according to some reports exposure to 7 %-10 % of CO_2 renders individuals unconscious within minutes even though the atmosphere contains enough oxygen to support life.

18.2.6.2 Carbon Monoxide

Carbon monoxide, a colourless, odourless gas, is universally recognised as being highly toxic. CO is rapidly absorbed through the lungs where it binds tightly to haemoglobin thus reducing ability of the blood to provide oxygen to the cells. There is evidence to support the view that exposure to concentrations of CO in the air much above 100 ppm for several hours will begin to have physiological effects on most individuals. The accepted TLV or WEL (section 18.1.2.2) has been set at half of this value. Carbon monoxide toxicology is covered in greater detail in section 18.3.2.

18.2.6.3 Hydrogen Cyanide

Hydrogen cyanide (HCN) may be produced when burning some of the nitrate esters such as propylene glycol dinitrate, an OTTO Fuel II component, as a monopropellant at up to 0.4 % in exhaust gases. HCN is a highly toxic substance and is a potent inhibitor of the vital respiratory enzyme cytochrome oxidase, thus stopping the utilisation of oxygen by the tissues of the body. At low doses the earliest symptoms are quickening of breathing, headache, confusion and sometimes vomiting and nausea. Hydrogen cyanide is absorbed extremely rapidly through the lungs and high concentrations (several hundred ppm) can prove fatal almost instantaneously.

18.2.6.4 Oxides of Nitrogen

Perhaps the most insidious of combustion products in explosion products are the oxides of nitrogen. These are effective at very low concentrations of producing delayed symptoms of lung damage in a manner similar to that of the chemical warfare agent phosgene. Although thermodynamics predicts that nitrogen gas is the most favourable product of explosion, studies of reaction products have found the presence of nitric oxide and nitrogen dioxide.

Nitric oxide is a colourless odourless gas. It can be formed by combination of nitrogen and oxygen of the air at elevated temperatures. The products of combustion of most fires and the gases produced during firing of high explosives or propellant charges contain varying amounts of nitric oxide. It is converted spontaneously, if slowly, in air to nitrogen dioxide. The WEL of nitric oxide is 25 ppm (30 mg m^{-3}). The chief effect of nitric oxide has been ascribed to the formation of methaemoglobin and subsequent action on the central nervous system. Animal experimentation suggests that nitric oxide is about one fifth as toxic as nitrogen dioxide.

Nitrogen dioxide (NO_2) is a reddish brown gas and in high concentrations is partly associated to the dimer dinitrogen tetroxide (N_2O_4) which is colourless. Varying amounts of nitrogen dioxide result from the detonation of nitro or nitrate explosives. Many deaths from pulmonary oedema, induced by inhalation of high concentrations of nitrogen dioxide, have been reported.

Brief exposure to 250 ppm causes coughing and increased difficulty in breathing; within 2 hours severe pulmonary oedema may develop and death may soon follow. In other cases there may be a latent period of 8 hours or more where the victim feels quite well, but after this interval the onset of pulmonary oedema is rapid. Latent periods of up to several weeks after exposure and then sudden symptoms and death are not unknown. The incidence of chronic effects, from long exposures at low doses, is less well defined: The WEL of nitrogen dioxide is 3 ppm (6 mg m^{-3}).

18.2.6.5 Hydrogen chloride/hydrochloric acid

When composite propellants containing ammonium perchlorate burn the efflux contains hydrogen chloride, which when mixed with moisture in the atmosphere is converted to a hydrochloric acid mist with a STEL (section 18.1.2.2) of 5 ppm.

18.3 TOXICOLOGY

This section is not comprehensive but provides an insight into the more prominent toxicological effects caused by explosives and their explosion products.

18.3.1 Methaemoglobinaemia

The ability of haemoglobin to carry oxygen depends on the iron it contains being in the ferrous state. Methaemoglobin is a changed form of haemoglobin in which the haem iron has been oxidised to the ferric state, which alters the oxygen binding curve so that it will no longer bond to the oxygen. In a normal individual the proportion of methaemoglobin does not exceed about 1 % - 2 % unless the individual smokes cigarettes when this can rise to between 5 % and 10 %.. Compounds containing inorganic and organic nitrogen can oxidise haemoglobin to methaemoglobin. The ferric pigment causes little ill effect in the victim up to a concentration of about 1 g per 100 ml (15 %) but beyond this level cyanosis sets in. First the extremities and then the whole body assumes a bluish hue and the patient complains of fatigue and difficulty in breathing. Symptoms of anoxia, headache and dizziness occur when the methaemoglobin level is 30 % - 40 %; at greater than 40 % vomiting usually occurs; more than 60 % - 70 % is a life endangering situation and death can occur from a breakdown of the respiratory function. Acute methaemoglobinaemia normally reverts at a rate of about 12 % per hour. In chronic cases of exposure to certain compounds the red blood cells can contain inclusions of precipitated methaemoglobin termed 'Heinz bodies'.

18.3.1.1 Organic amines

Aromatic amines such as aniline and its derivatives can be metabolised to hydroxylamines and nitroso compounds(42) and produce methaemoglobin with the formation of Heinz bodies. Many of these amino compounds can be absorbed through the skin. Acute exposure symptoms include cyanosis, giddiness, headache, nausea, vomiting and respiratory distress together with neurotoxic effects such as coma and convulsions leading to death. Chronic exposure victims can exhibit weakness, giddiness, loss of appetite, anaemia with occasional Heinz bodies and mild to severe cyanosis. Some amines e.g. acrylamide cause severe neurotoxic lesions, disturbance in gait, hallucinations and muscular atrophy. Exposure to aromatic nitro compounds and amines can also be responsible for liver damage. Among aromatic amines the phenylhydroxylamines are probably the most potent producers of methaemoglobinaemia induced cyanosis.

18.3.1.2 Organic nitro compounds

All organic nitro compounds act very similarly producing, at low concentrations, methaemoglobin, with cyanosis and the appearance of Heinz bodies. In addition, central nervous system and possible liver damage are quite common.

The aromatic nitro compounds oxidise haem by an indirect mechanism and intolerance to alcohol often occurs. Nitrobenzenes can be absorbed through the skin. Typical nitro poisoning symptoms include headache, cyanosis, vomiting, gastric colic, convulsions and coma. The lethal dose taken orally is usually a few millilitres and there is often a delay of several hours before symptoms occur. Nitrophenols inhibit oxidative phosphorylation leading to weight loss and for this reason they were once used in the treatment of obesity but have since been abandoned as being too toxic with damage to liver and kidneys being recorded.

18.3.1.3 Inorganic and organic nitrite and nitrate compounds

Nitrites relax smooth muscle. Sodium nitrite has been used orally, and amyl and ethyl nitrites by inhalation, as vasodilators in relieving angina pains.

Nitrites are very effective in oxidising the ferrous iron of haemoglobin to the ferric state to produce methaemoglobin in a direct reversible process, the mechanism of which is not very well understood. One mole of nitrite will oxidise 1 mole of haem. In contrast to the action of nitro compounds where no Heinz bodies are formed.

Inorganic nitrate is normally pharmacologically ineffective since, at physiological pH, the nitrate ion is a relatively poor oxidising agent and cannot convert haem to the +3 state. However, nitrates can be converted to nitrites by the intestinal flora of infants and cases of methaemoglobinaemia due to very low nitrate concentrations are not uncommon among newborn babies often called the blue baby syndrome.

Organic nitrate esters are very potent vasodilators(43), and can be absorbed orally, through the skin or by inhalation. Typical symptoms are:

a. Fall in blood pressure
b. increase in heart rate
c. headache ('nitro-head') and at higher doses
d. dizziness, nausea, production of methaemoglobin, cyanosis
e. even sudden death

Alcohol often potentiates the symptoms. Organic nitrates are rapidly broken down in the liver, and act pharmacologically as free nitrite ions produced by reduction by tissue sulphydryl groups. The typical tolerance that is built up by those regularly exposed to organic nitrates is due to depletion of sulphydryl groups with a consequent inability to metabolise the nitrate to the active nitrite form. Relatively short respites from exposure to nitrate esters allow the regeneration of free tissue sulphydryl groups and loss of 'nitro tolerance', which explains the habit of munitions workers of keeping a small piece of propellant in their clothing and handling it during weekends and holidays. Those working with EGDN pursued a similar practice with cloth impregnated with the substance. This tolerance effect probably explains the fact, noted above, that 105 mg kg^{-1}

is the LD_{50} for NG taken as one dose yet 1058 mg kg^{-1} day^{-1} can be tolerated by the test animal for two years with no obvious ill effects.

18.3.2 Carbon Monoxide

Carbon monoxide (CO) is colourless, odourless, tasteless and non-irritating. It is produced during the incomplete combustion of carbon and carbon containing compounds and oxygen deficient explosives. Carbon Monoxide binds to a haemoglobin molecule at the same sites as an oxygen molecule. Bour[44] states that CO has a binding affinity that is approximately 200-300 times greater than oxygen. If there is CO present it will bind more readily to haemoglobin regardless of the amount of oxygen available. Figure 18-1 shows the dissociation curves for both carbon monoxide-haemoglobin (carboxyhaemoglobin) and oxygen-haemoglobin (oxyhaemoglobin). A much smaller amount of CO is required to reach 100% haemoglobin saturation than oxygen. A normal partial pressure of oxygen is about 160 mm Hg. The curve demonstrates why low oxygen levels can be tolerated in the absence of carbon monoxide as the affinity of haemoglobin (Hb) for oxygen only starts to decline significantly below about 10% oxygen (80 mm Hg partial pressure).

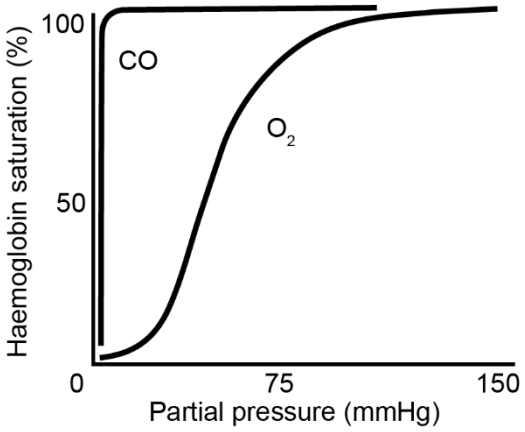


Figure 18-1 Carboxyhaemoglobin and Oxyhaemaglobin Dissociation Curves[45].

Oxygen usually binds 'imperfectly' to Hb. If it bound strongly it would not leave the haemoglobin when it was required to diffuse into the tissues it supplies[46]. Once one CO molecule is bound to a Hb molecule, it then gives Hb a higher affinity for O_2[47]. The oxyhaemoglobin curve shifts to the left[45] and the affinity is great enough that the O_2 will not leave the Hb to enter the tissues and supply them with the O_2 they need to survive. So a combination of fewer O_2 molecules bound to the Hb and a higher affinity of haemoglobin for oxygen is what causes the hypoxia, the deprivation of tissues of oxygen[47]. Once one molecule of CO is bound to a Hb molecule, Hb's affinity to CO will drop by two orders of magnitude[46]. This protects the body against poisoning by CO naturally produced in the body as this would take up a lot of the binding spaces if the affinity remained as high for all four sites per Hb molecule.

J. S. Haldane was the first person to confirm that the binding affinity of Hb is far greater for CO than oxygen. Haldane studied carbon monoxide and its effects on the body, usually his own body or those of his children, in great detail in the 1890s. He would subject himself to varying levels of carbon monoxide and note down the effects it had on him. He concluded "the effects to be similar to those produced by the lack of O_2"[48]. In partnership with Lorrain-Smith, Haldane developed what is now known as the Haldane Principle shown in Equation (18-1)[49].

$$\frac{[HbCO]}{[HbO_2]} = \frac{M.P_{CO}}{P_{O2}} \quad \textbf{(18-1)}$$

This equation, taken from Mcgrath[48], represents the relationship between haemoglobin, oxygen and carbon monoxide in blood. [HbCO] and [HbO_2] represent the concentration in blood of CO and O_2 respectively, PCO and PO_2 represent the partial pressures of CO and O_2 and M is the Haldane constant, which is the ratio of the affinity of blood for CO to that for O_2, and is approximately 250.

18.3.3 Phosphorus and Phosphine.

White phosphorus is extremely toxic whereas red and other forms such as black phosphorus are not classed as being toxic. White phosphorus is a small pyramidal molecule made of 4 phosphorus atoms whereas the other forms are polymeric chains. This makes them not susceptible to spontaneous ignition in air and not toxic. Both white and red phosphorus will produce phosphine when damp. Phosphine is a gas and thus has an inhalational route of entry.

It is important to separate the acute and chronic effects of phosphorus and phosphine. Unless it is ingested most exposure to phosphorus will be low level and chronic. Acute exposure to phosphine is possible and can lead to heart and lung damage as phosphine interferes with enzymes and protein synthesis. The US Agency for Toxic Substances and Disease Registry (ATSDR), in its leaflet about phosphine states[50] "Most deaths occur within the first 12 to 24 hours after exposure and are cardiovascular in origin. If the patient survives the first 24 hours the ECG typically returns to normal indicating that heart damage is irreversible. Deaths after 24 hours are usually due to liver failure."

Phosphine is also a central nervous system depressant. The Health Protection Agency (HPA) note that pure phosphine is odourless and that it is impurities that lead to the characteristic odour somewhere between garlic and decaying fish[51]. This means that the quoted odour threshold of 0.1 to 0.2 ppm (0.14 to 0.28 mg m^{-3}) is an unreliable indicator that phosphine is present and is not detected until just below the UK STEL (see 18.1.2.2) (15 minutes) of 0.3 ppm. The HPA say that 400 to 600 ppm of phosphine will be fatal after an exposure of 30 minutes to an hour[51]. They note that post-mortem evidence from 26 deaths found that lung oedema was the most common cause of death.

Chronic exposure to low levels of phosphine can cause bronchitis, gastrointestinal problems, visual and speech problems and the skeletal defects in the jaw and teeth noted from white phosphorus.

18.4 REFERENCES

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Appendix A GHS Classification

By 2015 all classification on Safety Data Sheets (SDS) should be as H statements. However, there are still many Material Safety Data Sheets (MSDS) in use that include risk (R) phrases and some safety documents include both R and H Statements together. The boundaries of the H statements are given below.

Acute Toxicity, Oral, LD_{50} (mg/kg)

1. H300 Category 1, 0 to less than or equal to 5
2. H300 Category 2, 5 < to less than or equal to 50
3. H301 Category 3, 50 < to less than or equal to 300
4. H302 Category 4, 300 < to less than or equal to 2000

Acute Toxicity, Dermal, LD_{50} (mg/kg)

1. H310 Category 1, 0 to less than or equal to 50
2. H310 Category 2, 50 < to less than or equal to 200
3. H311 Category 3, 200 < less than or equal to 1000
4. H312 Category 4, 1000 < less than or equal to 2000

Acute Toxicity, Gases, (ppm volume).

These are materials which are above or very close to their boiling point at the temperature of exposure (see below). This is not the same as the definition of a gas as a substance that is above its critical temperature.

1 H330 Category 1, 0 to less than or equal to 100 (0 to 0.01 %)

2 H330 Category 2, 100 < to less than or equal to 500 (0.01 % to 0.05 %)

3 H331 Category 3, 500 < to less than or equal to 2500 (0.05 % to 0.25 %)

4 H332 Category 4, 2500 < to less than or equal to 20000 (0.25 % to 2 %)

n.b. For many flammable gases the high end of category 4 will be in the explosive range.

Acute Toxicity, Vapours, (mg $litre^{-1}$).

A vapour is the gaseous form of a substance released from its liquid or solid state with the provision that if the liquid is so close to its boiling point that it cannot be held as a liquid in the open it should be considered as a gas.

1. H330 Category 1, 0 to less than or equal to 0.5 (0 to 500 mg m^{-3})
2. H330 Category 2, 0.5 < to less than or equal to 2 (500 to 2000 mg m^{-3})
3. H331 Category 3, 2 <to less than or equal to 10 (2000 to 5000 mg m^{-3})
4. H332 Category 4, 10 < to less than or equal to 20 (5000 to 20000 mg m^{-3}

Acute Toxicity, Aerosols, Dusts and mists (as mg/l).

A dust is a suspension of solid particles in air; a mist is a suspension of droplets in air. Both may have vapour associated with them but the concentration of the vapour from a mist will be generally higher than from a dust.

1 H330 Category 1, 0 to less than or equal to 0.05 (0 to 50 mg m^{-3})

2 H330 Category 2, 0.05 < to less than or equal to 0.5 (50 to 500 mg m^{-3})

3 H331 Category 3, 0.5 < to less than or equal to 1 (500 to 1000 mg m^{-3})

4 H332 Category 4, 1 < to less than or equal to 5 (1000 to 5000 mg m^{-3})

CHAPTER 19
ENVIRONMENTAL MANAGEMENT OF EXPLOSIVES

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19 ENVIRONMENTAL MANAGEMENT OF EXPLOSIVES

Authors – T J Temple and M K Ladyman (Cranfield University)

19.1 AWARENESS SUMMARY

The training with and, test and evaluation of Weapons, Ordnance, Munitions and Explosives (WOME) involves the release to ground, water and air of chemicals which could potentially have an adverse effect on the environment. Therefore cognisance needs to be taken of the broad legislative framework which governs environmental issues generally, and the way in which this applies from cradle to grave in the WOME life cycle.

Legislation cascades down from international conventions, treaties and protocols, through European directives and regulations to UK law. That legislation is then interpreted by the Ministry of Defence through its various Joint Services Publications.

At the international level there is a fundamental difference between the internationally agreed framework that applies in warfare under the Geneva Conventions and that which applies in peacetime for training, test and evaluation. The Geneva Conventions state that it is prohibited to employ methods or means of warfare which are intended, or may be expected, to cause widespread, long-term and severe damage to the natural environment. In peacetime there are more stringent restrictions, such as the MARPOL Convention which dictates what can be placed in the marine environment and the Oslo Convention which prohibits the dumping of WOME at sea.

At the EU level there is little legislation specific to the environmental consequences of manufacturing, functioning and disposal of WOME, albeit REACH legislation (see 1.3.2.4.6) does encompass some of the chemicals used in munitions.

UK legislation applicable to WOME includes the Environmental Protection Act of 1990 (EPA90) and the Environment Act of 1995 (EA95). The latter saw the establishing of the Environment Agency as the regulator for England and Wales and the Scottish Environmental Protection Agency for Scotland. Arrangements for Northern Ireland followed later. It deals with the liability for paying for the remediation of land contaminated by past activities of the Ministry of Defence and its predecessor organisations involving the use of WOME. The act also sets out the duty of the MoD toward the National Parks on which the Department does much of its training at locations such as Dartmoor and Otterburn. There are statutory limits on the permissible emissions to air for a range of potential pollutants, these including some of the products of functioning of WOME. The Water Resources Act states that a person contravenes the act if he causes or knowingly permits any poisonous, noxious or polluting matter or any solid waste matter to enter any controlled waters. This is important in the context of training and test and evaluation areas where WOME is used, given the possibility that explosives, heavy metals and the products of functioning of WOME may

migrate into controlled waters such as rivers, lakes and aquifers. The UK does not have threshold levels for explosives in drinking water, but in areas where there is the possibility of contamination from explosives the relevant authority may impose thresholds on nearby watercourses. These may be based on an agreed level, or by comparison with threshold levels imposed by other nations such as the United States.

Most breaches of environmental law are criminal offences. The penalties are usually a fine and/or imprisonment. For cases tried in the Magistrates' court, the maximum penalty is usually a fine and/or six months' imprisonment. In the case of the Crown Court, the maximum penalty is usually an unlimited fine and/or two years imprisonment.

Within Defence the policy relating to environmental protection is set out in Defence Safety Authority publication (DSA 01.1) "Defence Policy for Health, Safety and Environmental Protection", which describes in high-level terms the corporate system for the management of environmental protection and safety in the Ministry of Defence (MOD). Specifically it states that within the United Kingdom the Ministry of Defence will comply with all applicable environmental legislation. When operating overseas the Department will apply UK arrangements where reasonably practicable and, in addition, respond to host nations' environmental expectations. The policy goes on to state that where Defence has exceptions, derogations or dis-applications from environmental legislation, arrangements will be maintained that are, so far as reasonably practicable, at least as good as those required by UK legislation. Various Defence Safety Authority and Joint Services Publications sets out more detailed guidelines for the management of environmental protection in Defence.

The science underpinning the environmental impact of the functioning of explosives and munitions is a complex subject, with many factors contributing to the fate and effects of contaminants on the environment. These include the quantity of contaminant, the source and location of contamination, the local climate and the chemical composition of the munition. Nevertheless general behaviours and impacts of the most common explosive contaminants have been identified. This process is assisted by the use of the source-pathway-receptor (SPR) pollution linkages concept. This describes how a contaminant can enter the environment from a source, such as unexploded ordnance (UXO) or the products of functioning a munition in its design mode, and move through the environment by air, soil or water (pathway) to a receptor, usually defined as an entity that may be adversely affected by contact with a contaminant. A receptor can include flora and fauna, humans, as well as the ecology of an area. The contamination from specific explosives on ranges is highly dependent on the training or test and evaluation activity. For example soil at impact areas is most likely to be contaminated with RDX, HMX and TNT, whereas soil at firing areas is more likely to be contaminated with propellants such as nitroguanidine (NQ) and nitrocellulose (NC). Traces of explosives and degradation products have also found in nearby surface water, and/or groundwater indicating that explosives are able to travel through soil, and in water run-off. The extent to which this occurs depends upon the solubility of the

explosive in water, generally measured in milligrams per litre. Another factor affecting the fate and transport of explosives is the soil sorption coefficient which essentially describes the likelihood of the explosive to bind to soil particles. In both cases, solubilisation in water or binding to the soil, explosives are vulnerable to degradation by bacteria in the soil (biodegradation) or sunlight (photodegradation).

In order to assess the environmental impact of military materiel including WOME, the MOD has developed a bespoke platform known as the Project Orientated Environmental Management System (POEMS), which was designed to facilitate the application of an Environmental Management System (EMS) to specific MOD activities and equipment throughout the life cycle. POEMS is based on the international standards ISO 14001 and ISO 14040, the former representing the cornerstone of EMS and the latter covering life cycle assessment (LCA). POEMS comprises nine core procedures (see table 19-4).

One of the most important elements of POEMS is Serial 5 - the compilation of an environmental features matrix which ranks the environmental impacts in priority order to determine the most significant ones associated with any activity, each impact being scored in terms of its severity and frequency or duration.

The implementation of POEMS accordingly identifies those environmental impacts that exceed a minimal threshold score and require further investigation in the form of an Environmental Impact Assessment. Two approaches for conducting such an assessment are available; the first involves the bringing together a range of Suitably Qualified and Experienced Personnel (SQEP) who possess (a) a good knowledge of explosives chemistry and (b) have recent and relevant experience of the way in which WOME is used in the field. The second approach involves compiling numerical details of the materials used in a weapon system, and the chemical products of functioning that weapon. These are compared with statutory pollution limits.

A broader range of environmental procedures relevant to the estate and infrastructure is given in The MOD Sustainability and Environmental Appraisal Tools (SEAT) Handbook, which is the single point of reference for the suite of appraisal tool methodologies (see Table 19-3).

Where explosives are in constant use at a particular location, and pathways to receptors have been identified, it may be necessary to monitor receptors for traces of contaminants. Various sampling techniques are available for such monitoring; for instance multi-increment sampling is a method developed to overcome the difficulties with obtaining representative sample of very large areas of heterogeneously deposited contamination on soil. Instead of taking and analysing discrete samples which represent only a tiny portion of the entire area, multiple samples are taken and combined over several large areas of a range, thus smoothing out the heterogeneities. If significant contamination is identified, then remediation is required. That remediation may be chemical, physical or biological. Chemical remediation techniques include in situ chemical oxidation; physical remediation generally involves disposal of contaminants with

controlled fires, whereas biological remediation is undertaken through plant uptake and concentration of contaminants or metabolism or degradation into less toxic compounds.

Computer models are commonly used to attempt to predict source – pathway - receptor linkages for explosives. Environmental models use mathematical approaches to combine different forms of data, such as toxicological data and characteristics of the environment, into concise information suitable for environmental risk assessment, or to determine contamination levels in an area or environment.

Several countries, including the USA and Norway have developed databases of information for range management. At the current time, the UK does not have an established environmental database for WOME; however relevant research is undertaken when required on a case by case basis.

19.2 ENVIRONMENTAL LEGISLATION AND GOVERNANCE

19.2.1 Introduction

Within this section pertinent legislation is described. It is by no means exhaustive, but rather it is intended to give the reader a broad appreciation of the environmental legislative framework within which the Weapons, Ordnance, Munitions and Explosives (WOME) community must operate. It should be read in conjunction with Chapter 3 (Legislation). The chapter therefore aims to be a starting point for understanding the intricacies of environmental legislation and to guide the reader towards the legislation of relevance.

There is a legal requirement for all businesses, organisations and government departments to manage their environmental impacts. The MOD is not exempt from such legislation. Non-compliance with environmental law risks legal action which may include prison sentences or financial penalties. But beyond the legal compliance there are other benefits of compliance such as improved public perception, and financial gains due to reduction in energy use and waste production.

19.2.2 The Evolution of Modern Environmental Legislation

There is a hierarchy of legislation cascading down from international treaties and conventions through European legislation to UK law, which is then reflected in Defence-specific arrangements. These arrangements are illustrated in Figure 19-1.

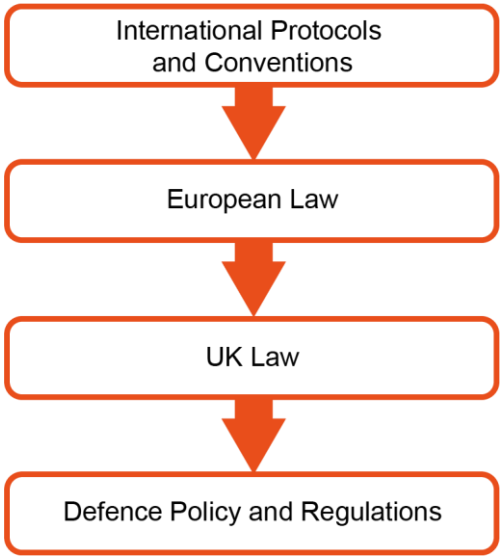


Figure 19-1 Hierarchy of legislation

19.2.3 International Environmental Legislation

International law is self-enforced by agreement to a treaty, also known as protocols, conventions and agreements. International Treaties seek to regulate issues as diverse as Climate Change, Ozone Depleting Substances (ODS) and International Waste Shipments as well as explosive governance in conflict situations and training.

19.2.4 Geneva Convention

Under International Humanitarian Law the United Kingdom is legally obliged to ensure that all weapons and associated equipment that it obtains, plans to acquire, or develops, comply with the UK's treaty and other obligations. This legal review process is mandated by Article 36 of The First Protocol of 1977 additions to the Geneva Conventions of 1949 (Additional Protocol I), which is the section on 'Methods and Means of Warfare', and to which the UK is a Party. Article 36 states:

"In the study, development, acquisition or adoption of a new weapon, means or method of warfare, a High Contracting Party (i.e. the UK) is under an obligation to determine whether its employment would, in some or all circumstances, be prohibited by this Protocol or by any other rule of international law applicable to the High Contracting Party."

Article 35 of the 1977 Additional Protocol I of the Geneva Conventions 1949 states that:

"It is prohibited to employ methods or means of warfare which are intended, or may be expected, to cause widespread, long-term and severe damage to the natural environment." MOD interpretation of Article 35 is that serious damage is caused to flora and fauna over tens of square kilometres lasting tens of years.

Article 55 of the 1977 Additional Protocol I of the Geneva Conventions 1949 states that:

"Care shall be taken in warfare to protect the natural environment against widespread, long-term and severe damage. This protection includes a prohibition of the use of methods or means of warfare which are intended or may be expected to cause such damage to the natural environment and thereby to prejudice the health or survival of the population."

A legal review is required to be undertaken to determine the legality of the use of military equipment in the context of international armed conflict. This review does not cover any domestic use of the equipment (i.e. within the UK). The process for the latter is explained in JSP 520 "Safety and Environmental Management of Ordnance, Munitions and Explosives over the Equipment Acquisition Cycle" Part 2 "Guidance", Vol 7 "Legislation Compliance".

Legal reviews are conducted on behalf of the MOD by the Legal Team at the Development, Concepts and Doctrine Centre (DCDC) at Shrivenham to whom all queries about the necessity or conduct of a legal review should be addressed. It should be emphasised that the Geneva Conventions only apply during armed conflict.

19.2.5 Training

When training is taking place in either the UK or overseas, much more stringent regulations apply. If the training is on land, then the host nation's legal framework applies and in most Western nations this is very rigorous.

If the training is at sea, then the International Convention for the Prevention of Pollution from Ships, 1973 as modified by the Protocol of 1978, known as the MARPOL (marine pollution) Convention, applies. MARPOL has six Annexes covering pollution by oil, noxious liquids, packaged harmful substances, sewage and garbage, also air pollution from ships.

19.2.6 Sea Dumping

Historically large quantities of OME were disposed of by sea dumping, much of this being after the Second World War. Estimates suggest that in excess of one million tonnes of munitions were dumped in Beaufort's Dyke in the Irish Sea between Scotland and Northern Ireland. This is a very deep trench, and in principle it should have been a safe place to dump munitions, but in practice many have subsequently been washed ashore, with some consequent injuries. Most probably this is because the ships which were tasked with dumping the munitions in the deep trench did not go far enough off-shore and left them in shallow waters, indeed anecdotal evidence supports this hypothesis, but there remains a degree of uncertainty over this. In addition some 168,000 tonnes were dumped in Skagerrak and some 300,000 tonnes in the North Sea. There are some 148 individual dumpsites spread from Iceland to Gibraltar as shown in Figure 19-2.

In 1972 The Oslo Convention for the prevention of Marine Pollution by dumping from ships and aircraft heralded the end of the practice. Dumping by the UK finally ceased in 1973 prior to the ratification by the Government of the Convention in 1975. This was later subsumed Into Convention for the Protection of the Marine Environment of the North-East Atlantic – the OSPAR Convention which was concluded in Paris on 22nd September 1992. This latter Convention entered into force on 25th March 1998.

It should be noted that, for the purpose of the Convention, "dumping" does not include “placement of matter for a purpose other than the mere disposal thereof, provided that such placement is not contrary to the aims of this Convention”. Therefore the firing of munitions from land, ships and aircraft into the sea is allowable both for training and Test & Evaluation (T&E) purposes.

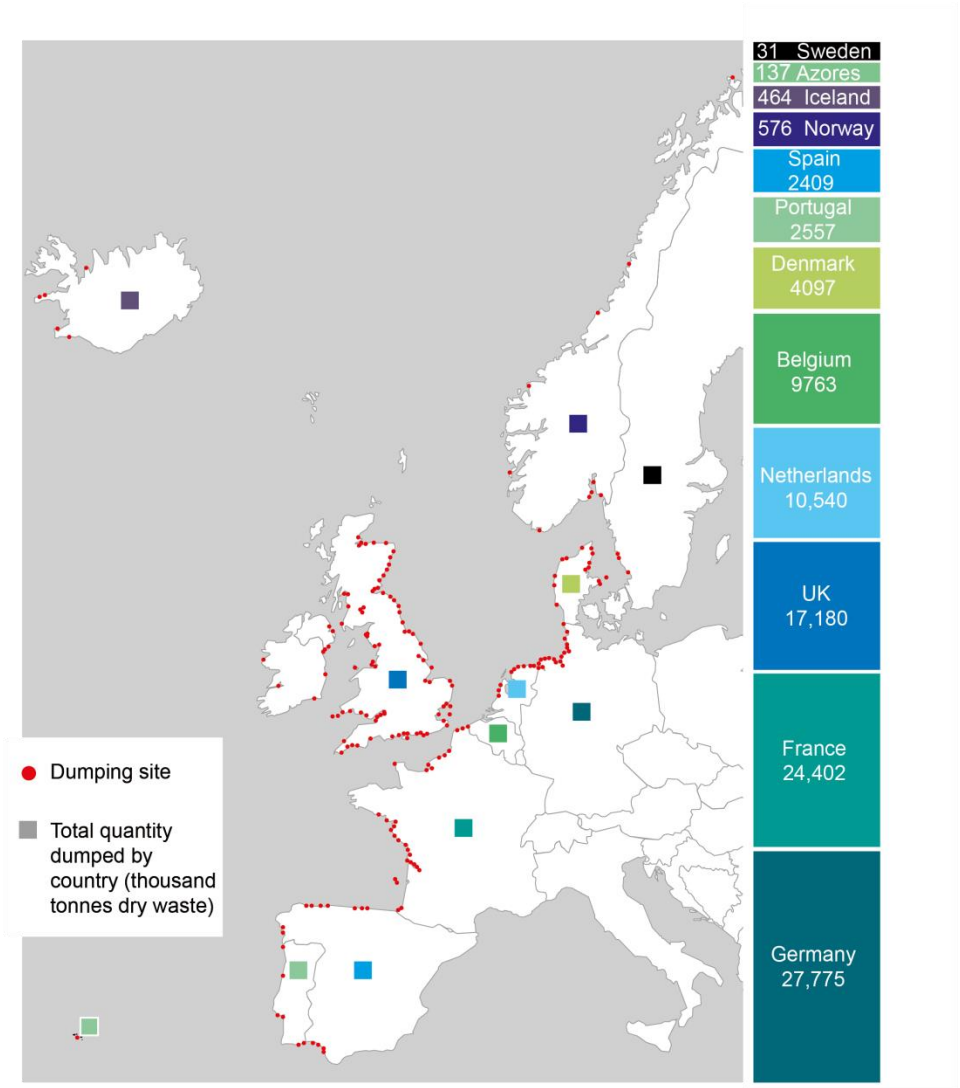


Figure 19-2 Sea dumping locations and quantities by country

19.2.7 European Environmental Law

At the time of writing the UK has voted to leave the EU and has invoked Article 50 of the Lisbon Treaty which triggered the withdrawal process. The terms of the interface arrangements with the EU after this has taken place have yet to be determined, and hence the requirement or otherwise to align UK legislation to EU Directives. In the interim a Repeal Act will transpose EU legislation into UK law pending determination as to whether EU Directives, etc. should in future remain part of UK legislation.

Since the UK joined the European Community in 1972 up until the UK referendum voted to leave the EU, European environmental legislation has increasingly shaped most domestic environmental laws. In turn European legislation has frequently been informed by international Protocols and Conventions. European law falls into a number of categories:

- Regulations are directly applicable laws in all member states
- Directives are legally binding documents which specify desired outcomes or objectives and specific dates for achievement of those outcomes. They leave the means of achieving the objectives to national governments.
- Decisions are directed at specific aspects and are legally binding on specific persons/institutions/procedures but are not generally applicable.
- Recommendations and Opinions are produced by the EU Parliament by the various committees and are not legally binding.

A series of single issue Directives were initially made but these have increasingly been replaced by “Framework” and “Daughter” directives. The aim of Framework Directives is to take a more integrated approach to environmental protection.

The Single European Act of 1986 requires under Article 130R that all policies of the EU should contain a component for environmental protection:

- Article 130R(1) covers measures to preserve, protect and improve the environment, to protect human health and to ensure utilisation of natural resources.
- Article 130R(2) embraces the principle of preventative action, that environmental damage should be corrected at source as a priority and that the polluter should pay.
- Article 130R(4) covers the "subsidiarity principle", that is that the EU should only take action when the objectives could be better achieved at community rather than national level

There are a number of EU Directives relating to OME, for instance Directive 2014/28/EU of the European Parliament and of the Council dated 26 February 2014 relates to the harmonisation of the laws of the Member States relating to the making available on the market and supervision of explosives for civil uses. There is, however, little EU legislation specifically referring to OME and the environment.

19.2.8 UK Environmental Legislation

There are three legal systems in the UK for England and Wales, Northern Ireland and Scotland. UK law comprises two elements; criminal and civil. Criminal is the body of law that deals with criminal offences. This may take the form of Statutes or Acts of Parliament. It may be delegated legislation such as Enabling Acts. It may also be through the mechanism of Statutory Instruments. Civil law governs relations between individuals or disputes between two parties.

19.2.9 Environmental Legislation Relevant to Activities involving Explosives

The principal UK legislation covering explosives is contained in the Explosives Regulations 2014 and the Pyrotechnic Articles (Safety) Regulations 2015. These are principally focussed on the safe use of explosives and pyrotechnics, and make no specific reference to the environment. Explosives legislation is covered in detail in Chapter 3. There is, however, much legislation which relates to and controls the use of OME. Arguably the two most important Acts of Parliament on environmental protection are the Environmental Protection Act of 1990 (EPA90) and the Environment Act of 1995 (EA95). EPA90 comprises seven parts:

1. Integrated pollution control
2. Waste on land
3. Statutory nuisance
4. Litter
5. Radioactive substances
6. Genetically modified food
7. Nature conservation

Of these, 1, 2, 3, 4, and 7 are pertinent to the functioning of OME on training and Test & Evaluation ranges. Statutory nuisance in this context includes noise and the creation of smoke and dust clouds.

EA95 expanded upon EPA90 and saw the establishing of the Environment Agency as the regulator for England and Wales and the Scottish Environmental Protection Agency for Scotland Arrangements for Northern Ireland followed later. EA95 covered other issues such as:

1. Contaminated land
2. National waste strategy
3. National parks
4. Air quality strategy
5. Minerals planning and abandoned mines
6. Water pollution measures
7. Statutory nuisance in Scotland

All of these with the exception of (5) are relevant to the functioning of OME.

EPA90 and EA95 brought together a range of earlier laws into a coherent whole, and subsequently more specific legislation on the various subject areas emerged.

Three areas within EA95 need explanation in terms of their relevance to OME use on training ranges.

19.2.9.1 Land contamination

EPA90 Part IIA provides the regulatory regime for the identification and remediation of contaminated land. EA95 Section 57 contains the provisions, which make up Part IIA of EA90, setting out a new regime for the identification and remediation of contaminated land. The Contaminated Land (England) Regulations (2006) under

DEFRA Circular 01/2006 “Contaminated Land” provides details of the provisions including the definition of contaminated land, identification and remediation; also the liability for who pays for remediation. There is a substantial legacy issue associated with contaminated land arising from the past activities of the Ministry of Defence and its predecessor organisations involving the use of OME.

19.2.9.2 National Parks

Over two thirds of the 240,000 hectares of land owned by the MOD is held for the purpose of training the armed forces. This land is the Defence Training Estate, and comprises 16 major armed forces training areas, and 104 other minor training areas, ranges and camps. Some of this estate is on National Parks, for instance Dartmoor and Otterburn, and significant precautions have to be taken to ensure that training activities do not conflict with the purpose of the parks.

The aims and purposes of National Parks are laid out in law in the form of the 1949 National Parks and Access to the Countryside Act.

There are slightly different aims and purposes for the national parks in Scotland and for the Broads National Park, compared to other national parks in England and Wales. When the aims and purposes conflict with each other, then the “Sandford Principle” is used to give more weight to conservation of the environment.

EA95 revised the original legislation and set out two statutory purposes for national parks in England and Wales:

- Conserve and enhance the natural beauty, wildlife and cultural heritage
- Promote opportunities for the understanding and enjoyment of the special qualities of national parks by the public

When national parks carry out these purposes they also have the duty to seek to foster the economic and social well-being of local communities within the national parks.

The 21st century brought two Scottish National Parks into existence, the Cairngorms and Loch Lomond & the Trossachs, created by the National Parks (Scotland) Act 2000. In 2005, the New Forest finally joined the National Park 'family'. The South Downs was established on 31 March 2010, and became fully functioning, including becoming the planning authority for the National Park, on 1 April 2011.

The duty of the MoD toward National Park purposes is set out in S62 (2) of the Environment Act 1995 and the Government Policy on Military Activity in National Parks in Circular 12/96. A Declaration of Intent between The Ministry of Defence and the Association of National Park Authorities (NPAs) has been established. The Declaration aims to set a framework for maintaining and enhancing working relationships between the MoD and the NPAs and its landlords and relates to any areas subject to MOD training or other rights in areas located in National Parks in Great Britain. The functioning of OME on the National Parks is necessarily a sensitive issue, and, quite apart from the need to operate legally, there are reputational issues to be considered.

19.2.10 Air Quality

Statutory Instrument 2010 No. 1001 “Environmental Protection - The Air Quality Standards Regulations 2010 came into force on 11th June 2010 These set statutory limits for emissions to air as shown in

Table 19-1.

In practice these limits are set for continuous or semi-continuous processes such as vehicle and industrial plant emissions and are very unlikely to be exceeded by the functioning of OME. In the UK the most relevant examples of a trial whereby there were likely to be longer term emissions were the disposal at the Shoeburyness Test & Evaluation range of 120,000 Barmines by open burning and the disposal at the same range of mixed natures of OME, also by open (cage) burning. Measurements of the resultant levels of atmospheric pollutants showed that natural dispersion rapidly reduced the concentrations to well below the statutory limits. Nevertheless, if calculations or measurements show that the statutory limits are being approached, then mitigation measures need to be put into place.

Table 19-1 Statutory Limits for Emissions to Air

Pollutant	Averaging period	Limit value
Sulphur dioxide	One hour	350 µg m^{-3} not to be exceeded more than 24 times a calendar year
	One day	125 µg m^{-3} not to be exceeded more than 3 times a calendar year
Nitrogen dioxide	One hour	200 µg m^{-3} not to be exceeded more than 18 times a calendar year
	Calendar year	40 µg m^{-3}
Benzene	Calendar year	5 µg m^{-3}
Lead	Calendar year	0.5 µg m^{-3}
PM_{10} (particulate matter which passes through a size-selective inlet with a 50 % efficiency cut-off at 10 µm aerodynamic diameter).	One day	50 µg m^{-3}, not to be exceeded more than 35 times a calendar year
	Calendar year	40 µg m^{-3}
Arsenic	Target value for the total content in the PM10 fraction averaged over a calendar year	6 ng m^{-3}
Cadmium		5 ng m^{-3}
Nickel		20 ng m^{-3}
Benzo(a)pyrene		1 ng m^{-3}
$PM_{2.5}$ (particulate matter which passes through a size-selective inlet with a 50 % efficiency cut-off at 2.5 µm aerodynamic diameter).	Calendar year	25 µg/ m^{-3}
Carbon monoxide	Maximum 8 hour daily mean	10 mg m^{-3}
Ozone	Maximum daily 8 hour mean	Target value 120 µg m^{-3} not to be exceeded on more than 25 days per calendar year averaged over three years

Table 19-2 Water and Soil Threshold levels for Common Explosives

Explosive/ degradant	Drinking water threshold µg L^{-1}	Recommended soil threshold mg kg^{-1}	Source
2,4-Dinitrotoluene (DNT)	100	1.6 (residential) 5.5 (industrial)	United States Environmental Protection Agency (DNT)
2,6- Dinitrotoluene (DNT)	40	0.3 (residential) 1.2 (industrial)	2012 Drinking Water Standards and Health Advisories tables
HMX	100	N/A	ATSDR factsheet
Nitrocellulose	Not considered toxic		
Nitroglycerine	Unregulated, but considered a candidate contaminant		EPA Drinking Water Contaminant List
Nitroguanidine	3500		2012 Drinking Water Standards and Health Advisories tables
Perchlorate	Drinking water: 1-18 Groundwater: 1-72	55 (residential) 720 (industrial)	US EPA Technical Factsheet
RDX	100	N/A	ATSDR factsheet
Trinitrotoluene (TNT)	20	19 (residential) 79 (industrial)	United States Environmental Protection Agency (TNT)

19.2.11 Water Pollution Measures

The Water Resources Act 1991 Chapter 57 “Offences of polluting controlled waters” states that *“a person contravenes this section if he causes or knowingly permits any poisonous, noxious or polluting matter or any solid waste matter to enter any controlled waters”*. ‘Causing' means not only deliberately releasing any polluting matter but also causing the pollution accidentally, by being the operator of a plant or process. “Controlled waters” in this context means any river, lake, pond or aquifer. The Water Act 2003 Chapter 37 “Contaminated land: pollution of controlled waters” amends the definition of "contaminated land" in Section 78A of the Environmental Protection Act 1990 so that it applies only where significant pollution of controlled waters is being caused, or there is a significant possibility of such pollution being caused. These Acts are important in regard to training areas where OME is used, given the possibility that explosives, heavy metals and the products of functioning of OME may migrate into controlled waters. An example is the Central Impact Area in the Salisbury Plain Training Area. This lies over an aquifer from which the drinking water for the city of Salisbury is extracted.

The UK does not have threshold levels for explosives in drinking water, but in areas where there is the possibility of contamination from explosives the relevant authority may impose thresholds on nearby watercourses. The threshold limits imposed may be based on an agreed level or by comparison to threshold levels imposed by other nations. Table 19-2 gives water and soil threshold levels for common explosives as recommended by the United States Environmental Protection Agency where UK figures are not available.

19.2.12 Penalties for Breaches of Environmental Law

Most breaches of environmental law are criminal offences. The penalties are usually a fine and/or imprisonment. For cases tried in the Magistrates’ court, the maximum penalty (2017) is usually a fine of £20,000 or £50,000 and/or six months’ imprisonment. In the case of the Crown Court, the maximum penalty is usually an unlimited fine and/or two years imprisonment. The main environmental regulators in England are the Environment Agency (EA) and local authorities, and Natural Resources Wales in Wales. The Scottish Environment Protection Agency (SEPA) is Scotland's principal environmental regulator. Northern Ireland Environment Agency (NIEA), which is part of Northern Ireland Executive's Department of Environment, is Northern Ireland's environmental regulatory body. Environmental regulators can, in some cases, serve an enforcement notice on a business requiring it to rectify a breach of environment law. The regulator may also have the power to order the closure or suspension of the business until the breach has been rectified. Breach of any of these types of notice is a criminal offence. Environmental regulators can, in some cases, serve a notice on a business requiring it to clean up any contamination, including water pollution, they have caused. Breach of this type of notice is a criminal offence. The regulators can also prosecute the business’ directors, managers, secretary or other similar officers or person purporting to

act in any such capacity, if it can be shown the offence was committed with their consent or connivance, or was attributable to their neglect. New legislation has given regulators, including the EA and local authorities, the power to impose civil penalties on businesses, as an alternative to prosecuting, for certain types of breaches, including breaches of environmental legislation. Civil penalties include fixed monetary penalties and enforcement undertakings. The civil penalties approach is more flexible and designed to fit the penalty more appropriately to the crime. It frees resources for criminal prosecutions while removing the burden from respectable companies that make a low level breach of regulations and raises the penalties for people who carry out deliberate environmental crimes.

19.3 DEFENCE POLICIES AND REGULATIONS

Within Defence the policy relating to environmental protection is set out in Defence Safety Authority publication (DSA 01.1) “Defence Policy for Health, Safety and Environmental Protection”, which describes in high-level terms the corporate system for the management of environmental protection and safety in the Ministry of Defence (MOD). It states that the MOD has as a fundamental objective to protect the environment when undertaking all defence activities. This includes the use, transport and destruction at end of life of explosives where there is potential for interaction with and contamination of the environment. Specifically it spells out the Secretary of State’s policy on environmental protection as follows:

1. Within the United Kingdom the Ministry of Defence will comply with all applicable environmental legislation.
2. Overseas the Ministry of Defence will apply UK arrangements where reasonably practicable and, in addition, respond to host nations’ environmental expectations.
3. Where Defence has exceptions, derogations or dis-applications from environmental legislation, arrangements will be maintained that are, so far as reasonably practicable, at least as good as those required by UK legislation.

More specific directions and guidance are given in Joint Services Publication (JSP) 418 “Management of Environmental Protection in Defence”.

JSP418 sets out guidelines for the management of environmental protection in defence and states that all MOD sites should be covered by an Environmental Management System (EMS). Part 2 of JSP 418 “Guidance” contains a series of leaflets 01 – 07 as shown in Table 19-3. Leaflets 01 – 05 are particularly relevant to the environmental impact of OME.

It is also MOD policy that all new acquisition projects must have a safety and environmental management system that defines the environmental impact of the acquisition throughout the lifecycle. The MOD procedures for ensuring that this takes place are in the Project Oriented Environmental Management System (POEMS). Further details of POEMS are given in Section 4 of this chapter. The specific application of an Environmental Management System to OME is

described in in JSP520 (part 2, volume 3) – “Safety and Environmental Management of Ordnance, Munitions and Explosives (OME) over the Equipment Acquisition Cycle”.

A broader range of environmental procedures relevant particularly to the estate and infrastructure is given in The MOD Sustainability and Environmental Appraisal Tools (SEAT) Handbook, which is the single point of reference for the suite of appraisal tool methodologies used on Estates related plans, programmes projects and activities such as military training within MOD. This contains eight Sections as shown in Table 19-4. Sections 2, 4 and 5 are particularly relevant to the environmental impact of OME.

Table 19-3 JSP 418 Guidance Leaflets

Document	Title
Leaflet 01	Environmental Management Systems
Leaflet 02	Pollution Prevention
Leaflet 03	Controlled Waste
Leaflet 04	Statutory Nuisance
Leaflet 04-1	Environmental Noise
Leaflet 05	Hazardous Substance and Restricted Materials
Leaflet 06	Fluorinated Greenhouse Gases
Leaflet 07	Ozone Depleting Substances

Table 19-4 MOD Sustainability and Environmental Appraisal Tools Handbook Sections

Document	Title
Section 1	Summary Booklet
Section 2	Sustainability Appraisal
Section 3	Strategic Environmental Assessment
Section 4	Environmental Impact Assessment
Section 5	Habitats Regulation Assessment
Section 6	Defence Related Environmental Assessment Method (DREAM)
Section 7	Climate Impacts Risk Assessment Method (CIRAM)
Section 8	Linked Tools

19.4 ENVIRONMENTAL SCIENCE OF EXPLOSIVES

19.4.1 Introduction

Many factors contribute to the fate and effects of contaminants in the environment such as the quantity of contaminant, the source of contamination, the location of contamination, the local climate and the chemical composition of the contaminant. It is impossible to predict the environmental impact of any one explosive in a given environment; however general behaviours and impacts of the most common explosive contaminants have been identified. Contaminated areas, and most likely transport pathways can also be established through a combination of site and literature knowledge and, if possible, computer modelling techniques. Armed with this knowledge, it is possible to determine when monitoring (section 19.6) or remediation (section 19.7) activities would be necessary, and which methods it would be appropriate to use.

The aim of this section is to give an overview of the complex environmental interactions and processes that contribute to the transport of explosive contaminants through the environment and the potential impact of specific explosives on the environment.

19.4.2 Source-Pathway-Receptor Pollution Linkages Model

One of the most useful ways to describe the fate and transport of contaminants in the environment is using the source-pathway-receptor (SPR) pollution linkages concept. It describes how a contaminant can enter the environment from a source, such as unexploded ordnance (UXO), and move through the environment by air, soil or water (pathway) to a receptor, usually defined as an entity that may be adversely affected by contact with a contaminant. An ‘entity’ can include flora and fauna, humans, as well as the ecology of an area such as a lake, or a Site of Special Scientific Interest (SSSI). For example, explosive residue from a damaged UXO (source) may be dissolved in water from rainfall and transferred into the soil. The explosive may then travel through the soil until it reaches an underground aquifer. In an isolated incident the concentration of explosive would be undetectable and in most cases would be unlikely to affect a receptor. However, if contamination from explosive residue is a frequent occurrence the quantities reaching groundwater may become significant and affect humans using the aquifer as a potable water source, or even contaminate downstream rivers or lakes and affect local flora and fauna populations (Figure 19-3).

The point at which a contaminant reaches and affects a receptor is when the contaminant can be said to cause an environmental impact. If the SPR linkages between the source and receptor are broken at any point then no environmental impact will be observed, that is, if the contaminant does not reach a receptor. When considering explosive contaminants in the context of the MOD the most likely source of contamination is from munitions containing explosives, and the most likely means by which explosives enter the environment is through training

or Test & Evaluation activities on ranges. Therefore much of the following discussion will focus on the environmental impact of explosives on such ranges; however the underlying environmental science would be applicable to explosive contamination at any site.

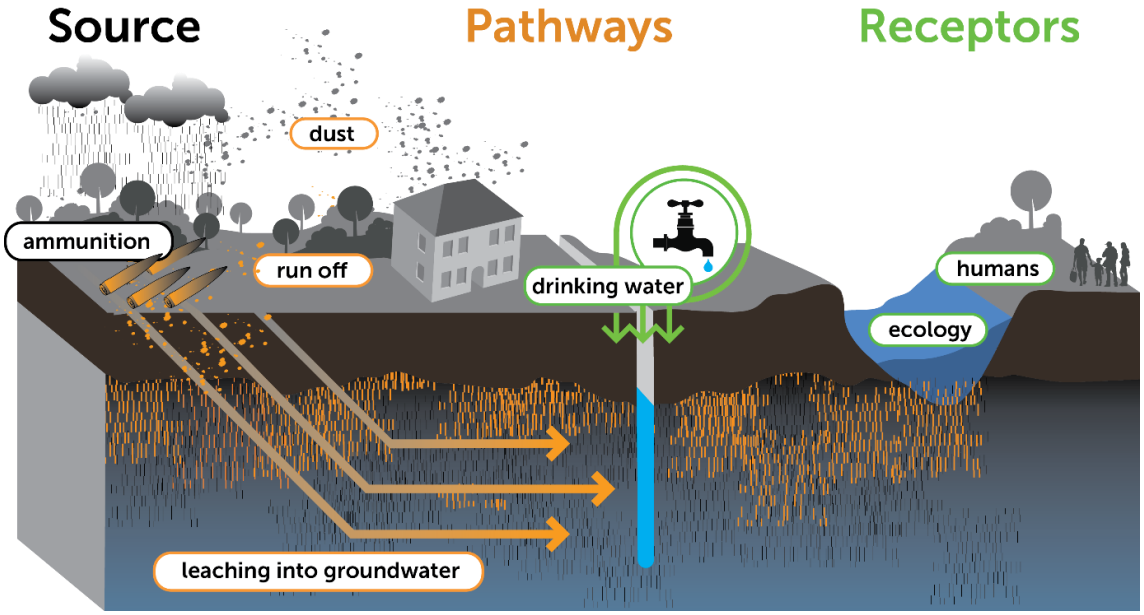


Figure 19-3 A schematic showing some potential source-pathway-receptor linkages model for unexploded ordnance on a range (Courtesy of Cranfield University)

The SPR concept should be used in risk assessments to link contaminant sources to potential exposure routes. The degree of risk to a receptor depends on the amount and frequency of contaminant exposure(1). For explosives the most common route for transport in the environment is through soil and water as any particulates released into the air are likely to fall back to the ground in close proximity to the site where the explosive initiated. Small isolated quantities of explosive residue that are carried further are unlikely to cause significant environmental impact. For explosives, contamination is usually due to the cumulative build-up of residue in areas of long-time explosive use, such as impact sites. Thus, when assessing munitions or explosives for environmental impact it is important to account for the cumulative impact of multiple detonations in specific locations.

19.4.3 Explosive Contamination on Ranges

19.4.3.1 Common explosive contaminants

Studies conducted at over 30 different military installations in the United States have demonstrated that explosive contaminants are present in surface soils on training ranges(2). These findings contradicted the long-time assumption that 99.99 % of the energetic material in munitions is consumed in the firing or detonation process. However, the baseline figures were determined by physical and chemical modelling on the assumption that all detonations are high-order.

More recent research has shown that although high-order detonations do almost completely consume the explosive materials, there are also a small percentage of munitions that do not undergo a high-order detonation when fired. In cases where detonation is not high-order, it has been shown that unconsumed explosive material may be scattered unpredictably on the soil as particulate residue[2–5]. It has also been recognised that sympathetic detonation of UXO can result in high quantities of explosive residue in the environment. In some cases munitions may become buried, and subsequently damaged leading to exposure of the explosive filling to the environment[6,7]. Finally, the destruction of end-of-life or damaged munitions through open burning or open detonation can leave high quantities of explosive and propellant residues at the burning ground.

The contamination from specific explosives on training ranges is highly dependent on the training activity. For example soil at impact areas is most likely to be contaminated with RDX, HMX and trinitrotoluene (TNT), whereas soil at firing areas is more likely to be contaminated with propellants such as nitroguanidine (NQ) and nitrocellulose (NC). There may also be traces of lead at the firing area. In most cases, soil has also been found to be contaminated with by-products of the explosives and propellants generated by biological or physical degradation. Traces of explosives and degradation products have also found in nearby surface water, and/or groundwater indicating that explosives are able to travel through soil, and in water run-off[8, 9].

Given the ability of explosives to travel sometimes significant distances in the environment it can be difficult to establish the source of the contamination, and even harder to determine the transport pathway. Transport in the environment is mainly determined by the chemical composition of the explosive combined with the local geology and climate[10]. Highly water soluble explosives could dissolve in rain water and enter the soil very quickly in wet climates, but if the explosive also tends to be absorbed by soil it will not travel much deeper than the surface. Extensive research has been conducted on the oldest and most common explosives and is discussed in the following sections, however it must be remembered that the environmental impact of a specific explosive depends, not only on its chemical properties, but also on the local climate and geology which are extremely variable. Therefore, whilst general trends can be established based on a wide range of global scientific research the effects of explosive contamination on the environment are likely to be unique to a particular location.

19.4.4 Fate and Transport of Common Explosive Contaminants

This section concerns the fate and transport of explosives in the environment, and the impact on environmental receptors including plants and animals.

There are several comparable properties of explosive behaviour in soil that allow some generalisations to be made about their environmental impact. Particularly significant is the solubility of the explosive in water, generally measured in milligrams per litre, literally meaning the maximum mass of explosive possible to dissolve in a litre of water at ambient temperature (20 °C

unless otherwise stated).Solubility is important because it is the most likely route for transport of explosives into groundwater and uptake by plants. Transport of explosives in water can be prevented if the explosive has a high soil sorption coefficient (K_{oc}), or in other words, a high likelihood of binding to soil particles. In both cases, solubilisation in water or binding to the soil, explosives are vulnerable to degradation by bacteria in the soil (biodegradation) or sunlight (photodegradation).

The potential of an explosive to bind to soil is dependent on the nature of the explosive, that is, it must contain appropriate chemical groups, usually nitro or amino groups, and on the soil type. Soils tend to be characterised according to the predominant particle size distribution within a sample and can be split into clay, loam or sand types. However, for sorption of explosives the most significant factor is thought to be the organic content (OC) which describes the percentage of living or decomposing matter in the sample.

19.4.4.1 Nitramines RDX and HMX

RDX and HMX are both nitramines with similar chemical structures, it follows that their properties in the environmental are also similar. HMX is less soluble than RDX (5-6.63 mg L^{-1} and 38.4 mg L^{-1} respectively at 20-25 °C), and solubility of both explosives increases with temperature. RDX (K_{oc}: 0.84-2.2) and HMX (K_{oc}: 0.54) do not sorb significantly to soil, but do tend to sorb more readily to soil with a higher OC[11]. Due to their low sorption to soil RDX and HMX are able to reach sources of groundwater in significant concentrations i.e. concentrations greater than threshold levels[12].

HMX can be photodegraded within a week forming nitrates, nitrites and formaldehyde. RDX can degrade into a variety of compounds in the environment such as methylenedinitramine and nitrodiazabutanal. It is worth noting that there have been far fewer studies into the fate and transport and environmental impact of these degradation products. However, due to the number of degradation products the concentrations of individual species are much lower than the initial concentration of RDX and may not be significant in all areas[13].

Of the two compounds, RDX tends to present more of a problem on training ranges due to its use in large quantities in munitions.

19.4.4.2 Trinitrotoluene

TNT is usually found as a crystalline solid in surface soils. It is soluble in water (130 mg L^{-1} at 20 °C), and tends to sorb to soil. If TNT not sorbed by soil it tends to be rapidly biodegraded into dinitrotoluene (DNT) and isomers of aminonitrotoluene and diaminonitrotoluene, therefore very little TNT tends to reach groundwater. If TNT is washed into surface water it can be degraded by sunlight (photodegradation) to give trinitrobenzene (TNB). High concentrations of TNT in surface water can be identified by a tell-tale pink tint, although contamination of that level is unexpected outside of manufacturing and processing plants[14]. TNT is commonly found on the soil surface at ranges

suggesting that the deposition rate is faster than the biodegradation and dissolution rates. TNT can be taken up by plants and tends to be metabolised quickly, such that bioaccumulation in higher mammals is not expected.

19.4.4.3 Propellants: nitrocellulose, nitroglycerine, nitroguanidine, dinitrotoluene, perchlorates

Propellants tend not to be completely consumed during burning and particles of unburnt propellant are deposited on the range, particularly around the firing areas[2]. Studies on several ranges in the US have found high concentrations of nitroglycerine (NG), nitroguanidine (NQ), perchlorates and dinitrotoluene (DNT) [15]. Although nitrocellulose is a commonly used propellant its presence on firing ranges has not been extensively investigated as it tends to be deposited as discrete fibres which are difficult to quantify. An added complication is the tendency for other explosives to sorb onto nitrocellulose, and so areas where high quantities of NC propellants are in use may be difficult to analyse[16].

NC is insoluble in water and therefore tends to be deposited on the soil surface in fibrous strands, rather than particles. However, NC is bio- and photodegradable. NC undergoes biodegradation to a non-energetic polymer through the loss of nitrogen[16]. NC is not toxic towards humans, animals or plants due to the difficulty of absorption through the intestines and insolubility in water [17]. Deposition of NC on ranges does not have a significant environmental impact on receptors, other than an unnatural presence in the environment.

NG is soluble in water, and does not tend to sorb significantly to soil so it is quite mobile in soil environments[16]. Under favourable soil conditions NG undergoes several stages of biodegradation and can ultimately form glycerol, and in some cases carbon dioxide. However, not all NG will be completely biodegraded, and in sandy soils where attenuation is poor it is unlikely that NG will be significantly biodegraded before migration to ground water[18]. Photodegradation of NG occurs more quickly when it is solubilised in water on the scale of weeks, rather than months. Some degradation products are more toxic than NG, therefore if NG contamination is suspected it is recommended that samples are also tested for mono and di-nitroglycerine [19].

NQ is fairly water soluble (2.6 g L^{-1}) and does not sorb significantly to soil. NQ has been found to be biodegraded in some soils giving ammonia and nitrous oxide particularly in soils with high organic carbon content but it may migrate too quickly through soil for any significant degradation to occur before reaching ground water[20]. Photodegradation of NQ gives guanidine, ureas and cyanoguanidine.

Perchlorate is a naturally occurring and man-made anion that contains one chlorine atom bonded to four oxygen atoms (ClO_4^-). It is commonly produced when energetic compositions in the form of ammonium perchlorate (AP), sodium perchlorate and potassium perchlorate dissolve in water. Perchlorates are generally soluble and stable in water and do not sorb significantly to soil therefore have a great potential to contaminate surface and ground water, and

in fact there are well documented incidences of significant ground water contamination from military use of perchlorates[9, 21]. A risk assessment of UK use of perchlorate highlighted that monitoring for AP in potable water sources is not widespread in the UK, but that high levels of AP were detected in the groundwater at Shoeburyness disposal range where 14.5 tonnes of propellant have been disposed of since 1993[22]. While drinking and ground water limits have not been set for the UK, where contamination has occurred the UK uses the limit of detection (1 µg L^{-1}) as an indication of acceptable levels. The presence of perchlorate in drinking water is a particular concern as it is known to cause abnormal thyroid function in humans[23, 24].

19.4.4.4 Primary explosives and less commonly used secondary explosives

Primary explosives, used in fuzes, and other less common secondary explosives are less frequently found in samples taken from training ranges. Primary explosives are used in very small quantities, and are typically completely consumed on initiation leaving only by-products of the explosive reaction, such as lead in the case of residue from lead azide and lead styphnate.

Tetryl (2,4,6-trinitrophenylmethylnitramine), a warhead booster explosive, was employed extensively in UK service munitions. It has been obsolete for some time, however, it can still be found in surface soil on UK ranges.

19.4.4.5 Pyrotechnics

Pyrotechnics can have a variety of uses from primer compositions to ignite gun propellants to heat, light and noise generating effects[25]. In order to achieve these affects metals are often added to the compositions. Metals most commonly used include aluminium, magnesium, zinc, barium, chromium and lead[26]. Metals do not biodegrade, and can therefore remain in the environment for very long periods of time. However, current research indicates that the concentrations of metal deposits are very low, even for devices initiated on the ground. For airborne devices the metal particulates are distributed by air currents over very wide areas, diluting their presence in the environment. For metal contamination from pyrotechnics to be a significant problem hundreds of firings must take place in the same area[26] or large quantities being subject to disposal by open burning.

Pyrotechnics contain a wide range of chemicals to produce their effects including not only the metals listed above but also a range of oxidisers. These can include nitrates, chlorates and perchlorates, the environmental impact of the latter[27] having been considered earlier (19.4.4.3). White phosphorus used to be widely used as an obscurant in pyrotechnics[28], but is known to be highly toxic and in one well documented case at a military training range in Alaska it was directly responsible for the death of thousands of waterfowl[29, 30]. Ingesting even a small amount of white phosphorus in contaminated soil or water can be fatal, and contaminated soil may cause mild chemical burns[31].

19.4.4.6 Insensitive Munitions

It is MOD policy to reduce the risks from UK munitions to levels that are either Broadly Acceptable or Tolerable and As Low As Reasonably Practicable (ALARP) by minimising the probability of inadvertent initiation and severity of subsequent collateral damage to weapon platforms, logistic systems and personnel when subject to unplanned stimuli. This is known as the Insensitive Munitions (IM) policy.

For warheads there are two main types of high explosive that are current candidates as having the necessary characteristics for filling IM munitions, polymer bonded explosives (PBX) and insensitive munitions explosives (IMX). The PBX explosives derive their IM characteristics from the physical properties imbued by the polymer matrix and include the familiar energetic materials RDX and HMX. The IMX explosives use more novel energetic materials such as 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO) which are both less sensitive to shock and heat than TNT and RDX[32].

Currently (2017) PBX materials are in common use in the UK, other European countries and extensively by the US Navy and US Air Force. The US Army now employ IMX-101 as a replacement for TNT, and IMX-104 in place of Composition B (RDX:TNT 60:40 % w/w). The environmental impact of these materials is still under investigation, but the current state of the art is summarised below.

19.4.4.7 Insensitive Munitions Explosives (IMX)

The two main IMX compositions currently in use in the US are IMX-101 (DNAN, NQ and NTO) and IMX-104 (DNAN, NTO and RDX). As with conventionally filled munitions only minimal explosive residues remain on a range after a high order detonation. In contrast, lower-order detonations may scatter up to 25 % of the energetics over a localized area, sometimes smaller than 100 m^2, [9, 33] and the residues may be of sufficient concentration to contaminate the soil and groundwater[34]. There is always a balance between providing an explosive that is more difficult to initiate from a safety perspective with the requirement of complete, reliable detonation.

RDX has been discussed in Section 19.4.4.1, and NQ in Section 19.4.4.3. NTO is more soluble than conventional explosives and will therefore dissolve more quickly in the environment[35]. NTO does not adsorb significantly to soil particles[36], although the rate of transport tends to be dependent on the soil pH, with adsorption decreasing as pH increases[37]. Laboratory studies have shown that NTO can be biodegraded[38], but the extent of biodegradation in the real environment is largely untested.

An additional concern with NTO is the acidity of aqueous solutions containing NTO, with the expectation that contaminated soil and water may exhibit increased pH known to cause leaching and migration of heavy metals in soil with low buffering capability. However, at the concentrations expected to be seen on ranges, no change in soil pH has been found[37].

NTO has low toxicity in mammals, but has been shown to cause reproductive toxicity in rats. In preliminary studies NTO has not shown significant aquatic toxicity and no water threshold levels have been identified.

DNAN is much less soluble than NTO (0.21 g L^{-1}), but does dissolve over time and has a low sorptivity to soil. DNAN therefore has the potential to quickly migrate into ground water(38). Several microbial degradation products of DNAN have been identified that may adsorb to soil(39). Further research by the same group indicated that although DNAN is more soluble than TNT, its hydrophilicity and tendency to form degradation products that sorb irreversibly to soil may make DNAN less harmful than TNT.

The environmental impact of these types of explosive has not yet been fully investigated despite their increasing use in munitions.

19.4.4.8 Polymer bonded explosives

In PBX munitions high explosives are used in combination with a polymer binder which encapsulates the explosive and improves the insensitivity profile of the material. In addition to a polymer binder, a small amount of plasticizer is usually added to the formulation to change the physical properties such as flexibility, the temperature at which the formulation becomes brittle and to permit easier processing(40).

It is generally thought that the polymer binder, which is not water soluble and slow to degrade, protects the explosive filling from environmental degradation. However, polymers are known to expand with increased temperature, and degrade when exposed to sunlight (UV) which may release the explosive filling- usually a nitramine explosive or ammonium perchlorate. Although the rate of release of explosive from a polymer matrix is slow under natural conditions, it should be noted that over time the encapsulated explosive will migrate into the soil, while the polymer is more likely to remain at the surface for much longer(41).

19.5 ASSESSING THE ENVIRONMENTAL IMPACT OF EXPLOSIVES USING PROJECT ORIENTED ENVIRONMENTAL MANAGEMENT SYSTEMS

The MOD has developed a bespoke platform known as the Project Orientated Environmental Management System (POEMS), which was designed to facilitate the application of an Environmental Management System (EMS) to specific MOD activities and equipment throughout the life cycle.

POEMS is based on the international standards ISO 14001 and ISO 14040, the former representing the cornerstone of an EMS and the latter covering life cycle assessment (LCA). LCA is a technique for assessing the environmental impact of a product throughout the entire lifecycle from extraction of raw materials to

disposal, often referred to as ‘cradle to grave’. Table 19-5 gives an outline of the POEMS 9 core procedures for implementation.

Table 19-5 POEMS Core Procedures

EMP No.	EMP Title	EMP Overview
1	**Environmental Management Plan**	An Environmental Management Plan (EMP) is developed so that potential environmental aspects and impacts are defined at the early stages of a project. The EMP better enables Project Teams to manage environmental performance and apply appropriate resource and support so that effective environmental management can be implemented.
2	**Stakeholder Communications**	To ensure that environmental impacts are identified and appropriately managed, information on relevant stakeholders, their needs and possible contribution to the project should be collated and documented.
3	**Standards Identification and Demonstration of Compliance**	It is important to identify standards that apply to specific projects so that compliance can be demonstrated. Relevant standards should be recorded and adjusted accordingly throughout the life cycle of the project.
4	**Screening and Scoping**	The purpose of this procedure is to identify and detail relevant aspects, impacts and potential risks of the acquisition. This provides an opportunity to influence procurement and design decisions.
5	**Impact Priority and Evaluation**	This procedure provides guidance on how to prioritise environmental impacts as high, medium or low. This helps to decide what impacts take priority and if further assessment is required. In order to document this Environmental Features Matrix (EFM) is developed.
6	**Objectives and Targets**	This procedure represents the first step of the Environmental Impact Management process which will assist project teams to manage their medium and high environmental priorities. Objectives and targets can represent mitigating activity and should be recorded in the EFM.
7	**Environmental Impacts Management**	This procedure is to help project teams to appropriately manage their medium and high priority environmental impacts. It also requires teams to continue to document and act where appropriate in relation to their low priority and positive environmental impacts and produce appropriate environmental reports.
8	**Operational Controls**	Operational control exists to ensure an activity is completed in the correct/desired way. This procedure should assist project teams in identifying where operational controls are required and checking the adequacy of operational controls. An operational control represents a mitigating activity and should be recorded in the EFM.
9	**Continuous Review**	Continuous review should ensure that POEMS outputs are kept up to date with overall project and other developments. A review should be part of a planned process of revision as the project progresses in order to incorporate improved or amended information, or as the result of audit findings. This procedure assists the project team in continuous review and improvements

		to their projects

One of the most important elements of POEMS is the compilation of an environmental features matrix which ranks the environmental impacts in priority order to determine the most significant environmental impacts associated with a piece of equipment. The Environmental Features Matrix considers each activity in turn, considering whether it is normal (planned and usual), abnormal (planned but unusual) or unplanned. For each of the activities an associated environmental aspect is ascribed. An environmental aspect is a feature or characteristic of an activity, product, or service that affects or can affect the environment. Depending upon the nature of the environmental receptor there will be an environmental impact. An environmental impact is a change to the environment and such change can be positive or negative. To assess potential impacts each potential impact is scored in terms of its severity and frequency or duration. The scores are on a scale of 1 to 5 for frequency/duration and are cross-referenced with the severity scored from ‘a’ to ‘e’ (Figure 19-4). These scores are aligned to high, medium and low priority environmental risks. An example of an Environmental Features Matrix template is given at Appendix A.

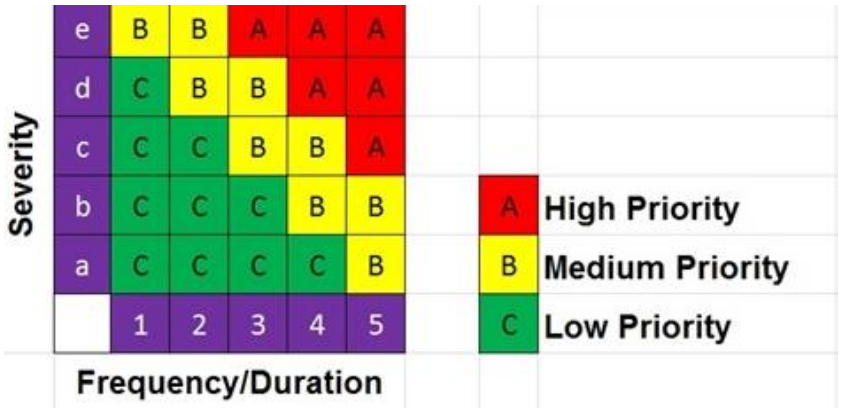


Figure 19-4 POEMS severity versus frequency and duration scoring matrix

The severity of an environmental impact is a measure of the degree of environmental damage that the impact represents. The lowest rating for severity is ‘Minor’ and the highest ‘Critical’. Frequency is defined as the number of times that the environmental impact is expected to occur, for example, once a week, once a day or once a year. The ‘duration’ is the length of time that the impact lasts for, for example, 30 minutes, 5 hours or continuous.

Once the methodology for priority evaluation is established, environmental impacts shall be prioritised using the categories chosen. The threshold score for further action is ‘B’ for medium priority impacts, with a higher threshold score of ‘A’ for high priority impacts. The two threshold levels are intended to give greater resolution between priority of impacts which require action and will assist the Project Team to make management decisions including whether or not to embark upon a full Environmental Impact Management (EIM) approach. Impacts scoring ‘C’ should not need any immediate further

action. Further details of the POEMS process can be found through the Acquisition Safety and Environmental Management System website[42].

The Ministry of Defence issues guidance on environmental issues that need to be taken into consideration in the design and operation of land ranges. This guidance is given in JSP 403 ”Handbook of Defence Range Safety” Volume 2 Chapter 2 “Range Design Criteria and Specification” Paragraphs 02102 – 02104.

19.6 MONITORING AND SAMPLING

Where explosives are in constant use, and pathways to receptors have been identified, it may be necessary to monitor receptors for traces of contaminants, usually by taking several samples and submitting them for laboratory analysis. Monitoring of receptors can be continuous, or can be carried out at regular intervals. For ranges it is rarely necessary to conduct continuous monitoring, rather nearby receptors such as rivers, potable water sources or ground water may be tested regularly if there is a likely SPR linkage between the source and the receptor. Alternatively, if a contamination problem has been discovered by some other means for example illness in a nearby animal population, a sampling strategy may be required to identify the source, or the pathway of the contamination. Here the need for different sampling strategies depending on the objective of the investigation, and the different methods available for monitoring and sampling different environmental receptors will be considered.

The sampling method for a specific area will depend on the desired outcome of the project. For example the sampling method for determining average concentration of a contaminant across a site, may be different from a sampling method to determine contaminant hotspots. The sampling method will also differ between area size, and medium including land, surface water, ground water or ocean beds. It is possible to sample air quality, but for outdoor explosive ranges this is unlikely to be necessary due to the quick dissipation of small quantities of gases over large distances and so will not be considered.

19.6.1 Sampling Methods for Monitoring Processes

Monitoring can occur when the contamination, and contamination source is known. Monitoring programmes usually monitor air, soil or water for specific contaminants that have been identified as possible contaminants and that may be harmful to environmental receptors, including local populations.

Whilst some explosives have threshold levels for drinking or surface waters, there are no UK threshold limits for explosive contamination in soil, and the limits for some newer explosives have not yet been determined. A threshold level does not necessarily mean that the levels are completely safe, and often even if trace amounts are detected in drinking water measures will have to be taken to ensure the concentration decreases, or at the very least does not increase.

19.6.1.1 Monitoring water

Ground water tends to be inaccessible unless there is a nearby outflow such as a well or natural spring. For monitoring purposes it is likely that the receptor will not be the groundwater itself, but will be nearby potable water sources, natural springs or rivers. In this case sampling will be conducted on a regular basis in the same way as surface water sampling would be conducted.

19.6.1.2 Sampling methods when investigating contamination

The main difficulty in investigating the source or extent of contamination is designing a representative sampling regime. The area under investigation may be very large so it can be difficult to choose which areas to sample, and how large a sample to take. When sampling land or water the depth of the collected sample also has to be considered, and whether the sample is taken at depth or is a cross section up to a specific depth. Some of these variables will be determined by the nature of the sampling area, and some will be determined by the objective of the investigation.

Another difficulty with sampling training ranges is the heterogeneity of deposited residues which can cause isolated hotspots. Detonation residues will be scattered over the range almost randomly, and will change depending on climate conditions, detonation method and the type of round detonated. Shrapnel will distribute differently to chemical and explosive residues, and when sampling an area it is likely that shrapnel, or even UXO’s fall into the sampling area. It is usual to discard any large items when sampling soil or water as these are not representative of contaminants in the medium; however it is likely that there will be higher concentrations of certain contaminants around these items particularly in soil.

19.6.1.3 Soil sampling strategies

Multi-increment sampling is a sampling method developed to overcome the difficulties with obtaining representative sample of very large areas of heterogeneously deposited contamination. Instead of taking and analysing discrete samples which represent only a tiny portion of the entire area, multiple samples are taken and combined over several large areas of a range. Within one sample there may be up to 100 ‘increments’, and each area is sampled up to three times to obtain three samples of up to 100 increments. Combining several sample increments increases the likelihood of identifying contamination, whilst eliminating heterogeneity by mixing samples. The protocol for sample collection and analysis is now well established, and has been shown to be highly repeatable. It has been identified as the recommended sampling method for many field studies, including some in the UK (Salisbury Plain Training Area, targeted land quality assessment document).

19.6.1.4 Surface and ground water

Ground water is usually sampled by drilling a series of boreholes and extracting water samples. To obtain a representative sample of groundwater it is first necessary to understand the hydrogeology of the area, mainly the extent of the ground water aquifer, so that samples can be taken from a representative area.

19.6.1.5 Ocean/ ocean bed sampling

Sea ranges present a particular problem for sampling and assessment of contamination due to the vast areas covered compared to land based ranges, the heterogeneity of firing patterns as there are no specific impact/firing areas and the natural currents that can move contamination and debris many thousands of miles. Localised contamination may occur near to sea dumping sites, but in general the first indication of a problem will be from impacts on the receptors, namely the aquatic flora and fauna.

Sampling for explosives in sea ranges is not available from the literature, but many other organic contaminants are monitored globally. One sampling method is the systematic sampling of large quantities of water, up to 1000 L at a time, using a technique called solid phase extraction in which contaminants can be adsorbed onto small fibres coated with a thin layer of polymer sorbent. Alternatively, discrete samples can be taken at intervals over the entire area and individually analysed for specific contaminants.

Often sampling oceans is not practically possible, but flora and fauna toxicity can be used as a good indication of a contamination problem. Local flora and deceased fauna can be analysed for indications of accumulation of the contaminant. This can be particularly useful for metals which are rarely metabolised.

19.7 RANGE MANAGEMENT

Prevention of contamination occurring is the preferred route for new site, and failing that a monitoring and mitigating programme that ensures legal compliance. However, for existing sites there will be contamination and remediation will be required at least upon vacation (see Section 6.4), or if a breach of legislation or a significant impact is identified.

Explosive contamination presents a particular problem in that there is rarely only one contaminant to remediate. As described in Section 19.4.4, the fate and transport is highly dependent on the chemical structure of the explosive, as well as the soil type and climate and so remediation techniques will have to be chosen for site specific problems, often several techniques will be required to ensure complete remediation(41).

19.7.1 Chemical Remediation

Chemical remediation techniques include in situ chemical oxidation (ISCO) remediation of matrices contaminated by explosives and other toxic aromatic compounds with nitro substituents. The pre-treatment step involves the injection or addition of a relatively inexpensive reducing agent (lactate or ethanol) which renders the contaminant more susceptible to conventional treatments such as with permanganate due to the conversion of one or more nitro substituents to an amine group. The pre-treatment step is applicable to soil and aqueous matrices.

19.7.2 Physical Remediation

The physical remediation of ground contaminated with explosives is referenced in the NATO Handbook on Reclamation of Contaminated Land Chapter 9-AVT197. This addresses the possibility of disposing of the contaminants in controlled fires. First combustible material in the form of dried plant material, wood chips, pine needles and the like are spread out in combination with glycerine and $KMnO_4$. This method has been shown to effectively reduce surface contamination of TNT and RDX(43). The challenge is that a temperature of over 250 °C is required for the explosive to be completely combusted. A lower temperature results in the TNT melting and migrating to deeper soil layers. In practice only a soil depth of a few centimeters attained the required temperature therefore this method is only effective if the explosive is located on or very near the surface(43).

19.7.3 Biological Remediation

The NATO Handbook on Reclamation of Contaminated Land Chapter 9 covers phytoremediation methods utilizing plants to degrade explosive residues by three main principles, which can be used individually and in combination.

- Phytoextraction - uptake and concentration of the contaminants from soil and water into plant biomass

- Phytotransformation - explosives are transformed as a result of the plant metabolism, leading to the formation of a less toxic product, degradation, or immobilization
- Phytostimulation – introduction of a plant that has micro-organisms living in the root zone of the plant able to degrade the explosives. This is also called rhizodegradation

Explosives are taken up through the roots of the plant. It is considered that nitramines such as RDX are transported to the leaves, while nitroaromatics such as TNT are more likely to accumulate in the roots. In practice phytoremediation is difficult to implement because it involves identifying a plant that is appropriate to a particular site and type of contamination, which may in practice not be possible.

19.8 SITE REMEDIATION

Explosives manufacturers are continually improving manufacturing processes to meet today's changing technical, safety and environmental requirements. In making these improvements, buildings within a manufacturing facility may become obsolete and must be decommissioned in a safe and environmentally acceptable manner. At times an entire facility may be phased out requiring the decommissioning of numerous explosives-contaminated structures. The decommissioning of such a structure may present less obvious hazards. For example, processing buildings in which explosive materials have been managed may contain explosives residues hidden within cracks, crevices, under floorboards, in ventilation ducts or behind wall panels. Explosive materials also may be present inside or in areas surrounding process machinery.

Decontamination of structures that have contained blasting agents composed of high percentages of water soluble, hygroscopic salts such as ammonium nitrate and fuels may be achieved by sweeping or other physical means. Water wash-down usually results in the safe decontamination of this building category. In certain cases, collecting and treating the wash-down water may be required. Open burning is not recommended for this explosives contaminated building category.

Decontamination of black powder and similar pyrotechnic mixtures may also be achieved by mechanical cleaning followed by water wash-down. However, due to the ease of ignition after drying, burning is recommended for this building category.

Water insoluble molecular explosives such as nitroglycerine, tetryl, TNT, PETN, RDX, and HMX require special decontamination and dismantling procedures. These procedures may include sweeping and physical removal followed by steam cleaning of equipment and the use of solvents, such as acetone, or a desensitising oil prior to the removal of threaded fittings. Trinitroresorcinol, lead styphnate, lead azide, mercury fulminate and other initiator explosives are sensitive to initiation by heat, impact and friction. These materials present the

supplementary problem of residual metal contamination after the criteria of reactivity is eliminated. Structures that have contained these two groups of explosives require soil monitoring to assure complete, safe closure of the site. It is highly recommended that buildings used to manufacture or process any of these two groups of explosives be burned to eliminate possible hazards associated with reactive materials that may have accumulated in cracks, crevices or larger spaces within the floors and walls. When it is planned to burn out a building, excessive plastic, asphalt, or rubber materials should be removed and treated separately to minimize heavy soot production and the associated environmental nuisance. Detonations of below-ground liquid explosives in underground drains have been known to occur hours after initiation of the fire, therefore a 48 hour waiting period before approaching the site is recommended.

The burning out of old explosives facilities carries with it potential risks to both human receptors and environmental receptors from the deposition of air borne particulates; these deposited materials could affect both soil and surface water bodies in the area surrounding the burn site. These might include nitrous oxide, carbon monoxide, asbestos, lead vapours and particulates, zinc, poly-aromatic hydrocarbons, and dioxins.

19.8.1 Remediation of contaminated soil

Historically at some explosives manufacturing facilities explosives wastewater was collected in washout pools or lagoons which accumulated contamination in the soil which subsequently migrated into underground aquifers. Explosives also entered the soil during transport and storage on the site. The chosen method to deal with this explosives-contaminated soil has been the use of a rotary kiln incinerator. In rotary kiln incineration soils are fed into a primary combustion chamber or rotary kiln where organic constituents are destroyed. The temperature of the gases in the primary chamber ranges from 450 ^{o}C to 650 ^{o}C, and the temperature of the soil ranges from 350 ^{o}C to 450 ^{o}C. Retention time in the primary chamber, which is varied by changing the rotation speed of the kiln, is approximately 30 minutes. Off-gases from the primary chamber pass into a secondary combustion chamber, which destroys any residual organics. Gases from the secondary combustion chamber pass into a quench tank and thence through a venturi scrubber and filters which remove acid gases and particulates prior to release from the stack. The treated product of rotary kiln incineration is treated soil which drops from the primary combustion chamber after organic contaminants have been destroyed. This product is routed into a wet quench or a water spray to re-moisturise it, then transported to a storage area.

The process is not without environmental concerns. The incinerator requires a large amount of fuel to produce the required heat and a powerful fan for air flow. There also is an attendant noise problem. Nevertheless the technique can achieve a 99.99 % destruction of explosives residues.

19.9 COMPUTER MODELLING AND ENVIRONMENTAL DATABASES

19.9.1 Computational modelling for predicting fate and transport

Computer models are commonly used to attempt to predict SPR linkages for explosives, and estimate the environmental risk for lifecycle assessment (LCA) or environmental management systems (EMS).

Environmental toxicity models use mathematical approaches to combine different forms of data, such as toxicological data and characteristics of the environment, into concise information suitable for environmental risk assessment, or to determine contamination levels in an area or environment. The typical inputs and outputs of an environmental toxicity model are summarized in Figure 19-5.

Several different modelling tools can be used to investigate the environmental impact of exposure to chemical contaminants. Fate and transport models are well-established tools that characterise the behaviour of contaminants in the environment. Fate and transport models have been parameterised at different spatial resolutions and can be used for either steady-state calculations (constant over time events or assumptions) or transient calculations (accounting for changes over time)[44]. The parameterisation of fate and transport models already encompasses factors such as temperature, rainfall, atmospheric circulation patterns, and degradation pathways[44–50].

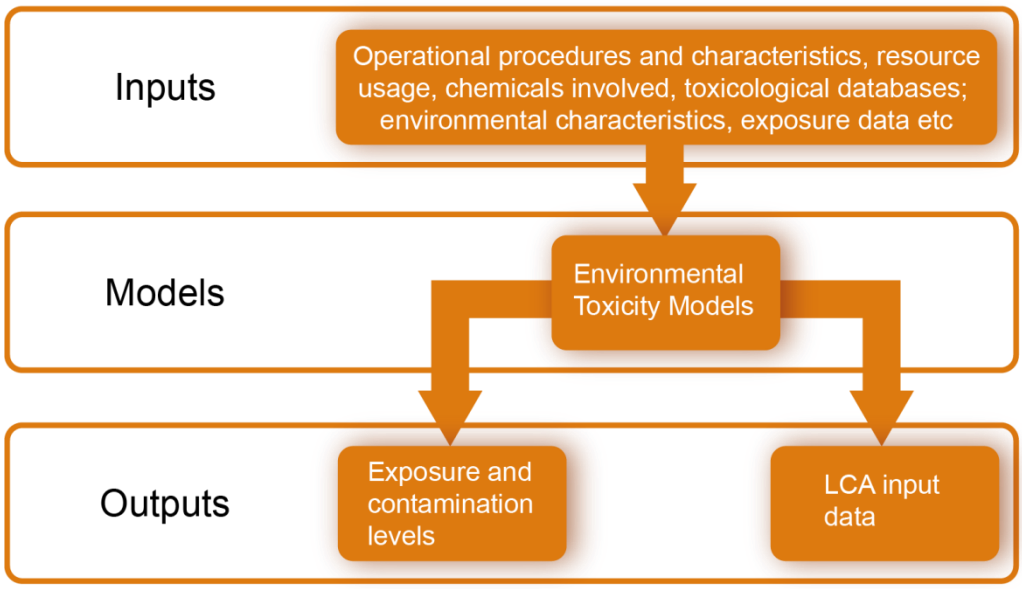


Figure 19-5 Inputs and outputs in an environmental toxicity model

Fate and transport models produce dispersion-related data and must be coupled with other tools, such as environmental toxicity models, in order to fully understand the environmental issues that are compiled in an Environmental

Impact Assessment (EIA) document. Therefore, the selection of a toxicity model plays a significant role in the overall EIA. In many cases the input data is available in databases, and are compiled from both experimental and predicted data.

Environmental modelling can be a very powerful tool when used to assess a specific, well defined problem. However, there are many different environmental modelling tools available which must be carefully chosen to suit the problem. In all cases the limitations and assumptions of the chosen environmental model must always be taken into consideration.

19.9.2 Information Databases

Some countries have developed databases of information for range management and munition disposal. One example is the Norwegian Defence Environmental Database (NDED) which is used to log ammunition usage on small arms ranges in order to calculate accumulation of specific contaminants(51).

The MIDAS Program was developed in 1992 by the U.S Department of Defence to identify alternatives to open burning/open detonation (OB/OD), and to provide a systematic approach to the disposal of unwanted munitions(52). The system has gone through several updates and is now known as “Web-based Munition Automated Environmental Analytical Capabilities.” The updated suite covers risk assessment, water dispersion and deposition, the permit repository and assets and more.

Although not specifically for munitions, The University of Rhode Island has an Explosives Database, funded through the auspices of the National Memorial Institute for the Prevention of Terrorism. The database is an interactive library of analytical data for explosive and energetic compounds arranged by name, and analytical technique(53). At the current time, the UK does not have an established environmental database for munitions but relevant research is undertaken when required.

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Appendix A Environmental Features Matrix

Table 19-6 Environmental Inputs

EMP04/F/01 – Environmental Feature Matrix										
In-Service										
Embodied Materials and Energies (Inputs)							**Priority Assessment**			Mitigation
Activity	Normal/ Abnormal/ Emergency	Aspect (Materials and Energies	Receptor	Impact	Positive/ Negative	Impact Codes	Severity	Frequency/ Duration	Priority Score (A, B, C)	Controls
Detonation upon target	Normal	Detonation of explosives	Land	Non-Renewable Resource Use	Negative	NR	b	3	C	
Functioning of gun at launch site	Norma	Burning of propellant	Land	Non-Renewable Resource Use	Negative	NR	b	3	C	

Table 19-7 Environmental Outputs

Emitted Materials and Energies (Outputs)							Priority Assessment			Mitigation
Activity	Normal/ Abnormal/ Emergency	Aspect (Materials and Energies	Receptor	Impact	Positive/ Negative	Impact Codes	Severity	Frequency/ Duration	Priority Score (A, B, C)	Controls
Detonation upon target	Normal	Noise	Humans	Nuisance	Negative	N	b	3	C	
Detonation upon target	Normal	Shell fragments	Humans	Human Health	Negative	H	b	3	C	
Detonation upon target	Normal	Lead fumes from fuze	Humans, Land, Air, Water	Human Health,	Negative	H, L, A, Wat	c	3	B	
Detonation upon target	Normal	Gaseous products	Humans, Air	Human Health, Air Pollution	Negative	H, A	b	3	C	
Firing the gun – launch site	Normal	Noise	Humans	Nuisance	Negative	N	b	3	C	
Functioning of gun at launch site	Normal	Lead fumes from propelling charge	Humans, Land, Air, Water	Human Health	Negative	H, L, A, Wat	c	3	B	

CHAPTER 20
QUALIFICATION OF ENERGETIC MATERIALS FOR PROCUREMENT OF MUNITIONS

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20 QUALIFICATION OF ENERGETIC MATERIALS FOR PROCUREMENT OF MUNITIONS

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20.1 AWARENESS SUMMARY

This chapter explains the procedures required to qualify energetic materials in accordance with the requirements of STANAG 4170(1) and AOP-7(2) for the purposes of the UK MOD. The Defence Ordnance Safety Group (DOSG) Science and Technology (ST1) section is the UK National Authority for the assessment of the safety and suitability for introduction into military service of energetic materials in compliance with STANAG 4170.

Explosive Qualification is defined as the assessment of the explosive material by the National Authority according to STANAG 4170 and AOP-7 to determine whether it possesses properties which make it safe for consideration for use in its intended role.

Explosive Qualification provides evidence to answer the following questions early in the CADMID cycle(3) of the munition:

- How does the munition work?
  - Chemistry, Physics, Engineering, Statistics etc.
- What is the munition ‘safe working envelope’?
- What are the safety critical failure modes that might exist/develop?
  - How can these be quantified or demonstrated during Qualification/Surveillance process?
- What other service life limiting failure modes might exist?

Qualification of an explosive for use in a specific application or munition is a separate process, called Type Qualification. Type Qualification is given when the explosive has been assessed as part of a single design and shown to be safe and suitable in that munition. Explosive Qualification assessment should be completed prior to Type Qualification and selection for a particular application.

There is no pass/fail criterion for Explosive Qualification; judgement will be by comparison with explosives that have been used satisfactorily in the same role. Explosive Qualification provides essential data on mechanical, physical, chemical, sensitiveness (see 20.2.1) and explosiveness (see 20.2.1) properties, which:

- Enables quantitative risk assessment to be carried out
- Identifies safety critical failure modes
- Provides baseline data for service life prediction/surveillance
- Establishes explosive ageing characteristics
- Candidate energetic materials can be ranked in terms of their properties
- Provides data required for munitions disposal, hazard and environmental considerations

- Increases energetic materials knowledge and identifies areas where research is required

Qualification is a requirement for all explosives including; primary explosives, booster explosives, high explosives, solid gun and rocket propellants, liquid propellants and pyrotechnics compositions. Each of these types of materials and the roles in which they are used, require that their responses to different accident or threat stimuli be evaluated in order to assess whether the materials are likely to be safe and suitable for introduction into UK service.

20.2 STANAG 4170 and AOP-7

Under STANAG 4170 participating Nations agree the requirement for Qualification of energetic materials for the purposes of ensuring safety and suitability for service in ammunition. Both the mandatory data requirements and general test guidance are included in NATO AOP-7. This guidance includes the types of tests and ageing protocols to be carried out for the various classes of energetic material. The guidance allows for some variation of test and test procedures by participating Nations. Direct read across between data from different nations will not always be possible therefore specific UK testing may be required. AOP 7 Chapter 10.7.15 details UK specific national test requirements. The UK national section cross references STANAG test methods alongside specific UK small scale sensitivity tests. Specific UK tests are discussed at length in Appendix B.

It is recommended that material Qualification should be completed before a decision is made to use the explosive material in a weapon design. The Qualification of a new explosive does not imply Type Qualification (see 20.5) for use in a particular weapon.

20.2.1 Definitions

The definitions in AOP-7 [(2)] are to be used during Qualification. Specific attention should however be drawn to the following definition:

New Explosive. The term ‘New Explosive’ encompasses the following:

- An explosive material that has not been previously qualified
- An explosive material for which the existing specification defining its composition, its material constituents or the process by which the composition is prepared has been modified
- An explosive material resulting from a change in manufacturer or manufacturing location
- An explosive material used in a role for which the explosive has not already been qualified

The following definitions are used when considering safety and reliability of explosives:

- **Sensitiveness.** A measure of the minimum level of a prescribed stimulus, relevant to an accident situation, required to ignite or initiate an energetic material. Such stimuli include, among others, impact, friction, and electric spark.
- **Sensitivity.** A measure of a prescribed stimulus required to achieve reliable functioning of an energetic material in its designed mode.
- **Explosiveness.** This describes the degree of violence shown by an energetic material when it responds to a prescribed stimulus relative to an accident situation. It is dependent on the nature of the energetic material, its mass, physical state, configuration and confinement.
- **Compatibility.** Absence of reactions between explosives and other component within a munition, leading to unacceptable changes in physical properties, sensitiveness or sensitivity of explosives in the munition as detailed in STANAG 4147(4).

20.2.2 General Advice

It should be noted that the safety and suitability characteristics assessed and interpreted for Qualification purposes relate to an energetic material or composition in a specific role and that the data presented from a Qualification programme may also assist the Regulatory Authority in its assessment for granting a storage and transport hazard classification certificate. It should also be noted that any estimation of service life and detailed performance parameters are not part of the Qualification process.

Qualification of a new composition does not imply any recommendation for use in a specific weapon system, but any evidence of significant change of properties on ageing will be included as a proviso, so that the change may be considered during subsequent assessment of the munition containing the composition.

A new energetic material having a characteristic rendering it unsuitable for Qualification in one role does not necessarily excluded its consideration for another. In these circumstances particular care will need to be taken in determining an appropriate trials programme in order to Type Qualify (see 20.5) the material in a particular munition.

The safety and suitability of the weapon system is demonstrated separately by relevant safety and environmental tests. This will include Type Qualification of the energetic material for the particular application in Accordance with the Allied Ammunition Safety & Suitability for Service Publication (AAS3P).

20.3 COMPOSITION DETAILS, USE AND SAFETY: MANDATORY REQUIREMENTS

When considering an energetic material for Qualification full details of the manufacturing specification and composition should be supplied and should include the percentage of individual ingredients, specifications and manufacturing source(s) of each of the ingredients, relevant toxicity and known

hazard data. These requirements are referenced and discussed at length in Appendix A and are STANAG 4170 Explosive Hazard Data Sheet requirements.

It is accepted that the composition of an energetic material, processing method and any controlling specifications may be modified during the material development programme. This may be necessitated by scale-up considerations or by changes required to accommodate issues identified during Type assessment trials. To enable the continued applicability of any existing Qualification certification the National Authority should be informed of any such changes and any additional testing requirement should be identified and undertaken.

Historically many explosive materials consisted of a well-defined formulation with reproducible micro-structure and physical properties. However, the drive to improve munition safety characteristics, particularly with respect to vulnerability, has led to the greater use of Polymer Bonded Explosive (PBX) type materials where a single explosive or a mixture of energetic components is bound in a polymer matrix that incudes plasticisers. These compositions are necessarily highly heterogeneous. Widely differing mechanical properties (e.g. strain capability) can be produced by relatively minor modifications in cross-link agent concentration or cure conditions. Since material Qualification data must be representative of the properties of the energetic material as actually presented for service use Design Organisations should ensure that samples tested for the purposes of Qualification are materially representative throughout the explosive. It may be required to test samples extracted from munitions to verify that this requirement is fulfilled.

20.3.1 Origin of Energetic Materials

Historically the majority of UK energetic compositions were of UK design and manufacture, however this no longer the case with the majority being supplied from abroad as are the explosive substances used in their manufacture such as RDX, HMX and nitrocellulose.. Where an energetic composition or its key components are of overseas origin, the available test data for these materials may not entirely fulfil the requirements of DOSG ST1 as the National Authority. So far it has not proven possible to fully standardise test procedures internationally. Those used by individual NATO nations are listed in AOP-7[(2)] in the relevant Chapter 10 national sections. Some nations' tests are less well understood in the UK and where this presents difficulties for Qualification programmes, specific requests identifying the data shortfall will be made to the Design Organisation.

A programme of extra testing may be required should any Qualification data supplied be considered insufficient to establish material characteristics. If tests cannot be carried out in the country of origin, then it may be necessary to provide samples of the energetic composition for testing in the UK. This may be in the form of specifically manufactured test material or material extracted from actual munitions.

20.3.2 Change in Manufacture

Re-qualification of a material will also become necessary when there is a change of manufacturer and/or manufacturing site and using a particular manufacturing process. It is now quite normal for repeat production of explosives and munitions to be open to competition and obsolescence driven changes in manufacture are occurring with increased frequency. When this occurs, advice should be sought from the National Authority as to the extent of the re-qualification exercise.

In reaching a decision on whether their original advice for safety and suitability for service needs to be amended the National Authority will be guided by the principles that explosives and munitions subject to a change in manufacture:

- Must remain safe and suitable for service, and continue to have a service life acceptable to the MOD Project Team
- Materials are assumed not to have the same characteristics as the original

A change in manufacture will have occurred when there is a change in one on more of the following:

- The drawings or specification
- The manufacturing process
- The source of type of raw materials
- The source of components
- The manufacturer or manufacturing site
- A break in production which could have led to a loss of manufacturing expertise

Changes to drawings, specifications and manufacturing processes are normally recorded, assessed and approved by the MOD QA Authority and/or technical authority prior to implementation. On those occasions where safety may be affected advice should be sought from DOSG or the DE&S Weapons Operating Centre (WOC).

20.4 PRELIMINARY ASSESSMENT AND HAZARD DATA

Prior to Qualification a preliminary safety assessment is carried out which, in the UK, results in the issue of an Explosives Hazard Data Sheet (EHDS) conforming to the requirements of STANAG 4170, Defence Standard 07-85[(5)] and Defence Standard 13-129[(6)]. DOSG ST 1 as the National Authority uses this information when qualifying energetic materials. A more detailed examination of the requirements for EHDS is covered in Annex A. Qualification of energetic materials new to UK service is determined by assessing the compositional details together with the physical, chemical, mechanical, sensitiveness (see 20.2.1) and explosiveness (see 20.2.1) properties. Properties are compared with those of energetic materials which have been used in a similar role in UK service and for which a high level of confidence has been established. Test data derived from energetic material Qualification

should be used to inform design of Type Qualification and Surveillance test programmes.

The extent of Qualification testing may range from nothing, where an explosive's characteristics can be read across from similar materials, to a full range of Qualification tests where a new explosive contains one or more of the following:

- New ingredients not previously used in explosives
- Ingredients new to this type of composition
- A substantially different ratio of major and minor ingredients
- Substantially different physical properties (e.g. particle size, density etc.)

20.4.1 Energetic Material Test Requirements

The testing required can be broadly categorised as follows: compositional; chemical; physico-mechanical; and hazard (small scale & charge scale) tests. Guidance on this is outlined below.

20.4.1.1 Chemical properties

The energetic material must demonstrate adequate chemical stability. Information from a variety of tests should have been obtained during a UK development programme and additional tests are not normally required by DOSG for Qualification purposes.

The overall thermal stability of the composition needs to be established for Qualification. Thermal stability can be determined relatively easily and data should normally have been obtained during the development programme. Techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA), Heat Flow Calorimetry (HFC) and Accelerating Rate Calorimetry (ARC) provide a great deal of information regarding the thermal behaviour of a composition and its constituents.

Properties such as melting points, phase changes, decomposition temperatures and ignition temperatures can be obtained from DTA and DSC, with the latter also providing the total energy output on decomposition. TGA on the other hand only indicates temperature of decomposition and changes, which affect mass, such as loss of water or volatiles.

Nitrate esters, for example in nitrocellulose based propellants, are known to degrade with time, and the products of the degradation catalyse further degradation, which can eventually lead to self-ignition of the propellant. In order to prevent this, sacrificial stabilisers are included in the formulation to remove some of the products of the degradation. The chemical stability of the explosives can thus be measured by monitoring the level of the stabiliser(s) and/or the presence of the degradation products.

In practice a variety of tests are used, assessing the range of decomposition modes. Together these indicate the safe chemical life of the explosive and may

be used as part of the determination of the service life. The methodologies as described in STANAG 4620[7] are well established and strongly preferred as this enables comparison with many service compositions tested previously and the application of common sentencing criteria. Determination of chemical compatibility (see below) will be in accordance with the STANAG 4147[4]. Where specific STANAGs are not available, the chemical stability assessment regime will need to be agreed with the National Authority.

In addition to the risk of self-ignition, the gaseous degradation products of the nitrate esters can induce gas cracking in rocket propellants. The likelihood of this occurring for a given set of conditions is dependent on a number of parameters, including: the effectiveness of the stabiliser, the propellant formulation, the mechanical properties and the charge geometry. The vulnerability to gas cracking needs to be assessed using a test regime agreed with DOSG.

The overall chemical stability of composite propellants should also be assessed using vacuum stability and thermal stability tests, in accordance with STANAGs 4556[8] (Explosives, vacuum stability tests) and STANAG 4515[9] (Explosives, thermal analysis using DTA, DSC, HFC and TGA).

20.4.1.1.1 Compatibility

Stability testing of explosives is concerned with the inherent stability of the chemical components of the explosive against spontaneous decomposition. Compatibility testing considers the potential for a non-explosive material in contact or close proximity to the explosive material to cause a chemical reaction that compromises the stability of the explosive.

There are three issues to be considered when assessing the compatibility of materials with explosives:

1. Inert materials present in design interacting with the explosives and destabilising them causing an immediate safety issue.
2. Inert materials present in design interfering with some aspect of explosive performance without diminishing explosive safety characteristic causing an indirect safety issue.
3. Explosive material interacting with inert material to either increase hazard of inert materials or influence ‘Type’ performance.

When assessing these factors contact between the materials can be ‘direct’ or ‘vapour path’. Current DOSG ST1 doctrine states that unless there are two reliable seals between materials their compatibility should be tested and they are included in the compatibility test matrix. Table 20-1 is an example compatibility matrix for the munition shown in Figure 20-1. Explosive to explosive compatibility must also be proven.

Most compatibility tests are modified stability tests. An example of compatibility testing is a variation of the Vacuum Stability Test, where an explosive test sample is held at a given temperature under a starting pressure no greater than 6.7 mbar for a given time period. Assessment of the pressure increase in a

known apparatus volume allows calculation of the volume of gas given off by the explosive. As a stability test this gas evolution is compared against a specification, for example in a Defence Standard. Typical test conditions are 40 hours at 100 °C for high explosives and 240 hours at 80 °C for double base propellants.

Table 20-1 Compatibility Test Matrix for the Munition Shown in Figure 20-1

Energetic Material (EM)	Inert Material (IM)	Contact Type	Test
Torpex 9	Polyurethane Type X	Contact	Vacuum Stability & HFC
Torpex 9	Heat Insulating Layer Type Y	Contact	Vacuum Stability & DSC
Torpex 9	Steel Body Grade 2568	Possible Vapour/ Manufacturing	None (by analogy), EM and IM common from Mark I, UK Service

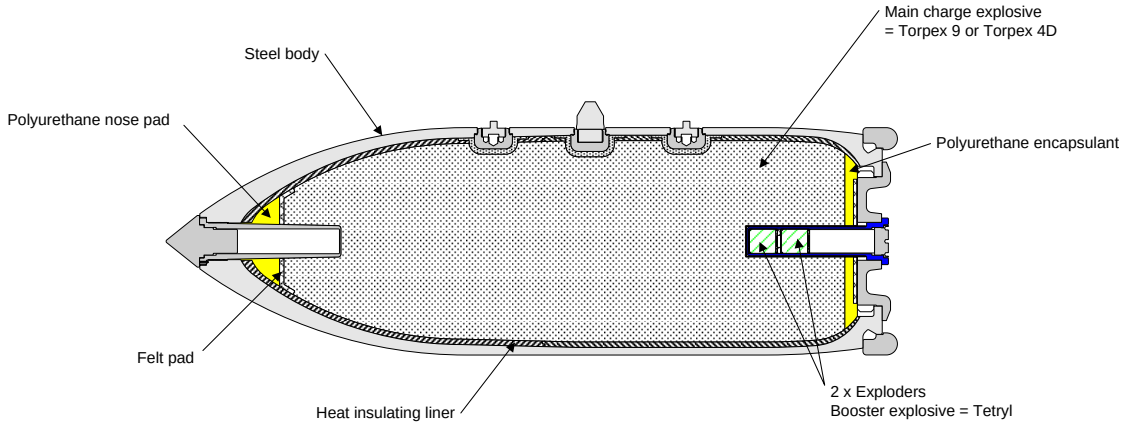


Figure 20-1 Example munition showing potential physical contact and vapour path contacts that require compatibility testing

To assess compatibility 2.5 g of the explosive is tested and gas evolution measured. Also 2.5 g of the material being assessed for compatibility is tested. This latter material is sub-divided in to small pieces. Finally 2.5 g of the material and 2.5 g of the explosive are intimately mixed and tested. If the gas evolved from the mixture is 5 cm^3 or more compared to the addition of gas evolution from the material and explosive separately the combination is incompatible.

20.4.1.2 Physical and mechanical properties

In addition to the chemical deterioration/mechanical property interaction, other physical changes may occur. Any evidence of phase changes or exudation

needs to be considered. Plasticisers and desensitisers may become mobile under thermal or mechanical stressing conditions and transfer energetic material into screw threads or other close fitting joints. The likelihood of this occurring should be assessed.

Solid propellant must demonstrate satisfactory mechanical properties over the expected service temperature range. The suitability of the mechanical properties will depend on the intended role and the physical form (whether thick web charge, thin web charge, granular or powder, etc.). Most rocket motor propellants and many explosives in charge form will require both tensile and dynamic mechanical properties to be assessed across the expected service temperature and humidity range. Where it is relevant, mechanical property testing will be carried out in accordance with STANAG 4717[10] (Energetic materials mechanical test methods). Other mechanical properties may need to be assessed and further mechanical testing may be required by DOSG to fulfil the requirements of the Qualification process.

Composite propellants also degrade with time; the rubbery matrix can be subject to oxidation which gives rise to a degradation of mechanical properties. In order to reduce this, sacrificial antioxidants can be included in the formulation. If this is the case, the level of these antioxidants will need to be monitored. The soluble fraction of the binder also provides a measure of the extent of its oxidation and hence it is necessary to determine this also, in accordance with the STANAG 4581[11] (Assessment of ageing characteristics of composite propellants containing an inert binder). Where specific STANAGs are not available, the assessment regime will need to be agreed with the National Authority.

Historically, secondary explosives were generally of very limited mechanical capability and mechanical testing was often only performed at ambient temperatures. Modern PBX compositions generally have much superior mechanical capabilities across wide temperature ranges and their characterisation for Qualification should include testing of relevant parameters across the range of service environments to be encountered. Variations in density may affect the overall hazard characteristics of High Explosive components manufactured by pressing and this should be quantified early in the development programme.

In addition, explosives will become brittle when the temperature falls below the glass transition temperature (Tg). It is therefore essential that relevant mechanical properties of PBXs be characterised both before and after ageing in order that these effects may be assessed.

By definition a booster composition is used as a component in the initiation train of a main High Explosive charge and will often be used in small quantities and with mechanical support. For this reason often only limited mechanical property testing is required.

The density, including percentage of theoretical maximum density, of the explosive material batch(es) used for the assessment is generally required by the National Authority.

20.4.1.3 Properties after ageing

Qualification requires demonstration that required properties are maintained throughout service life. AOP-7[(2)] contains guidance on the UK preferred temperature/time storage requirements to demonstrate this. It is strongly recommended that these be agreed with DOSG prior to the start of the test programme.

The temperature used to promote artificial ageing of energetic compositions must be carefully selected. The majority of the DOSG ST1 national data base contains ageing data at 60 °C for 3, 6 and up to 12 months and use of these regimes makes comparison with in service compositions straightforward. Whilst selection of higher temperatures may enable more rapid achievement of 'age equivalence', it risks promoting ageing modes unrepresentative of those encountered in service and such test results may prove unsatisfactory and require repeat ageing at lower temperatures.

20.4.1.4 Sensitiveness and Explosiveness

The principle environments under which energetic materials are assessed are:

- Impact sensitiveness
- Friction sensitiveness
- Ignition temperature
- Electric spark (electrostatic discharge sensitiveness)
- Fragment attack
- Explosive shock
- Explosive response when ignited (confined and unconfined)

Subjecting the candidate material to small scale and charge scale tests assesses the response of energetic materials to abnormal environments. The difference in sensitiveness (see 20.2.1) and explosiveness (see 20.2.1) between loose and consolidated samples is reflected in the tests necessary to provide the required information for a Qualification assessment to be made. This methodology is discussed further in Appendix A.

The larger charge scale tests (See Appendix A) subject the energetic material to stimuli, where appropriate, comprising:

- Heating under confinement
- High velocity fragment impact
- Explosive shock
- Ignition under confinement

Test regimes have been devised for National Authority assessment of energetic materials and aim to satisfy the requirements AOP7[(2)]. Unless otherwise specified, each of the tests listed in a particular regime against a particular

serial should be conducted on the candidate material. If the National Authority is satisfied that there is sufficient evidence of equivalence, it may consider reading across some of the charge scale test results from relevant compositions. In these cases, the test programme will be reduced accordingly.

A booster needs to exhibit higher sensitivity than a main charge and thus will also invariably exhibit higher sensitiveness (see 20.2.1) than the associated main charge but it is considered unnecessary to determine some of the hazard characteristics of booster compositions in charge configurations when, by the very nature of the materials, they will not see service in that form. Booster materials are used in significantly smaller quantity than main charges and therefore their exposure to mechanical stress is much reduced. If the booster is likely to be used in pellet form then further mechanical and physical tests may be required to assess the likelihood of powdering and thus any consequent hazards.

20.5 APPROACH TO QUALIFICATION

Three approaches to qualifying explosives can be identified. Qualification followed by Type Qualification or Type Qualification alone. The third is a middle route.

Qualification of an explosive followed by Type Qualification of the explosive in the weapon is the standard route under which the National Authority provides advice, and is mandated in AOP 7[(2)].This methodology has generally been the most cost effective route to provide advice when sought at a sufficiently early stage in the procurement process.

In some instances however it may be acceptable not to qualify the explosive in its own right but to undertake a more thorough Type Qualification instead. This is more likely to apply when good read across from similar explosives is available or when potential hazards have been assessed as low, for instance where weapons have only a small explosive content.

In other instances a limited amount of Qualification testing may be considered sufficient. These are when:

- Some, but insufficient Qualification data are available
- Limited read across is available
- The weapon or device in which the explosive is to be used is assessed as not presenting a significant hazard

In making a choice between the above approaches the risks of failure at a late stage in development must be considered, including the implications for the user of a weapon not being assessed as safe and suitable for service (S^3), and the overall cost to the manufacturer or supplier of the weapon if not accepted in to UK service.

Guidance in the form of a report with test schedules, indicating the level of enhanced testing required for Type Qin the absence of material Qualification testing is required and the final decision as to whether the Qualification step can be omitted remains with the UK National Authority DOSG ST1 in the UK.

When an explosive composition has been produced and qualified to STANAG 4170[(1)] by another nation, due account should be taken, both of the Qualification methods and of the amount of data released to support it.

DOSG continues to request that other nations disclose Qualification data both to enable Qualification of new explosives to be completed with the minimum of extra testing and associated costs and to assist in the development of internationally agreed standard Qualification tests. Often further information cannot be made available by the National Authority due to manufacturer's commercial confidentiality issues or ITAR constraints. Until greater cooperation is achieved the full benefits in terms of risk reduction and time and cost saving of STANAG 4170[(1)] will not be fully realised.

In order to facilitate the maintenance of a UK database it is important that all Qualification reports and safety cases contain a formal statement regarding the Qualification status of all explosives used.

20.6 QUALIFICATION REPORTING

At the end of the Qualification programme the results of the small scale tests are normally presented in the form of an Explosive Hazard Data Sheet (EHDS) along with further trials reports documenting the results of the charge scale tests and any extra testing or analysis performed.

In the UK, after consideration of all the evidence in support of Qualification, the National Authority will issue a Qualification report detailing their consideration of the evidence and generally comparing the candidate energetic material with current or historic UK service materials used in similar applications. Since this will generally require inclusion of data from multiple sources, intellectual property and/or security considerations will prevent general issue. Where required, DOSG ST1 will issue a summary report suitable for more general distribution via the relevant project team.

An explosive Qualification certificate in accordance with the format suggested in AOP-7[(2)] will be issued for each energetic material approval. The certificates will generally contain only limited formulatory information and are generally suitable for unrestricted distribution. The National Authority keeps a database of all UK Qualified energetic materials. To ensure control of intellectual property and adherence to security requirements the issue of this list is controlled by the Head of Energetic Materials in DOSG ST1.

The requirements for testing of in-service energetic materials to gain Qualification can be waived at the discretion of the National Authority DOSG ST1. This is specifically permitted within AOP-7[(2)] providing there has been no

change to the specification, explosive material already in service for which there is a history of satisfactory application may be considered Qualified by the National Authority for use in the same role (e.g. main charge filling, booster, initiator, rocket motor propellant, gun propellant, pyrotechnic, etc.), without further testing. The National Authority will define the need for any restrictions of the role and for any further testing in specific cases. Given the significant changes to the UK MOD energetic material supply base it is unlikely that continuity of specification, process and expertise will have been maintained for significant numbers of explosives which have not already been presented for Qualification by DOSG ST1 in the past decade. Therefore, material Qualification requests which are not fully supported with specific and recent (i.e. within 5 years of date of request for Qualification) test data will not generally be considered for UK Qualification.

The Qualification status of energetic materials, when fully qualified, shall be reviewed on a five-yearly basis. The Design Organization or Project Team will be requested to confirm continuity of specification, supply and process should evidence not be fully available. Where evidence supporting continuing Qualification status beyond five years is not available for munitions and delivery to MOD is still underway or is planned, the National Authority DOSG ST1 will request the Design Organisation or Project Team ensure that the Munition Safety Case is amended to reflect the position.

20.7 PRIMARIES AND PYROTECHNICS

As the UK National Authority DOSG ST1 has not qualified primary explosives and pyrotechnic materials for many years, this is entirely due to the historic nature and formulation of these types of materials. Their current UK Qualification status can be considered satisfactory and they are included in the National Authority Qualified status list.

Many devices fitted to platforms include small quantities of primary explosives or pyrotechnics whose general use is not associated with weapon effect which include aircraft fire suppression, hydraulic activation and emergency escape systems. These devices are identified for consideration by DOSG ST1 though it is accepted that in many cases the quantities of energetic material employed are small and the safety risks associated are limited to the effectiveness of device.

20.8 REFERENCES

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Appendix A Qualification Methodology and Explosive Hazard Data Sheet (EHDS) Requirements under STANAG 4170

A.1 Part 1: Methodology and General Characteristics

STANAG 4170 outlines the requirements for material Qualification within NATO nations, and combined with the requirements of AOP 7 defines the tests requirements to provide small scale and charge scale hazard data for an EHDS.

STANAG 4170 contains the following terms and definitions which must be applied when qualifying explosive materials and selecting data for an EHDS:

- Assessment. The evaluation of the properties of an explosive material, including the results of appropriate tests, to determine its relationship, with particular regard to safety, to other known explosive materials already in service use.
- Explosive Material. An explosive material is a substance (or mixture of substances) which is capable by chemical reaction of producing gas at such a temperature and pressure as to cause damage to the surroundings. Included are pyrotechnic substances even when they do not evolve gases. This document will refer only to those explosive materials whose application requires that they shall react reliably on demand. The term “explosive” thus includes all solid and liquid materials variously known as high explosives and propellants, together with igniter, primer, initiatory and pyrotechnic (e.g. illuminant, smoke, delay, decoy, flare and incendiary) compositions.
- Qualification. This is the assessment of the explosive material by the National Authority according to this STANAG and AOP-7 to determine whether it possesses properties which make it safe and suitable for consideration for use in its intended role.
- Qualified Explosive Material. An explosive material which has successfully completed the Qualification process of a National Authority. This is an intermediate risk reduction stage prior to Final (or Type) Qualification.
- Final (or Type) Qualification. Final (or Type) Qualification relates to the use of the explosive material in a specific application or munition. Final Qualification is given when the explosive has been assessed as part of the design of the specific munition, and predicted to be safe and suitable for military operational or training use in that role. The database of results is a means of undertaking “Risk Assessment”.
- New Explosive Material. The term “New Explosive Material” encompasses:
    - An explosive material not previously Qualified;
    - An explosive material for which the existing specification defining its composition, its material constituents or the process by which the composition is prepared has been modified;

  - An explosive material resulting from a change in manufacturer or manufacturing location;
  - An explosive material used in a role for which it has not already been Qualified.
- Comparison Explosive. An in-service explosive with proven safety characteristics whose properties are used to assess the relative safety and suitability of a new explosive intended for use in a similar role.
- Intended Role. The main roles are listed as follows. Nations may define other roles or add to specific information for the intended application of a particular explosive material.
  - Primary Explosive. Substance, or mixture of substances, used to initiate a detonation or a burning reaction. In their intended role these materials are sensitive to a range of thermal, mechanical and electrical stimuli.
  - Booster Explosive. Explosive material used to augment and transmit the reaction (initiated by the primary explosive) with sufficient energy to initiate a detonation reaction in the main charge.
  - High Explosive. Material which is used as a detonating final charge.
  - Solid Gun Propellant. Substance or mixture of substances which is required to burn in a controlled manner within a gun combustion chamber producing hot gases capable of propelling a projectile at high velocity. Combustible cases may also be included as they contribute to the overall energy of the propellant.
  - Solid Rocket Propellant. Substance, or mixture of substances, which is required to burn in a controlled manner within a rocket motor producing hot gases which are vented through a nozzle to propel the munition.
  - Liquid Propellant. Substance or mixture of substances, which is required to react in a combustion chamber in a controllable manner in order to generate propulsive force. These may be mono-propellants, bi-propellants or hybrids comprised of liquids and solids.
  - Pyrotechnic Compositions. Substances, or mixtures of substances, which when ignited undergo an energetic chemical reaction at a controlled rate intended to produce on demand and in various combinations, specific time delays or quantities of heat, noise, smoke, light or infrared radiation. Pyrotechnic compositions may be used to initiate burning reactions such as in igniters.

Note: Pyrotechnic compositions may be Qualified for specific role(s) such as time delay, illuminating flare etc. The Qualification status is not valid for other pyrotechnic roles for which the composition has not been assessed.

A.1.1 Methodology for Qualification of new explosive materials

For assessment of new explosive material leading to its Qualification, the following shall be identified and form the basis of an EHDS to support material Qualification;

- The explosive composition and its intended role;

- The characteristics of the explosive material which are relevant to its intended role and any specific application that is envisaged;
- The characteristics of the explosive material in its powdered state, as-used condition and after possible degradation due to ageing and the service environment;
- The effect of temperature, particularly on the safety and performance characteristics of explosive materials;
- Characteristics of particular interest include thermal, mechanical, and electrostatic discharge sensitiveness, rheological and physical properties (for example, for thermal sensitiveness), the ignition temperature and effects of confinement, charge size and heating rate should be known;
- In the case of mechanical sensitiveness, the sensitiveness to shock, friction, impact, or to a non-penetrating object, such as a crush or drop, or the effect of confinement and charge size on explosiveness should be known;
- For electrostatic discharge, the materials sensitiveness to static electricity should be assessed;
- Knowledge of the variation of rheological and physical properties with temperature and age of the material;
- The toxicity and disposal data on the explosive material, its components, and its reaction products, in-so-far-as possible.

The National Authority shall identify the minimum data requirements necessary to fulfil the conditions of the test programme. This shall include, but not be limited to, the mandatory tests (for the intended role) given in STANAG 4170.

Table 20-2 provides explosive material characteristics that need to be determined. Additional tests may also be further referenced in AOP-7. Procedures and equipment detailed in appropriate STANAGs shall be used to conduct the test methods.

AOP-7 contains guidance on procedures where STANAGs for explosive material properties are not available; this is referenced in AOP-7 Chapter 10 National sections where individual national test requirements are mandated.

STANAG and AOP methods define appropriate tests and procedures for Qualification, and are used in conjunction with and cross reference UK Energetic Material Testing and Assessment Policy (EMTAP) test procedures. These are described in AOP 7 UK Chapter 10 test methodology and the UK EMTAP manual of tests. Reference should always be made to STANAG 4170 and AOP 7 UK Chapter 10 when qualifying energetic materials for UK service.

Table 20-2 Composition Details, Use and Safety – Mandatory Requirements

Composition and Safety - Mandatory Requirements		Type of Information
1	Details of the composition and its ingredients shall be given.	Composition and specification. Method of manufacture. Source of ingredients.
2	Details of its intended role and explosive type shall be specified.	Main warhead filling, booster charge, primary explosive, pyrotechnic, propellant etc.
3	Details of its form as used in service shall be given.	Pressed, cast, extruded, machinability etc.
4	Chemical and physical properties shall be given.	Acidity, alkalinity, density (also as percentage of theoretical maximum density), melting/softening point, etc.
5	Comparisons to other similar compositions (if any) already in service shall be specified.	Service applications of closely related compositions and their status in regard to Qualification.
6	Information pertinent to material toxicity and disposal shall be specified.	Inherent toxicity data and information on the ability to be reused, recycled or destroyed with minimum effect on health and environment.
7	Compliance with National Health and Safety requirements shall be given.	Material Hazard Data Sheet, etc.

A.1.2 General characteristics

Any EHDS will only relate to an energetic material made by a given manufacturer, by a specific method of manufacture, to a given specification, and at a given place of manufacture.

Energetic materials will be supplied with an Explosive Hazard Data Sheet (EHDS) which consists of two parts,

Part 1: *Contains general characteristics that must include:*

- Designation
- Physical form
- Manufacturers name, address and contact details
- Ingredients
- Chemical stability
- Incompatibility with other materials
- Health hazards
- UN hazard division data
- Fire extinguishing agents

- Recommended method of destruction
- Packaging and storage methods

Part 2: *Contains the sensitiveness characteristics such as:*

- Sensitiveness to mechanical nipping / impact between hard surfaces
- Sensitiveness to friction
- Ignition by flash
- Behaviour on inflammation
- Ignition by electric spark
- Additional information
- Explosiveness and charge scale sensitiveness
- Name of test centre carrying out the assessment

In some cases the National Authority may be supplied with Material Safety Data Sheets (MSDSs) which do not contain specific small scale hazard test information contained in Part 2. MSDS data can be used when assessing an energetic material for Qualification but full Qualification will not be achieved without sufficient small scale hazard classification data being provided.

A.2 Part 2: Sensitiveness Characteristics.

Part two of the EHDS shall contain sensitiveness (see 20.2.1) characteristics of the energetic material and as outlined shall give the results of the tests for sensitiveness to impact, friction, and ignition by electric spark and igniferous flash. It shall also give the temperature of ignition of the energetic material, its behaviour on inflammation and any additional precautions that are considered necessary.

Sensitiveness is the UK term for a measure of the level of a prescribed stimulus, relevant to an accident situation, required to ignite or initiate an explosive material. Such stimuli include, among others, impact, friction and electric spark. The significance of the word is thus in terms of the hazard characteristics of the explosive material.

Sensitiveness and Explosiveness test methods and interpretation of results are specified in appropriate STANAGs and the UK Energetic Material Testing and Assessment Policy (EMTAP) test procedures, Manual of Tests. A fuller appreciation of the main tests required for Qualification is contained in Appendix B.

Table 20-3 Sensitiveness Characteristic Tests Described in the EMTAP Manual

EMTAP Test No.	Scale *	Major Stimulus	Duration of Stimulus	Confinement**	Info***
1a Rotter F of I	VS	Crushing a thin layer	ms	T Heavy	S
1c Grit sensitisation	VS	Crushing a thin layer	ms	T Heavy	S
2 Mallet friction	VS	Shearing a thin layer	ms	T Moderate	S
3 Temp of ignition	VS	Heat	seconds to mins	Light	Thermal Stability
4 Bickford fuze	S	Hot particles and gases	~100 ms	Light	S, X
5 Train	S/M	Flame	s	Light	S, X
6 + 7 Electric spark	VS	Electric spark	µs	Light	S
33 Rotary Friction	VS	Shearing a thin layer	ms	T moderate	S

* VS up to 0.5 g, S 0.5 – 25 g, M 25 g – 0.5 kg

** T = Transient, *** S = sensitiveness, X = explosiveness

A.3 Part 3: Explosiveness and Charge Sensitiveness Characteristics.

Information from larger scale tests for explosiveness (see 20.2.1) and charge sensitivity, where the energetic material is in charge form, is not normally required for an EHDS but will be required as a part of the final Qualification of the energetic material.

Explosiveness is the UK term which describes the degree of violence shown by an explosive material when it responds to a prescribed stimulus relevant to an accident situation. It is dependent not only on the nature of the explosive

material, but also on its mass, physical state, configuration and confinement. The significance of the word is thus in terms of the hazard characteristics of the explosive material.

The sensitiveness and explosiveness testing of materials in charge-form and in quantities greater than those used in Part 2 may highlight specific situations where the hazard is high, or may cause the apparent hazard derived from Part 2 results to be modified. Charge test results are more relevant to the hazard present when larger quantities of material are handled.

Table 20-4 Explosiveness and Charge Sensitiveness Characteristic Tests Described in the EMTAP Manual

EMTAP Test No.	Scale*	Major Stimulus	Duration of Stimulus	Confinement **	Info***
22 Large Scale gap	M	Shock	µs	Moderate	SDT
35 Tube test Internal ignition	M	Hot particles and gases	50 ms	Heavy	X
36 Fragment impact test	M	Fast fragments	µs to 100s µs	Moderate	S,X
41 Tube test-fast heating (Fuel fire)	M	Heat	seconds to mins	Heavy	X
42 Tube test (Electrically heated)	M	Heat	seconds to mins	Heavy	X

* M 25 g – 0.5 kg

** T = Transient, *** S = sensitiveness, X = explosiveness, SDT = sensitiveness to shock initiation (shock to detonation transition)

A.4 Explosive Hazard Measurement

Sensitiveness and explosiveness information is used to monitor the potential hazard. Data is obtained from the small-scale (powder) and larger-scale (charge) tests previously mentioned. Results from tests can be compared with those from well-known compositions for which considerable experience has shown to give long and satisfactory service. The information is used in a formal sense to produce the EHDS, for the Qualification of explosives for service use

and in determining the classification of the explosive for storage and transport under the UN International System.

Traditionally, it has been assumed that explosives intended to fulfil a specific function possessed broadly similar safety properties (i.e. the designations - propellant, high explosive, pyrotechnic, initiator or booster could imply various degrees of potential hazard). Today it is realised that this is no longer necessarily so, and sensitiveness and explosiveness should be evaluated for each material of interest. In the search for increased performance, propellants are being produced which, compared to their predecessors, have reduced sensitiveness but increased explosiveness.

In the search for high explosives with lower potential hazard, polymer-bonded and other new secondary explosives are being produced which, compared to their predecessors, have increased sensitiveness and reduced explosiveness. Thus in hazard terms, and as a consequence in formulations, are blurring the distinction between propellants and high explosives. Similarly, some modern pyrotechnics are sensitive enough to be classed as primary explosives. Figure 20-2 shows typical regions in the sensitiveness/explosiveness plane occupied by the various types of explosive. The most hazardous materials are those furthest from the origin.

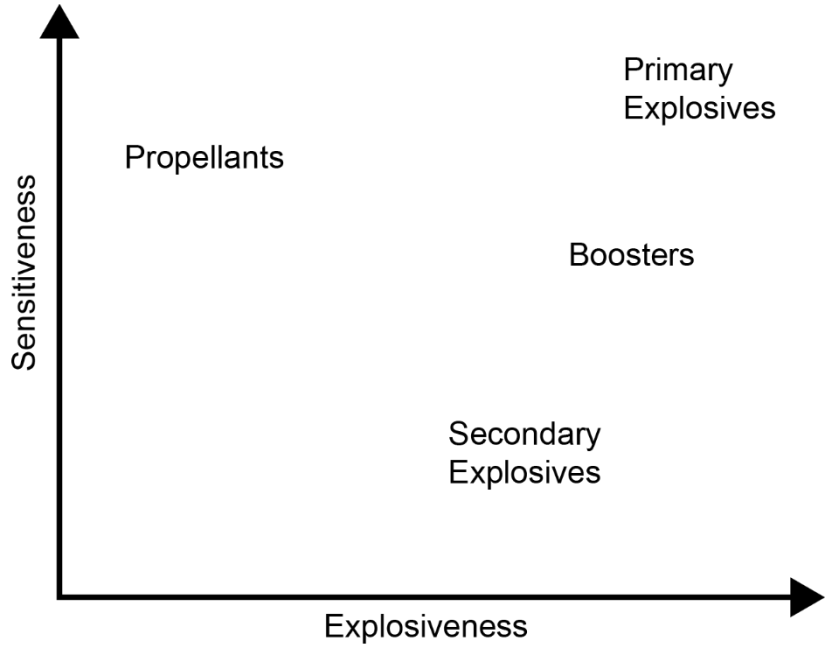


Figure 20-2 Sensitiveness/Explosiveness diagram

Apart from the monitoring of potential hazard, it is also desirable to gain a predictive capability in any hazard situation. It is clear that the probability of an event occurring is related to sensitiveness, whereas the magnitude of the event is related to explosiveness. Other factors such as explosive mass, confinement, physical form and environment also greatly affect hazard.

A.4.1 The Ideal stimulus/response curve

The ideal explosive would have a stimulus/response curve as shown by the dotted line in Figure 20-3 where no events occur below a critical stimulus level and above that level events occur in all tests. In a real situation, random variations in the explosive samples, in the state of the test machine and in the operator result in an 'S' shaped (sigmoid) stimulus/ response curve as shown by the solid line. Often data are analysed to give the '50% level', the value of the stimulus at which events would occur in 50% of the tests, e.g. Rotter Impact, Gap and Friction tests, using a technique such as the Bruceton Staircase (EMTAP Manual of tests). Although this is a useful concept for comparing explosives, it is often essential to have some idea of the probability of an event at low levels of stimulus. In this situation it is useful to analyse data by Probit Analysis so that extrapolation to low probabilities can be made using reasonably small sample sizes.

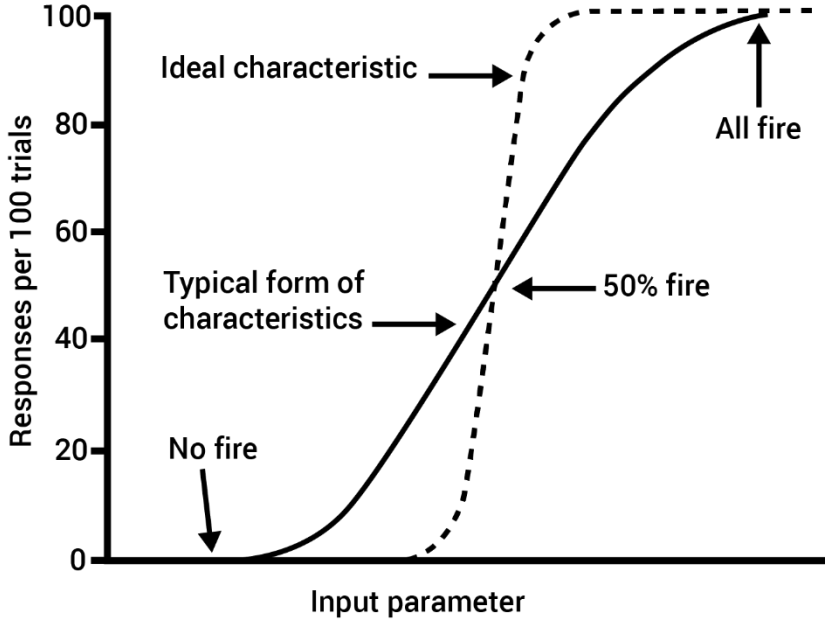


Figure 20-3 Basic stimulus-response characteristics of explosives

A.4.2 Probit analysis

In theory the sigmoid curve does not attain zero or 100 % response except at infinitely low or infinitely high stimuli respectively, whereas in practical tests it is usually found that there is a realistic lower limit at or below which no explosive substance or article will fire and a similar upper limit at or above which all explosive substances or articles will fire. The problem confronting the experimentalist with samples of limited size is the realistic evaluation of these limits. To obtain the limits it is usually necessary to extrapolate beyond the range of experimental observations.

Appendix B Material Qualification Tests from the EMTAP Manual

B.1 Introduction

The methods are specified in the Energetic Materials Testing and Assessment Policy Committee Manual of Tests (2016) (hereafter referred to as EMTAP Manual).

B.2 Safety tests

B.2.1 EMTAP Manual Test No 1: Figure of insensitiveness (F of I)

The Rotter Impact test assesses the impact sensitiveness of solid energetic materials. This is achieved by the transfer of energy from a falling drop-weight into a small test sample held within a gas tight system whilst monitoring the sample response. The drop-weight is 5 kg and drop heights vary between ~ 5 and 240 cm dependent on the susceptibility to ignition that the sample exhibits. Ignition is monitored by measurement of the evolved gas volume from reaction or from secondary ignition criteria (e.g. smoke, sample discoloration etc.).

The Rotter Impact test was originally developed to study the impact sensitiveness of crystalline secondary explosives. In the course of time and with appropriate modifications in procedure the test has been applied to all types of solid energetic materials and is now considered to be of universal application. It is a reproducible and versatile test, requiring only small quantities of explosive, and the basic action of the test is readily understood. The test can be used to quantify sensitiveness to impact, to assess relative sensitiveness and to investigate the effect of gritty contaminants on sensitiveness. A major advantage of the Rotter Impact test apparatus over other impact machines is the availability of gas volume data from ignition events and this gas volume data can be used to quantify small scale explosiveness.

The sensitiveness trials result in the calculation of a value termed the Figure of Insensitiveness (F of I). Ranking of F of I results from a range of explosives allows an order to be found that has been shown to correspond with practical experience in the handling of explosives. Surprise is often expressed at the relatively high sensitiveness (low F of I) to impact of double based propellants containing nitrocellulose and nitroglycerine where impact initiation is perceived to be Comparatively Insensitive. However accident data from such materials have shown that they are very sensitive when impacted in thin layers as is the case within the Rotter Impact test.

For the purposes of the UK MOD Explosives Hazard Data Sheets F of I results are divided into three categories shown in Table 20-5.

Table 20-5 Categories of Rotter Impact Sensitiveness

Figure of Insensitiveness (F of I)	Sensitiveness level
≤30	Very Sensitive
35-90	Sensitive
>90	Comparatively Insensitive

Grit sensitisation

This test assesses the sensitiveness of the explosive in the presence of grit and indicates the degree of hazard that would arise should an explosive filling become accidentally contaminated with hard foreign matter.

This method is as described in the Figure of Insensitiveness Rotter Impact Test No 1C with 0.1 % w/w and 1.0 % w/w grit by weight added to and intimately mixed with the test material. The EMTAP Committee on request will provide information on the nature and consistency of the grit to be used in this test and other details of the test.

B.2.2 EMTAP Manual Test No 2: Mallet Friction Test

The basic purpose of the Mallet Friction test is to provide part of the data needed to classify explosives into three main sensitiveness groups and this is achieved by the use of a series of mallets and anvils to obtain a graded response. Results from the mild steel surfaces may be taken to apply to any metal/metal combination. Results from the Yorkstone anvil may be taken to apply to concrete flooring.

Explosives giving ignitions on wooden surfaces are either inherently very sensitive to friction or sensitised by the addition of abraded wood/plastic particles which act as fuel. As a general rule, if 0 % ignitions are obtained on the mild steel anvil/mallet combination, the composition should not present handling difficulties from a frictional viewpoint, but care should be taken to avoid contamination from potential fuels.

In this test a small sample of explosive is spread onto an anvil and struck a glancing blow with a standard wood, steel-tipped, or nylon-tipped mallet held in the operator's hand. Approximately 0.1 ml of the test material is spread to give an area of about 6 mm by 12 mm on various anvils made of softwood, hardwood, Yorkstone and of mild steel, aluminium bronze and naval brass. The test material is struck up to 5 times using a standard wood mallet (for the wood and stone anvils) or a mild steel mallet (for the metal anvils). When an ignition takes place (shown by a crack, spark or flash), a fresh trace is tested. The operation is performed 10 times on each of the anvils.

The three main categories are classified as shown in Table 20-6.

Table 20-6 Categories of Mallet Friction Test Sensitiveness

A	Very Sensitive	100 % ignitions on metal and at least 50 % ignitions on Yorkstone and hardwood
B	Sensitive	All results excepting those in A & C
C	Comparatively Insensitive	No ignitions on any surface combination

Extreme care is required in handling compositions classed as “very sensitive”. Friction and impact between materials harder than softwood for those compositions classed as "sensitive" must be avoided. For “comparatively insensitive” compositions it is usual to recommend that blows between hard surfaces be avoided, but simple transfer between metal containers through pipes and valves is permitted.

B.2.3 EMTAP Manual Test No 3: Temperature of ignition

The actual values of “Temperature of Ignition” are meaningful only under the particular conditions used, as alterations in the rate of heating or quantity of explosive will give different results. Small weighed quantities of the explosive under test are heated in borosilicate test tubes placed in a steel block, the temperature of which is controlled to rise at a steady rate, until an event occurs. In this test a sample of the test explosive, 0.2 gram (or 0.05 gram for initiators) is heated in a test-tube held in an electrically heated metal block. The rate of heating is controlled to obtain a temperature rise of 5 °C per minute. The temperature of ignition is the temperature at which the sample inflames, explodes or undergoes rapid combustion.

Explosive samples giving results in the range 140 °C to 170 °C are found, in general, to have short service lives. Such samples need to be subjected to regular surveillance testing and must not be stored in close proximity to steam-heated pipes and radiators. A negative result, i.e. that reported as “not under 400 °C” should be treated with caution. It does not mean that the material has not decomposed, nor does it mean that it cannot be ignited, e.g. Pyrotechnic composition SR 371C does not inflame below 400 °C but is readily ignited in the Ease of Ignition Test (EMTAP Test No 4). Samples containing organic compounds that appear to give a negative result would normally be reported as “decomposes slowly”.

This test is also useful for:

- Screening candidate explosives (e.g. those with a “T of I” of less than 140 °C are not usually stable enough for Service use and can be ruled out);
- Distinguishing primary explosives from other classes (primary explosives explode at their Temperature of Ignition).

It is not a substitute for systematic stability testing.

B.2.4 EMTAP Manual Test No 4 Ease of Ignition (Safety Fuze) test

This test, previously called the Bickford Fuze Test, is used to assess the ease of ignition of an explosive by incendive sparks and to ascertain whether it burns or explodes. The hazard category is affected by these two observations.

If a material ignites under the conditions of light confinement of this test it must be assumed that any non-electric spark will ignite it, the electrostatic risk being determined separately. Many flammable materials are not ignited by the short flash from the Safety Fuse so flammability, as opposed to ease of ignition, should be determined from a consideration of both this test and the Train Test. The physical form of the material can affect the results of the test, e.g. with certain pyrotechnic compositions, changes in the grain size of the individual ingredients, coupled with small changes in formulation, are enough to cause a change from “burning vigorously” to “explosion”.

If a material explodes in this test, it must be assumed that the material will explode on inflammation. A negative result must be supported by data from larger-scale tests, e.g. the sealed vessel tests and the tube tests.

In this test a sample of the powdered test material (3 gram) is put into a test-tube with a length of Bickford fuze resting on the surface of the material. The behaviour of the material is noted when the gunpowder core of the Bickford fuze burns through and the brief flash output impinges on the test material. The result is categorised as follows:

- fails to ignite
- ignites and burns quietly
- ignites and burns vigorously
- explodes

B.2.5 EMTAP Manual Test No 5: Train Test

This test determines whether an unconfined material in powder form will ignite if a flame is applied to it and assesses the degree of hazard arising from the ignition. An unconfined train of material is heated at one end by a naked flame for up to 2 minutes, and observations are made of the liability of the sample to burn and how vigorously it does so.

Many materials that are not ignited in the Ease of Ignition Test (EMTAP Test No 4) will burn when subjected to a naked flame of several seconds duration. Therefore, this test is used to determine whether a loosely or lightly confined material will ignite if a flame is applied, and to assess the hazard arising from an ignition.

The physical form of the material can affect the results of this test though the effect on the results is less than that experienced in EMTAP Test No 4. If an explosion is obtained under the conditions of this test then the material must be treated as an explosive risk. If the material burns vigorously, i.e. burns rapidly with or without sparks, or more slowly with copious sparks, it will obviously lead to a rapidly spreading fire. However, such a reaction does not necessarily

mean that the material will not exhibit an explosive risk when stored in bulk. The test is incapable of deciding this, and differences between explosive and fire risks are best made by means of sealed vessel tests, and/or tube tests. This aspect must also be considered in relation to materials placed in other categories by this test, since it has to be remembered that this test is carried out at virtually atmospheric pressure, whereas, in the real case, sufficient confinement may allow an increase of pressure leading to an increase in rate of burning.

The resultant behaviour of the explosive is observed and recorded as follows:

1. Fails to ignite (FI)
2. Ignites but fails to support train for more than XX mm
3. Ignites but supports train fitfully (ISTF)
4. Ignites and supports train steadily throughout (ISTST)
5. Ignites and supports train vigorously throughout (ISTVT)
6. Explodes (E)

B.2.6 EMTAP Manual Test No 6 and 7: Ignition by Electric Spark

This test has been devised to provide a fairly simple means of distinguishing between those explosive materials which need a relatively high energy for ignition by electrostatic sparks and those which need a relatively low energy. The dividing line between two such groups of risk was suggested by the maximum amount of electrostatic energy that can be accumulated on a person in the UK which is believed to be 0.02 J. In this test the lowest energy was fixed at 0.045 J, i.e. a safety factor of approximately two. Energies of ten times and one hundred times this were chosen for the higher levels, i.e. 0.45 J and 4.5 J. However, it has been found that this energy of 0.02 J is rarely attained and it is more realistic to regard 0.001 J as being the likely maximum. Consequently, a subdivision into three groups of risk is more appropriate for the UK, but this will not necessarily apply in other countries as the ability to store and discharge an electrostatic charge depends on several factors including humidity.

The highest energy group comprises those compositions needing energies in excess of 0.45 J and for which First Degree Precautions are sufficient. Compositions in this group are classified as "Comparatively Insensitive" to electrostatic spark. Full Second Degree Precautions are necessary for those compositions that have a ‘minimum ignition energy of less than 0.001 J, i.e. those classified as "Very Sensitive".

Those compositions having ignition energies in the range 0.45 J to 0.001 J, are classed as "Sensitive", and form an intermediate class in which the precautions to be applied are gradually increased from First Degree towards Full Second Degree Precautions as the minimum ignition energy decreases from 0.45 J to 0.001 J.

The tests are carried out in two stages. The first stage is to determine whether an electrostatic spark with an energy of 0.045 J ignites the material. If the material is sensitive to a spark of that energy, then the second more searching

test is carried out to determine the minimum energy required for ignition. In each test the discharge from a charge capacitor is passed through the material, which is normally tested in a powdered or granular state.

B.2.7 EMTAP Manual Test No 22A. (The Large Scale Gap Test).

The Large Scale Gap Test is used to compare the shock detonation sensitiveness of a wide range of explosive materials having critical diameters up to approximately l00 mm. A witness plate is used to distinguish detonation of the test explosive from sub-detonative reactions.

The test uses a reproducible attenuator material accurately calibrated in terms of attenuator thickness versus shock pressure using a standard explosive donor. Following the US convention, the results are expressed as the pressure just inside the attenuator at the attenuator/acceptor interface at the gap thickness which produces a 50 % probability of detonation in the test explosive.

The test is based on the US Naval Ordnance laboratory (NOL) Large Scale Gap Test, and results obtained can be compared with the published US data. The material under test, in the form of a cylindrical pellet or casting (140 mm x 36 mm) is subjected to the shock generated by the detonation of a standard donor pellet. The donor pellet is Rowanex 3601 (50 mm x 50 mm) pressed to a density of 1600 kg m^3. The test explosive is confined in a steel tube which is inserted into a cardboard tube containing the Rowanex 3601 pellet. Interposed between the donor or acceptor pellet is a barrier of polymethylmethacrylate (PMMA) (50 mm diameter) of density 1186 ± 1 kg m^{-3} and thicknesses ranging from 5 mm to 70 mm in 1 mm increments.

A steel witness block is used to assess the reaction of the test material. The thickness of the barrier is varied to determine the thickness at which there is a 50 % probability of detonation of the material under test. The criterion used to distinguish between a detonation and a non-detonation is that for detonation a clean hole is punched in the witness plate.

B.2.8 EMTAP Manual test No 33: Rotary Friction Test

This test is designed to provide a quantitative assessment of the friction sensitiveness of a wide range of solid explosives. Unlike the Mallet Friction Test (EMTAP Test No. 2) there is no element of impact in the stimulus. Although any wheel and block materials of interest can be used, the standard test uses mild steel blocks and wheels of standard surface roughness. Results are expressed relative to those for standard RDX by assigning a value of 3.0 to the Figure of Friction for the standard RDX. This value was chosen because it is close to the actual median peripheral wheel velocity (m/s) when testing the standard RDX.

Energy stored in a flywheel imparts an impulse to the wheel assembly, causing it to rotate. This rotation generates high shearing forces in the sample, which is under a pre-set load between the wheel and the stationary block

In this test a Bruceton Staircase procedure is used over 50 trials to establish a median flywheel angular velocity for the test material. Results are expressed in terms of Figures of Friction relative to standard RDX.

For MOD Explosives Hazard Data Sheets the Figure of Friction is normally quoted to two significant figures. Broad sensitiveness categories can be assigned as shown in Table 20-7 to conform to those used in the Explosives Hazard Data Sheet.

Table 20-7 Categories of Rotary Friction Test Sensitiveness

Very sensitive	Cat A	FoF < 3
Sensitive	Cat B	FoF >3 but <6
Comparatively insensitive	Cat C	FoF > 6

B.2.9 EMTAP Manual test No 35: Tube Test – Internal Ignition

A sample of explosive, confined in a steel tube, is ignited by means of a charge of propellant. The degree of fragmentation of the tube is used to assess the relative explosiveness of the composition under test.

The internal ignition version of the Tube Test can be used to evaluate the explosiveness of solid high explosives and propellants. It assesses the behaviour of explosive charges when ignited under confinement. The level of violence of this reaction, and its potential to cause damage to the surroundings, is referred to as "explosiveness".

Explosiveness is influenced by several variables including the nature of the stimulus, the temperature and physical form of the explosive and its confinement. The Internal Ignition Tube Test has been developed to assess explosiveness under one set of well-defined conditions. These conditions are more representative of a moderately confined explosive in munitions such as shells but the data generated form a basis for comparing the relative explosiveness of energetic materials. Because the test is relatively cheap and simple to perform it is used routinely in assessing the potential hazards of new explosive formulations.

In this test the explosive may be cast, pressed, extruded, or pre-machined to shape and fitted into a mild steel tube 253 mm long, i.d. of 31 mm and a wall thickness of 6 mm. The ends of the tube are sealed with heavy, mild steel, screw caps. The charge is ignited at one end using an electric match head and a 1 g charge of Bullseye or M9 propellant.

The number of fragments recovered provides the most useful indication of the relative explosiveness of the material under test. In those experiments where less than 100 % of the test vehicle is recovered, the number of body fragments may be divided by their fraction of the intact vehicle to give a "normalised number of body fragments". This number is then used to assign a reaction

category to the event using the descriptions listed in Table 20-8. For clarity, the reaction description should be included as well as the category when reporting the results

Table 20-8 Description of Tube Test Reaction Categories

Category	Reaction Description	Observation
0	No Reaction	From weighting
0/1	Burning decomposition	No disruption of test vehicle
1	Pressure burst due to burning/decomposition	Assembly ruptured but one fragment approximates to original weight
2	Deflagration	2 to 9 body fragments
3	Explosion	10 to 100 body fragments
4	Detonation	>100 test vehicle body fragments showing evidence of detonation

B.2.10 EMTAP Manual Test No 36: Fragment Attack Test

The fragment attack of confined explosive charges invariably produces disruptive events at velocities much below those required to initiate detonation via a shock mechanism. It is important to assess the vulnerability of explosives to fragment attack in this lower velocity region since the occurrence of a violent deflagrative event in a munition may pose a hazard equal to that of a detonation and in some cases it may be possible for an initial deflagration to burn to detonation (link to 5.1.2.1). The processes which control the response of an explosive to fragment attack are complex and are very susceptible to changes in test parameters such as case thickness, charge size and fragment mass. However, it is possible to obtain a preliminary assessment of the vulnerability of explosive compositions to fragment attack by selecting a standardized set of test parameters. The Fragment Attack Test has been designed for this purpose and allows the study of fragment-initiated reactions to be undertaken at velocities up to 2500 m s^{-1}.

The projectile employed is a 13.15 mm diameter, 25.4 mm long mild steel cylinder. It is fired from a smooth bore gun at velocities in the range 400 to 2000 m s^{-1} to impact normally on the septum of the assembled test vehicle. Greatest control of fragment impact velocity is achieved by employing a modified 0.5 in (12.7 mm) Browning gun for velocities up to 1000 m s^{-1} and a modified RARDEN (30 mm) gun with a saboted projectile for higher velocities. However, a gas gun or other gun giving similar control to the above over velocity and fragment orientation may be used.

The response of the explosive charge to the projectile impact is assessed in terms of the damage done to the test vehicle according to the categories listed in Table 20-9.

Table 20-9 Description of Fragment Attack Test Reaction Categories

Category	Reaction Description	Observation
0	No Reaction	No visible sign of reaction after penetration of the septum by the projectile.
1	Burning	Hint of a burning reaction which has faded rapidly, no obvious consumption of explosive.
2	Deflagration	Detachment of the septum, up to 20 % of the explosive consumed.
3	Explosion	Septum detached, vehicle intact or broken into large fragments, more than 20 % of explosive consumed.
4	Detonation	100 % of explosive consumed in a very violent reaction characterised by breaking up of vehicle into very many small fragments showing evidence of shear failure.

SERVICES TEXTBOOK OF EXPLOSIVES - GLOSSARY OF TERMS

This Glossary of Terms covers the various terms and acronyms, etc. covered in the chapters of this Textbook. It also incorporates some of the terms used in the 1988 version of the Services Textbook of Explosives and from Allied Ordnance Publication 38 “Glossary of Terms and Definitions Concerning the Safety and Suitability for Service of Munitions, Explosives and Related Products” (AOP-38) which may be of use to the reader.

A

AAS3P	Allied Ammunition Safety & Suitability for Service Publication
Abel Heat Test	A test introduced by Sir Frederick Abel to assess the stability of guncotton by detecting oxides of nitrogen by starch-potassium iodide paper
ABOL	All Burnt On Launch - Normally referred to in connection with motors of Shoulder launched GW: rapid burning motor which expels all exhaust products before the missile leaves the launcher
Accelerated Test	A test in which the applied stress level is chosen to exceed that stated in the reference conditions in order to shorten the time required to observe the stress response of the item or magnify the response in a given time. To be valid, an accelerated test must not alter the basic modes and/or mechanisms of failures, or their relative prevalence
ACGIH	American Conference of Governmental Industrial Hygienists, an American advisory body which sets the standard for Threshold Limit Values
Action Time	The elapsed time from application of primer initiation energy to the moment of projectile base exit from the muzzle of the barrel
Activation Energy	The energy difference between the average energy of activated molecules (i.e. those which are able to react) and the average energy of normal molecules. In essence, it is the minimum amount of energy which must be supplied to a chemical system to initiate a chemical reaction
Actuator	A mechanism that furnishes the force required to displace a control surface or other control element
Acute Toxicity	Toxicological effect produced after a short exposure
Adiabatic Change	A change undergone by a system such that no heat enters or leaves the system. In the adiabatic expansion of a quantity of gas the temperature falls because the external work is done at the expense of the internal energy of the gas
Adiabatic Flame Temperature	The maximum thermodynamic standard state temperature ideally achievable during combustion under adiabatic conditions
ADN	Ammonium dinitramide - a potential replacement for ammonium perchlorate in composite propellants and more environmentally

	friendly compared with propellants based on AP
ADR	"Accord européen relatif au transport international des marchandises dangereuses par route" - regulates the carriage of dangerous goods, including explosives, by road
All-Arm Distance	After firing the munition, the minimum distance between the weapon and the launched munition where the fuze is armed
All-Fire Level	The value of a stimulus which, under specified conditions, is predicted to cause an explosive material or an explosive component to function, with a stated probability
All-Function Level	The minimum value of a stimulus which, under specified conditions, is predicted to cause a device or component to function, with a stated probability and confidence level
Amatol	Ammonium nitrate and TNT mixed in various proportions (e.g. 80/20) for use as a shell filling
Ames Test	A test, using micro-organisms, which is used as an indicator of possible mutagenicity
Ammonal	An explosive comprising a mixture of TNT, ammonium nitrate and aluminium
Ammunition	A device charged with explosive, propellant, pyrotechnic, initiating composition or nuclear, biological or chemical material for use in connection with offence, or defence including demolitions. Certain ammunition can be used for training, ceremonial or non-operational purposes
Ammunition Compatibility Grouping	A system of classifying bulk explosives and live ammunition into twelve groups, so that items which would, if accidentally initiated, increase the hazards by their interaction are not stored or transported together
AN	Ammonium Nitrate - a white crystalline solid with the chemical formula NH_4NO_3
Anaemia	A reduction in the normal concentration of haemoglobin or red cells in the blood
ANAL	Ammonium nitrate and aluminium powder
ANFO	Ammonium nitrate + fuel oil, a common, inexpensive blasting agent
Angina	Severe chest pain caused by lessening of blood supply to the heart muscles
ANNIE	ammonium nitrate nitrobenzene improvised explosive
ANS	Ammonium nitrate and sugar
Antioxidant	A substance which prevents or retards oxidation. For example, antioxidants are used in nitrate ester propellants to reduce the effect of the auto oxidation of the compositions
AOP-7	Allied Ordnance Publication 7 - Principals and methodology for the qualification of explosive materials for military use
AP	Ammonium Perchlorate – extensively used as an ingredient for composite propellants for rocket motors
Aplastic Anaemia	Anaemia as a result of damage to bone marrow
Approving Authority	For the Qualification of explosives, the approving authority is defined in STANAG 4170. The National Authority for the United Kingdom is the Defence Ordnance Safety Group

ARC	Accelerated Rate Calorimetry – used to measure the thermal and pressure properties of exothermic chemical reactions
Arkadite II	N-methyl-N',N'-diphenylurea – a stabiliser for nitrate ester propellants
Arm	To make a fuzing or firing system ready for functioning by removal of all the safety constraints thus permitting the munition to be fired on receipt of a specified firing stimulus and to function as intended
Armed	The state of the (sub)-system when all safety breaks and switches have been made ineffective with the exception of the single function which would initiate the intended operation of the system
Arrhenius Equation	An important equation in physical chemistry which expresses the way in which the rate constant of a chemical reaction is influenced by temperature
Arming Delay	A time delay between launch initiation and fuze arming by which time a safe separation distance should have been reached
Article (Explosive)	An article containing one or more explosive substances
ASA	A disruptive, flash sensitive, primary explosive composition containing lead azide, lead styphnate and aluminium in specific proportions
Assessment	The evaluation of the properties of an explosive, including the results of appropriate tests to determine its relationship, with particular regard to safety, to other explosives already in Service use
Attenuate	To reduce in force or value. The term is often used to describe the weakening of a shock wave by decreasing its amplitude or duration
Augmenting Cartridge	A small quantity of propellant in a container which may be added to the primary cartridge to make up propellant charges for mortar ammunition
Audit	An evaluation of a system, organisation, process, project or product. An audit is often carried out with a view to achieving an improvement in performance
Availability	The probability an item is in operable and committable at the start of a mission when the mission is called for an unknown (random) time

B

Bachmann Process	A method used for the manufacture of RDX using nitric acid and ammonium nitrate or nitric acid, ammonium nitrate, glacial acetic acid, and acetic anhydride. The process produces HMX as a by-product
Backblast	The rearward blast of (hot) propulsion gases when the weapon is fired, escape from the muzzle brake of recoil weapons and from the aft opening (venture) of recoilless weapons. The blast

	may contain fragments and particles swept up from the ground
Ballistic Coefficient	An index relating size, shape and weight of a projectile to its aerodynamic drag
Ballistic Modifier	Any additive incorporated in a propellant composition to alter its rate of burning
Ballistic Mortar	A device for measuring the power of an explosive
Ballistics	The science or art that deals with the motion, behaviour, appearance or modification of missiles or other vehicles acted upon by propellants, wind, gravity, temperature, or any other modifying substance, condition or force
Ballistite	A double base propellant in the form of flakes, used in mortars and small arms. It is composed of nitrocellulose and nitroglycerine, blended together with diphenylamine, which acts as a stabilizer
Ball Powder	A type of small arms propellant, usually single base, manufactured in the form of small spheres
Baratol	Barium nitrate and TNT mixed in various proportions for use in grenades and anti-tank mines, also in some wave shaping applications
Barium Styphanate	Barium 2,4,6-trinitroresorcinate – a relatively insensitive primary explosive which is difficult to ignite by electric spark. It is less sensitive to impact and friction than lead azide or lead styphnate
Base Bleed	Reduction of the aerodynamic drag of a shell by means of an auxiliary device in the shell consisting of propellant in a combustion chamber. The propellant gases flow out into the wake behind the shell, enhancing the pressure and thereby reducing drag
Base Charge	The increment of secondary high explosive (commonly tetryl, PETN or RDX) in the base of a composite detonator, which enhances the shock wave produced by the primary explosive.
BDNPA	Bis(2,2-dinitropropyl)acetal (BDNPA) $C_8H_{14}N_4O_{10}$ is an energetic plasticizer used in propellant and explosive applications
BDNPF	Bis-Dinitropropyl formal, $[CH_3.C(N0_2)_2.CH_20]_2.CH_2$
BDNPA/F	Bis(2,2-dinitopropyl)acetal/formal $C_{7.5}H_{13}N_4O_{10}$ is used in LOVA gun propellants. It is typically used in a 50/50 mixture as a plasticiser
Biazzi Process	Named after the Italian Mario Biazzi – a continuous process for the manufacture of nitroglycerine
Biodiversity	The number and variety of living organisms on the planet
Bipropellant	A propellant composed of two components, a fuel and a liquid oxidiser. Generally neither substance is explosive
BKW	Brinkley-Kistiakowsky-Wilson, an empirical equation of state for the detonation products of condensed explosives that is widely used for practical calculations
Black Powder	Gunpowder comprising potassium nitrate, charcoal and sulphur. Usually 75/15/10
Blast	A supersonic wave produced in the surrounding atmosphere by

	an explosion. A blast wave comprises a shock front with an area of high pressure air behind it, followed by a rarefied zone
Blast Impulse (or Positive Impulse)	The time integral of the overpressure exerted by a blast wave
Blasting Agent	A commercial explosive mixture of fuel(s) and oxidant(s) containing no ingredient which in considered to be separately explosive. Examples are ANFO and some water based slurries. The distinction between blasting agents and explosives is economically important in the different safety regulations which apply
Blasting Gelatine	A commercial explosive comprising a very high proportion of nitroglycerine (about 92%) with sufficient nitrocellulose to render it gelatinous, and a little chalk. It has a high detonation velocity and is totally waterproof
Boltzmann Constant	Named after Ludwig Boltzmann, it is a physical constant relating the average kinetic energy of particles in a gas with the temperature of the gas
Bonding	The strength of the adhesion of an explosive filling to its receptacle
Booster (Explosive)	A high explosive element sufficiently sensitive so as to be actuated by small explosive elements in a fuze or primer and powerful enough to cause detonation of the main explosive filling
Booster (Propulsion)	An auxiliary or initial propulsion system which travels with a missile or aircraft and which may or may not separate from the parent craft when its impulse has been delivered. A booster system may contain or consist of one or more units
Bridge-wire	An electrical filament which can be used to ignite a pyrotechnic or primary explosive which is in contact with it, normally inside an igniter or detonator. Unless specified as an 'exploding bridge wire ' it can be operated in a low tension circuit
Brisance	The shattering property shown by an explosive. The property is estimated by firing explosives in contact with metals or other solids and measuring the deformation or shattering. The effect is associated with the detonation pressure and the characteristics of the shock wave produced in the material in contact with the explosive
Brixal	Bridgwater explosive, aluminised. A variant of Debrix containing up to 30% of aluminium. Can be produced as a free flowing powder
Bruceton Staircase	A statistical technique used to determine the Figure of Insensitiveness (F of I) of energetic materials
Bubble Pulse	The repeated secondary shockwaves emanating from an underwater detonation of an explosive charge
Burning	The propagation of combustion by a surface process involving conduction, convection and radiation
BWX	Beeswax, used as a desensitiser in some HEs

C

CAB	Cellulose acetate butyrate – an inert polymeric binder
Calorimetric Value	The amount of heat evolved by the combustion of a propellant in a closed vessel in the absence of air or oxygen gas. By convention, the result is based on the assumption that the water formed during combustion is in the liquid state, which is not true in the case of a gun
CAN	Calcium Ammonium Nitrate - a mixture of AN and calcium carbonate that has a nitrogen content of 27%
Canister	A case containing substances designed to release or emit pyrotechnic smoke, harassing or casualty producing material. It may be a complete store in itself or may be a component of another store
Cap	A small metal container filled with a flame producing explosive composition
Carbamite	Diphenyl diethyl urea, known outside the UK as ethyl centralite. A common stabiliser/plasticiser/collant in gun propellant compositions
Carcinogen	A cancer producing substance
Cartridge	Definitions of cartridge are given as follows: (1) A cased quantity of propellant complete with its own means of ignition. The term is also used to describe a complete round of shell and cartridge when applied to small calibres, in the small arms range, of fixed or semi fixed ammunition. (2) A complete fixed round with propelling assemblage consisting of charge case, charge and primer. Also applicable to mortars and not restricted to small calibres
Case Cartridge	A container of brass, steel or other material to contain a propellant charge for use with automatic and semi-automatic ordnance, small arms and recoil-less weapons. The base is designed to take a primer or igniter
Case Bonding	The gas tight adhesion of a rocket propellant grain to the walls of the combustion chamber of the motor
CAS	Chemical Abstracts Service – ascribes reference numbers
Cavity	The portion of the projectile that accepts the fuze
CCC	(1) Cap conducting composition (2) A marking on British coloured smoke pyrotechnics, printed in the colour of the smoke produced. (3) Combustible charge container. Used in some large guns to contain the propellant charge, the container is completely consumed during firing and contributes to the ballistic performance
CDB	Cast double base (rocket propellant). British examples are propellants AY, BY, CY etc.
CE	Composition Exploding – also known as Tetryl (2,4,6 trinitrophenylmethylnitramine)
CERU	Cartridge Ejector Release Units used to provide a release and

	separation of a missile from the aircraft
Characterisation	The determination of attributes of a material or a substance to fulfil particular requirements
Charge	There are two definitions for this term: (1) The amount of propellant required for a fixed, semi fixed or separate loading projectile, round or shot. It may also refer to the quantity of explosive filling contained in a bomb, mine or the like. (2) In combat engineering, a quantity of explosive prepared for demolition purposes
Chamber Pressure	The pressure existent within the weapon chamber at any time as a result of the burning of the propellant charge
Chapman-Jouguet (C-J) Surface	A plane behind the initial shock front of a detonating explosive where material is receding from the wave front at the local sonic velocity. In a high order detonation the chemical reaction (and energy release) has effectively been completed. In a low order explosive the end of the reaction zone may be behind the C-J plane
CHEETAH	CHEETAH is a thermochemical computer code and is a physics- and chemistry-based computational tool that can reliably predict the performance of ideal and non-ideal high explosives and explosive formulations
CHIP	Chemical Hazard Labelling and Packaging
Chronic Toxicity	Toxicological effect produced as a result of long term exposure
Chuffing	The characteristic of some rockets to burn intermittently and with an irregular noise
CL-20	Hexanitrohexaazaisowurtzitane, also called HNIW - an explosive with detonation shock pressure greater than HMX
Closed Detonation	To place a munition in a closed chamber and to initiate it with an explosive charge. The evolved gases and solid residue can then be collected and treated in an environmentally safe manner
CLP	Classification, Labelling and Packaging Regulations - adopts the United Nations' Globally Harmonised System on the classification and labelling of chemicals (GHS) across all European Union countries, including the UK
Classification Of Hazardous Goods	A United Nations scheme for classifying goods into nine classes according to their hazardous nature. Explosives form Class 1
CLC	Charge Linear Cutting - A linear shaped cutting charge of high explosive encased in a metal tube which has a groove on one side. When detonated groove inwards against sheet metal it produces a cutting effect
Closed Vessel Test	A test in which the pressure time relationship, resulting from the combustion of a standard weight of propellant in a stout steel vessel of fixed volume, is used to indicate the ballistic properties of the propellant
CMCDB	Composite modified cast double base (rocket propellant).

	Ammonium Perchlorate and aluminium are added to CDB compositions via the casting powder. CMCDB may also contain RDX or HMX
CNS	Central Nervous System, comprises the brain and the spinal cord
COER	2.2.5 The Control of Explosives Regulations 1991 - regulates any person (including a body corporate) who acquires; has access to; possession of or control over any explosives
Combustion	An exothermic oxidation reaction producing flame, sparks or smoke. The oxidant may be part of the material as in a propellant, or oxygen from the atmosphere or other source
Comparison Explosive	An in-service explosive material with proven safety characteristics whose properties are used to assess the relative safety and suitability of a new explosive intended for use in a similar role
Compatibility	Compatibility of two or more items or components of equipment or material to exist or function in the same system or environment without interference
Compatibility Grouping	See Ammunition Compatibility Grouping
Complete Round	Ammunition which contains all the components necessary for it to function
Composition Exploding (CE)	See CE. The Service name for the explosive trinitrophenyl methylnitramine. It is used in, for example, fuzes such as an Intermediary explosive. Also called Tetryl.
Composite Propellant	A solid propellant, usually for rockets, which comprises an inorganic oxidant (typically ammonium perchlorate) and a polymeric fuel/matrix. The wide diversity of candidate polymers and additives gives a range of physical properties and performance. They can be subdivided into three classes; 'plastic', 'rubbery' and 'pressed', the latter no longer being used widely now. Plastic propellants generally featured a polyisobutene (PIB) binder whereas composites use Polyurethane (PU), Polybutadiene (PB) or Polybutadiene acrylic acid acetonitrile (PBAN)
Composition A	A mixture of RDX 91% with beeswax 9% as desensitiser. (US term)
Composition B	A mixture of RDX with TNT, usually 60/40 (US term).
Composition C	A mixture of RDX with oil and/or polymeric material in proportions e.g. 88/12 to give a plastic explosive (US term)
Conducting Cap	An initiatory component (eg of a gun cartridge) in which the passage of an electric current through a small quantity of conducting composition heats it to its ignition temperature. The use of a bridge-wire is thus eliminated
Conducting Cap Composition	A initiating composition, containing graphite and initiating composition, which allows the flow of an electrical current between the pole pieces. As the current flows, sufficient heat is

	generated to function the composition
Confinement	The characteristics of the casing of a charge which restrict the expansion of the decomposition products when the explosive substance reacts
Consumable Case	A cartridge case, made of a suitable combination of ingredients, that will enable the case to be completely consumed during the firing event but which does not significantly contribute to the energy of the system
Continuous-rod warhead	The warhead casing features long pre-formed rods which are linked to produce an expanding hoop
Controlled Fragmentation	The munition casing or the explosive charge is modified to cut the metal into relatively uniform shapes and sizes
Cook-off	The premature explosion of an enclosed explosive by the conduction of heat through its container. Applicable to e.g. munitions exposed to fires, or to live cartridges left loaded in hot guns
Cordite	Double base propellant for small arms, guns or rockets, in the form of extruded cords or tubes. The use of the term cordite in British service was discouraged from 1950 but still persists. The correct designation of such compositions is simply "Propellant" followed by the identifying letters, e.g. “Propellant WM”.
Cordtex	Proprietary name for one type of detonating fuze produced by NEC Ltd
COSHH	Control of Substances Hazardous to Health
Critical Characteristic	A characteristic (tolerance, surface finish, material, manufacture, assembly) of a product, material or process which may result in the failure of a critical item in the event of non-fulfilment of requirement
Critical Diameter	The diameter of an explosive charge below which it will not detonate
Cryolite	Potassium aluminium fluoride or sodium aluminium fluoride, both used to reduce flash in gun propellants
CS	The compound 2-chlorobenzalmalononitrile (also called o-chlorobenzylidene malononitrile) (chemical formula: $C_{10}H_5ClN_2$), a cyanocarbon, is the defining component of CS gas, which is used as a riot control agent
CTMTNA or R-salt	Cyclotrimethylenetrinitrosamine - similar in structure to cyclotrimethylenetrinitramine (RDX), the difference being the presence of nitroso groups rather than nitrate groups.
CTPB	Carboxy terminated polybutadiene
Cutting Charge	A charge which produces a cutting effect in line with its plane of symmetry
Cyanosis	Blue colouration of the mucous membranes and the skin caused by low oxygenation of the blood
Cyclonite	US name for RDX
Cyclotol	US name for RDX/TNT, usually 75/25

D

DADP	Diacetonediperoxide - a white powdery solids which is extremely sensitive to shock, friction, electrostatic spark and flame
Danger Area	A specified area above, below or within which there may exist potential danger for personnel and/or equipment
DATB	1,3-Diamino-2,4,6-trinitrobenzene, $(NH_2)_2.C_6H.(N0_2)_3$, a high-melting secondary HE
DBP	Dibutyl phthalate – plasticiser historically used in propellants – now restricted under REACH
DBX-1	Copper(I) 5-nitrotetrazolate - an environmentally friendly (lead-free) primary explosive which is a drop-in replacement for lead azide and has a similar sensitivity profile and equivalent or better output when replacing LA in the same volume
DCDC	Development, Concepts and Doctrine Centre - based at Shrivenham
DDNP	Diazodinitrophenol; alternatively named 4,6 dinitrobenzene 2 diazo l oxide, a primary high explosive
Deactivation	To return an armed fuzing system to unarmed mode by the issue of a specific command or after a pre-set delay
Dead Pressing	A phenomenon whereby the sensitiveness of an energetic material is reduced at high pressing densities
Debrix	"Desensitised Bridgwater Explosive". A range of compositions in which RDX or HMX is desensitised by a small but efficiently admixed proportion of wax. Suggested for use in exploders, HEAT warheads and HESH projectiles
Deflagration	Subsonic combustion propagating through heat transfer; hot burning material heating the next layer of cold material and igniting it. When applied to articles: Ignition and burning of the confined energetic material leads to non-violent pressure release of a low strength case or venting through case closures (leading port/fuze walls, etc). The case might rupture but does not fragment; closure covers might be expelled, and unburned or burning energetic material might be thrown about and spread the fire. Pressure venting can propel an unsecured test item, causing an additional hazard. No blast or significant fragmentation damage to the surroundings; only heat and smoke damage from the burning energetic material
DDT	Deflagration to Detonation Transition - the transition to detonation from an initial burning reaction
DEFRA	The Department for Environment, Food and Rural Affairs. Defra are a government department responsible for environmental protection
DEGDN	Diethyleneglycol dinitrate, a propellant constituent. $(O_2NOCH_2CH_2)_2O$
Delay Element	An intermediate item in an explosive train to lengthen the function time of the train
Demilitarisation	The act of removing or otherwise nullifying the military potential

	of a munition. Demilitarisation is anecessary step for military items prior to their release into a non-military setting
Demolition	The destruction of structures, facilities or material by the use of fire, water, explosives mechanical or other means
Demolition Charge	An explosive charge designed to destroy material, structures or installations by means of explosive effects such as blast, fragmentation or cutting
Dermatitis	Inflammatory reaction of the skin to contact with toxic substance
Design Principles	The fundamental rules to be adhered to in the process of recognition and problem solving associated with the creation of a product
Design Safety State	A system state that provides the maximum degree of safety within the constraints of the administrative, operational or logistic phase
Detasheet	A plastic explosive in sheet form based on PETN and manufactured by DuPont of USA.
Detent	A catch, latch, stop pin, metal pin or similar feature supported or retained by a spring which prevents the movement of a functional fuze part, e.g. an interrupter or striker, until the restraint is removed due to the effect of the launch environment of the weapon
Detonating Fuze	Flexible tubing filled with powdered secondary high explosive, which will transmit a detonation wave over any required distance
Detonation	A type of combustion involving a supersonic exothermic front accelerating through a medium that eventually drives a shock front propagating directly in front of it
Detonation Pressure	The dynamic pressure in the shock front of a detonation wave. Its magnitude for a particular explosive can be calculated or can be determined experimentally using the Hopkinson machine. This parameter should not be confused with Pressure of Combustion
Detonator	An explosive device for starting detonation in a disruptive explosive train. It is small in size and may be designed for initiation by one of several methods, e.g. bridgewire, flashing stabbing, etc.
Detonics	The study of detonation and related phenomena
DFRMO	Defence Fire Risk management Organisation – MOD's single, integrated, regionally based fire risk management organisation; part of HQ Land Forces
Differential Thermal Analysis	A laboratory method for studying those physical and/or chemical changes which occur in a substance when its temperature is progressively raised and which result in the adsorption or emission of heat
DINA	Diethylnitramine dinitrate, a secondary high explosive. $(O_2NOCH_2CH_2)_2N.NO_2$, also used to replace NG in gun propellants

Dinitrogen Pentoxide	N_2O_5 – a nitrating agent used in the preparation of explosives
DIPAM	3,3` Diamino 2.2`,4,4`,6,6` hexanitrobiphenyl
Diphenylamine	$(C_6H_5)_2NH$ Diphenylamine is the most common stabilizer used in smokeless powder that prevents build-up of deteriorating matter
Disarm	To restore a fuzing system to a non-armed condition from an armed condition, either reversibly to permit re-arming, or irreversibly and permanently (sterilization)
Disruptive Explosive Train	That type of explosive train which is designed to terminate in a detonation
Dissociation, Thermal	As applied to explosives, the decomposition of gas molecules at high temperature into other species, which may recombine at lower temperatures if conditions permit. Of particular relevance to the combustion products of propellants
DNAN	2,4-dinitroanilisole - an explosive which is less sensitive to shock and heat than TNT and RDX
DNB	1,3-Dinitrobenzene, a weak secondary high explosive. $C_6H_4(NO_2)_2$
DNT	Dinitroluene (mixed isomers, usually) a coolant and moisture-repellent additive in some gun propellants. $CH_3.C_6H_3(NO_2)_2$
DOA	Dioctyl adipate – a propellant plasticiser
DOS	dioctyl sebacate - a propellant plasticiser
DOSG	Defence Ordnance Safety Group - the UK National Authority for the assessment of the safety and suitability for introduction into military service of energetic materials
DOSG ST1	Defence Ordnance Safety Group Science and Technology 1 – the section within DOSG responsible for advising on explosives safety
DOSR	Defence Ordnance, Munitions and Explosives Safety Regulator - responsible for regulating the majority of explosives and ordnance related activities in MOD
Double Base Propellant	A propellant based on nitrocellulose and nitroglycerine
DPA	Diphenylamine – a stabiliser for nitrate ester propellants
Driving Band	A band of metal or other material pressed round a projectile which, when engaged with the rifling of the barrel centres the projectile in the bore, imparts spin to the projectile and also prevents forward escape of the propellant gases
DSA	Defence Safety Authority - an independent organisation, empowered by charter from MOD's S of S to undertake the roles of regulator, accident investigation and Defence Authority for safety
DSC	Differential Scanning Calorimetry - a thermos-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature
DSHAR	2.2.3 Dangerous Substances in Harbour Area Regulations

	(DSHAR) 1987 - regulates all classes of Dangerous Goods including explosives (Class 1) for carriage, loading, unloading and storage in harbours and harbour areas
DTA	Differential Thermal Analysis - a thermos-analytic technique that is similar to differential scanning calorimetry. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference.
Dud	Explosive munition which has not armed as intended or which has failed to explode after being armed
Dynamic Pressure	Pressure resulting from some medium in motion, such as air following the shock front of a blast wave
Dynamite	Dynamite can be either of the gelatine or non-gelatine type. The former is defined separately. The latter contains nitroglycerine (10-50%) an inorganic oxidant and woodmeal. The cohesion of the cartridge is due only to compaction and its waterproofing is by wax coating . If the oxidant is ammonium nitrate as distinct from the sodium salt, the composition is called an ammonia (or ammon) dynamite)

E

EA	Environment Agency - an executive non-departmental public body, sponsored by the Department for Environment, Food & Rural Affairs
EA95	Environment Act 1995 - saw the establishing of the Environment Agency as the regulator for England and Wales and the Scottish Environmental Protection Agency for Scotland Arrangements for Northern Ireland followed later.
EBW	See Exploding Bridge Wire Detonator
EDB	Extruded double base propellant, usually referring to a type of rocket propellant. British examples are propellants PU, SU and VU
EDC Compositions	A series of high performance military explosives
EDNA	Ethylene dinitramine (Haleite), a secondary HE with some use in the USA. Alternative name ethane- 1, 2-dinitramine. $O_2N.NH.CH_2CH_2NH.NO_2$
EED	See Electro-Explosive Device
Effluent	Liquid waste from sewage treatment or industrial processes
EFM	Environmental Features Matrix – used to identify significant environmental impacts
EFP	Explosively formed projectile – A shallow dished metal plate in the warhead inverts to form a fast solid slug of metal travelling at high speed
EGDN	Ethylene glycol dinitrate – used as a replacement for NG in gun propellants
EH40	EH40/2005 “Workplace Exposure Limits”, available on-line via HSE website

EHDS	Explosives Hazard Data Sheet
EIA	Environmental Impact Assessment. Process required by UK planning legislation for certain projects detailing the significant environmental effects of a proposed development
Electric Detonator	A detonator initiated by electrical means
Electrochemical Reduction	Treatment of organic wastes by generation of highly oxidising species in an electrochemical cell and utilising these to oxidise the waste to carbon dioxide and water
Electro-Explosive Device	A one shot explosive or pyrotechnic device used as the initiating element in an explosive or mechanical train and which is activated solely by the application of electrical energy
Electromagnetic Radiation Environment	The intensity, frequency and time distribution of the RF radiation in the range 200 kHz to 40 GHz existing at a location
EMCDB	Elastomer modified cast double base propellants - a type of rocket propellant. The colloidal mixture used for double base propellants is modified by the introduction of an elastomer to confer good mechanical properties at low temperatures
Emissions	The release of a substance such as gas into the environment, for example the burning of coal releases Carbon Dioxide into the atmosphere, referred to as Carbon Dioxide emissions
EMS	Environmental Management System
Endothermic Compound	A compound of which the formation entails the absorption of heat from the surroundings. By convention, the heat (enthalpy) of formation of such a compound is positive. Single explosive compounds can be either endothermic or exothermic
Endothermic Reaction	A chemical reaction accompanied by the absorption of heat from the surroundings. The heat (enthalpy) change for such a reaction is, by convention, positive
Energetic Material	A material making a positive contribution to an explosive, propellant or pyrotechnic process
Enforcement Notice	Can be issued by the Environment Agency or a Local Authority with regard to Environmental issues. It gives notice that an organisation must act to avoid further penalty or closure.
Entropy	A condition of a chemical system which, under certain circumstances, is related to the degree of disorder within the system
Environmental Aspect	An Environmental Aspect is a feature or characteristic of an activity, product, or service that affects or can affect the environment
Environmental Impact	Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organisation's activities, products or services
Environmental Testing	Product testing under specified conditions of environment likely to affect performance
EOS	Equation Of State - a constitutive equation which provides a mathematical relationship between two or more state functions

	associated with the matter, such as its temperature, pressure, volume, or internal energy
EPA90	The Environmental Protection Act 1990
Equation of State	The equation which expresses the relationship between the temperature of a quantity of gas and the product of its pressure and volume. For the extreme conditions of temperature and pressure produced by high explosives and propellants, modifications of the ideal equation are necessary
ER14	Explosives Regulations 2014 - consolidated and therefore revoked a number of explosives regulations. It has brought together the requirements of health and safety related explosives legislation into a framework based around common topics such as authorisation, safety, security and placing on the market
Erosion	Removal of metal by gas action on the bore, including the possible contributory effects of chemical action by gases, corrosion or mechanical action by the driving band. When the effect is general it is Erosive wear, where the characteristic local effects are evident it is Erosive Scoring. The term is also used to describe the removal of metal by gas action on the projectile
ES	Exposed Site - any facility, service or civilian, exposed to and thus hazarded by the effects of an explosion or fire at a PES
ESD	Electro-static discharge
Ethyl Centralite	1,3-diethyl-1,3-diphenyl urea – a stabilisers for nitrate ester propellants. See also Carbamite
Ethridge Equation	A simplified version of the Friedlander equation, to describe the pressure time curve at a given location for the detaonation of an explosive charge in air
EU	European Union
EU Directive	Directives are legally binding documents which specify desired outcomes or objectives and specific dates for achievement of those outcomes. They leave the means of achieving the objectives to national governments.
EU Framework Directive	A Framework Directive establishes a framework or template for subsequent legislation in an area
EU Regulation	Regulations are directly applicable laws in all EU member states
Excitation Time	The period for which current must be supplied to an electro explosive device to ensure functioning
Exothermic Compound	A compound of which the formation entails the loss of heat to the surroundings. By convention, the heat (enthalpy) of formation of such a compound is negative. Single explosive compounds can be either exothermic or endothermic
Exothermic Reaction	A chemical reaction accompanied by a loss of heat to the surroundings. The enthalpy change for such a reaction in, by convention, negative
Exploder	This term has two definitions: (1) When applied to a Booster or Gaine; A charge of secondary explosive designed to amplify the

	detonation wave produced by a fuze detonator or magazine, to ensure efficient detonation of the main charge in a shell, bomb, etc. The exploder may be a pressed pellet or a filled container (also known as a Booster or Gaine). (2) Otherwise a portable electric generator designed for use with electro explosive devices
Exploding Bridge Wire (EBW) Detonator	A detonator in which a secondary explosive filling is detonated by electrically exploding a fine wire embedded in it
Exploding Foil Initiator (EFI)	An electro-explosive device with a low resistance bridge which, when subject to a high energy short duration electrical pulse, converts the electrical energy into kinetic energy to project a high velocity flyer plate which, on impact, causes a detonation in a relatively insensitive explosive material which is not in direct contact with the bridge.
Explosion to Detonation Transition (XDT)	A delayed transition of an unstable violent reaction into detonation
Explosive	A chemical substance or mixture which can react to produce an explosion
Explosive Classification	A division of explosives according to the risks they present when initiated in storage or transport. The Hazard Divisions and Compatibility Groups are given in ESTC's paper 'Classification of Explosives for Storage and Transport' (ESTC/220/Leaflet No 2)
Explosive D	US name for ammonium picrate, used in the US as a secondary high explosive. This compound is also used as a coolant/burning rate moderant in plastic rocket propellants. $NH_4^+[OC_6H_2(NO_2)_3]^-$
Explosive Hazard Data Sheet	Supersedes Explosive Safety Certificate. A document which describes those properties of an explosive which are important for its safety during manufacture, handling, filling and disposal.
Explosive Ordnance	All munitions containing explosives, nuclear fission or fusion materials and biological and chemical agents. This includes bombs and warheads; guided and ballistic missiles; artillery, mortar, rocket and small arms ammunition; all mines, torpedoes and depth charges, demolition charges; pyrotechnics; clusters and dispensers; cartridges and propellant actuated devices; electro explosive devices; clandestine and improvised explosive devices and all similar or related items or components explosive in nature
Explosive Ordnance Disposal	The detection, identification, field evaluation, rendering safe, recovery and final disposal of unexploded explosive ordnance. It may also include the rendering safe and/or disposal of explosive ordnance which have become hazardous by damage or deterioration when the disposal of such explosive ordnance is beyond the capabilities of personnel normally assigned the responsibility for routine disposal
Explosive Power	The product of the heat of explosion and the volume of gas

	produced in an explosive reaction
Explosively-formed projectiles	See EFP
EPP	Explosives Precursors and Poisons - licence is required before these chemicals can be supplied to the public
ESTC	Explosives Storage and Transportation Committee - the UK Competent National Authority for the classification of military explosives. The Secretary ESTC is delegated as the Ministry of Defence Classification Authority
Explosive Train	The initiation train (transfer mechanism) beginning with the first explosive element (primer, detonator) and terminating in the main charge (munition functioning mechanism, high explosive, pyrotechnic compound)
Explosiveness	This describes the degree of violence shown by an energetic material when it responds to a prescribed stimulus relative to an accident situation. It is dependent on the nature of the energetic material, its mass, physical state, configuration and confinement
Extreme Service Conditions Pressure (ESCP)	The chamber pressure developed when firing the specified system under extreme service conditions (cannon systems)

F

F	Propellant force constant – also known as the propellant impetus
Fail-Safe	A characteristic which prevents faults from becoming critical faults. A fail-safe design is one which ensures the system is put into a safe condition if a fault occurs. In a fuzing system it is a design feature which renders the munition incapable of arming and functioning upon malfunction of safety feature(s) or exposure to out of sequence arming stimuli or operation of components
Failure Mode Effects (and Criticality) Analysis (FMEA, FMECA)	An analytic procedure to evaluate the effects (probability and criticality) of failure modes
FAX	Fuel air explosive – liquids, slurries, gases or dust particles which exhibit explosive properties when mixed with air
F of I	Figure of Insensitiveness
FEFO	Bis (2-fluoro-2, 2-dinitroethyl formal), a secondary high explosive. Otherwise bis(2,2-dinitro-2-fluoro-ethyl) formal. $[(NO_2)_2CFCH_2O]2CH_2$
FHN	Flash-less, non-hygroscopic (sic): a particular single base artillery gun propellant of US origin.

Film Bridge Initiator	An electro-explosive device where the power dissipated by the passage of current through a resistive vacuum deposited film or foil of very small dimensions is used to initiate by heating a primary explosive which is in intimate contact with the film or foil
Final (or Type) Qualification	Final qualification relates to the use of the explosive material in a specific application or munition. Final qualification is given when the explosive has been assessed as part of the design of the specific munition, and predicted to be safe and suitable for military operational or training use in that role
Firing Circuit	The complete system including the electro-explosive device (EED), power supply and associated electrical and electronic circuitry necessary for normal EED firing
Firing Energy	Energy available in a munition or a weapon system to cause its firing
Firing Interval	The time lapse between two successive firings during a sustained firing of cannons, mortars or automatic weapons
Firing Stimulus	A stimulus that will initiate the first explosive element in an explosive train
Firing System	The aggregate of devices in a munition and its associated weapon system (including cannon, launcher and munition launch platform) which generate and control the operating signal to cause the propelling charge or the propulsion system to function
Fixed Ammunition	Ammunition in which the cartridge case is permanently attached to the projectile until the round is fired
Flame	Luminous phenomenon accompanying gas phase combustion
Flash	The definitions for this term are: (1) A brief radiation pulse accompanying an explosion. (2) A short lived flame used to ignite safety fuze, a detonator or igniter
Flash Inhibitor	A substance added to a propellant composition to reduce muzzle flash
Flash Suppresser	Device attached to the muzzle of a weapon which reduces the amount of visible light or flash created by burning propellant gases
Flash Receptive Detonator	A type of fuze detonator which is initiated by a flash (short lived flame) from another component of the fuze
Force, Or Force Constant	The work capacity of an explosive, usually applied to gun propellants. It can be calculated for high explosives or propellants and in the case of the latter it can be determined experimentally by the use of the Closed Vessel
Form Function	The mathematical function describing how the surface area of a propellant grain of particular shape changes in the course of combustion
FOX-7	1,1-diamino-2,2-dinitroethene $C_2H_4N_4O_4$ - an insensitive high explosive
FOX-12	N-Guanylurea dinitramide (GUDN) - a low sensitivity explosive with good thermal stability and potential candidate for Insensitive Munitions

Fragmentation	The shattering effect of an explosive upon its container, e.g. fragmentation of a shell case by its explosive filling
Frank-Kamenetskii Theory	Named after a Russian scientist David A. Frank-Kamenetskii, the theory explains the thermal explosion of a homogeneous mixture of reactants, kept inside a closed vessel with constant temperature walls.
Friedlander Equation	An equation that describes the pressure-time curve at a given location resulting from the detonation of an explosive charge in air
Fuze	There are three definitions for this term: (1) Cord or tube for the transmission of detonation or flame. See Detonating Fuze and Safety Fuze respectively. (2) A compact, engineered assembly of explosive components, means of initiation and safety devices, to initiate the main charge of a munition. (3) An electric filament (bridge-wire) which is part of an electro explosive igniter
Fuze Assembly	A number of components or sub-assemblies or any combination thereof, joined together to perform a specific individual technical function. Examples: Antenna assemblies, mechanical assemblies, electronic assembly. Note the distinction between an assembly and a sub assembly is not always exact an assembly in one instance may be a sub assembly in another where it forms a portion of an assembly
Fuze Cavity (Pocket)	A recess in a charge for receiving a fuze
Fuze Safety System	The aggregate of devices included in the fuze to prevent its arming and functioning until a valid launch environment has been sensed and the arming delay has been achieved
Fuze Setter	A device for setting a unique and required function of the fuze
Fuzing System	A physical system designed to (a) sense a target or respond to one or more prescribed conditions, such as elapsed time, pressure or command; (b) initiate an explosive train in a munition: (c) provide as a primary role safety and arming in order to preclude munition arming before the desired position or time

G

Gaine	In proximity fuzes, the component part which contains the explosive components together with certain safety devices
GAM	A primary explosive comprising a mixture of **G**elatin, Lead **A**zide and **M**olybdenum disulphide
GAP	Glycidyl azide polymer – an energetic binder
Gas Actuator	Device intended to perform one or several mechanical actions using the gases from the reaction of an explosive
Gas Constant	See Molar Gas Constant

Gas Generator	A munition or a subsystem of a munition that generates gases to be used for a purpose other than providing thrust for direct rocket motor propulsion of the host munition
Gastritis	Inflammation of the lining of the stomach
Gelatine Dynamite	Generic term for a commercial explosive containing 25-55% nitroglycerine, 1-5% nitrocellulose, woodmeal and one or more inorganic nitrates as oxidant. The gelatinous NG/NC matrix provides high density and detonation velocity, also good waterproofing. If the oxidant is sodium or potassium nitrate the composition is called a "straight gelatine", or gelignite. If ammonium nitrate is used instead of, or in addition to, other nitrates, the composition is a "special gelatine" (in NEC nomenclature), or ammon gelatine dynamite, or ammon gelgnite. This type is somewhat less waterproof than the "straight" type
GHS	Globally Harmonised System of Classification and Labelling of Substances within the European Union
Global Warming	The average annual increase in temperature on earth caused by the activities of mankind
GPS	Gunpowder substitute
Grain	A discrete portion of a propellant composition, usually of a precise geometrical shape
Grenade	A self-contained fragmenting, blast, smoke or gas munition used at short ranges either thrown or projected
GUDN	See FOX-12
Guided Missile	A missile whose trajectory through the atmosphere can be controlled during flight
Guncotton	Nitrocellulose with a nitrogen content above 12.9%.
Gunpowder	A mixture comprising potassium nitrate, charcoal and sulphur. Usually 75/15/10.
Gun Propellant	A substance or mixture of substances which is required to burn in a controlled manner within a gun combustion chamber producing hot gases capable of propelling a projectile at high velocity. Combustible cases may be included as they contribute to the overall energy of the propellant
Gurney Equation	An equation to predict the velocity of fragments from warheads of various geometries

H

Haem	The part of the haemoglobin molecule which contains the oxygen binding iron atom
Haemoglobin	The oxygen binding pigment present in red blood cells containing iron in the 2+ valency state. See Methaemoglobin
Haemolytic Anaemia	Anaemia resulting from destruction of red blood cells
Hand Emplaced Munition (HEM)	A munition that is hand emplaced at, or hand-thrown to, the point of its intended function, and requires user action both to

	commit it to arm and to achieve safe separation
Hang Fire	An undesired delay in the functioning of a firing system
Hardening	The process by which a munition mat be protected against potentially hazardous effects induced by the environment, by inducing particular features in the design
Hazard	A situation that in particular circumstances could lead to harm, where 'harm' is the loss to a human being (or human population) consequent on damage
Hazard Classification Code	A code derived from a combination of Hazard Class/Hazard Division and Compatibility Group
Hazard Assessment	The assessment, by means of various empirical tests and treatment of results, of the degree of hazard posed to personnel and property by the storage, handling, transportation and use of a particular explosive
Hazard Divisions	A system of classifying bulk explosives and live ammunition into six categories, based on the nature of the hazard(s) which they would pose to personnel and property if accidentally initiated; e.g. mass explosion, violent burning etc.
Hazard Probability	The aggregate probability of occurrence of the individual events that could create a specific hazard
Hazard Severity	The extent of the consequences which could be caused by a hazard
Hazardous Waste	Waste with the potential to adversely affect the environment or human health. All hazardous wastes are listed in the regulations and include, but are not restricted to, substances which are highly flammable, an irritant, toxic or carcinogenic e.g. batteries, oils, solvents and chemicals etc
HBX	A series of US explosives designed for underwater use
HCE	Hexachloroethane, on which a type of pyrotechnic screening smoke mixture is based
HE	High Explosive
Heat of Formation	The amount of heat absorbed from, or given up to, the surroundings, when one mole of a substance is formed from its elements at 298K and 1.01325 x 105 Nm^2 (1 atmosphere) pressure
Heat Capacity	The amount of heat absorbed by a substance when its temperature is raised by 1K. The unit of substance may be one of mass, giving a 'specific heat capacity'. Alternatively, if the substance is an element or single compound the unit can be the mole, giving a 'molar heat capacity'. The molar heat capacities of gases, which are of special interest in explosives chemistry vary with temperature, but a mean value for a large temperature rise can be calculated. This is called 'mean molar heat capacity' and is a valuable aid in thermochemical calculations. The heat capacity of a gas can be measured either at constant pressure (Cp) or constant volume (Cv). The value of Cp is greater than the corresponding Cv because some of the

	heat supplied is used up as work in expanding the gas to maintain constant pressure. The difference between the corresponding values, for one mole of an ideal gas, is numerically equal to the molar gas constant R in SI units
Heat Capacity Ratio (γ)	The ratio of heat capacity at constant pressure to that at constant volume, Cp:Cv. For a diatomic gas its value is 1.4 and for a triatomic gas 1.33. In internal ballistics the value of γ is specially calculated because of the peculiar conditions obtaining, and is called 'gun γ'. It depends on the chemistry of the propellant and is less than the foregoing figures
Heat of Explosion	The liberation of heat under adiabatic conditions when an explosive is initiated either to burning or detonation
Heat of Formation	The heat released or absorbed during the formation of a pure substance from its elements at constant pressure
Hexamine	Hexamethylenetetramine or methenamine is a heterocyclic organic compound with the formula $(CH_2)_6N_4$ – a precursor in the manufacture of RDX
Hexogen	German name for RDX
Heinz Bodies	Small accumulations of abnormal haemoglobin seen, after staining with a dye, in red blood cells; typically caused by organic nitro or amino compound toxicity
HFC	Heat Flow Calorimetry
HIAP	High ignition temperature propellant
High Energy Gun Propellant	Triple base gun propellant with the addition of RDX or HMX.
High Explosive	An explosive which is capable of detonation under the normal conditions of use
High Order Detonation	Detonation at a velocity approaching the maximum stable velocity of detonation for the system. Usually applied to high order NG based compositions
HME	Home Made Explosive
HPLC	High performance liquid chromatography
HPOM	Hydrogen Peroxide Based Mixtures
HITP	High ignition temperature propellant
HITP/SEAP	High ignition temperature propellant, self-extinguishing at atmospheric pressure
HME	See Home Made Explosives
HMTD	Hexamethylenetriperoxidediamine - $C_6H_{12}N_2O_6$ - a powerful explosive, but it is not easy to handle. Shock, friction, heat, and reaction with common metals can cause it to detonate
HMX	HMX, $(C_4H_8N_8O_8)$ also called octogen, is a powerful and relatively insensitive nitroamine high explosive variously listed as High Melting Explosive, Her Majesty's Explosive, High-velocity Military Explosive, or High-Molecular-weight RDX
HNAB	Hexanitroazobenzene 2,2',4,4',6,6'-hexanitroazobenzene a secondary HE. $C_{12}H_4N_8O_{12}$
HND	Hexanitrodiphenylamine, a secondary HE, also known as hexyl. $(NO_2)_3C_6H_2.NH.C_6H_2(NO_2)_3$
HNIW	See CL-20 - a more powerful explosive than HMX

HNS	Hexanitrostilbene (1,3,5-Trinitro-2-[2-(2,4,6-trinitrophenyl)ethenyl]benzene) – generally used as an anti-cracking additive in TNT based fillings. It also is heat resistant with a melting point in the range 316-320 °C
Hollow Charge	A charge, usually cylindrical, having a cavity opposite the point of initiation to exploit the Munroe effect. The cavity may be lined with metal to enhance the effect
Hopkinson-Cranz Scaling Law	Also known as the cube root scaling law, this describes how the air blast from an explosive can be scaled by dimension
Hot Spot	A small, localised region in an explosive substance which is characterized by a temperature much higher than that of its surroundings. This is relevant to mechanisms of initiation
HSE	Health and Safety Executive
HTP	High test peroxide – a 80% - 90% solution of hydrogen peroxide in water, used as a liquid monopropellant
HTPB	Hydroxyterminated polybutadiene
Hugoniot	The Rankine–Hugoniot conditions, also referred to as Rankine–Hugoniot jump conditions or Rankine–Hugoniot relations, describe the relationship between the states on both sides of a shock wave in a one-dimensional flow in fluids or a one-dimensional deformation in solids
Hydrazene	Anhydrous hydrazine (N_2H_4) is a colourless, mobile liquid generally used as a monopropellant in propulsion units for space probes. Hydrazene is normally utilised by decomposition on a spontaneous (cold start) catalyst
Hydrogen peroxide	Until the mid-1960s hydrogen peroxide (H_2O_2) was the most widely used liquid monopropellant, as well as an oxidant in bipropellant systems. Subsequently Hydrazene found preference as a monopropellant
Hydrolysis	The decomposition of a compound by the action of water. This is of particular relevance to the chemical stability of explosives, and also to the formation of pyrotechnic smokes
Hypergolic	Term describing certain liquid bipropellant combinations which ignite spontaneously on mixing

I

IED	Improvised Explosive Device – a bomb constructed and deployed in ways other than in conventional military action. It may be constructed of conventional military explosives, such as an artillery round, attached to a detonating mechanism. IEDs are commonly used as roadside bombs
Igniferous Explosive Train	That type of explosive train which functions throughout in a burning mode as distinct from a detonative one. Such trains are found in, e.g. gun cartridges, carrier projectiles and pyrotechnic devices
Igniter	A device for starting the burning of the next component in an

	explosive train
Igniting Component	A device which deflagrates but which does not detonate, producing either hot gas or hot particles, or a combination of both
Ignition	The onset of burning
Ignition Delay	Time lapse between the moment of administration of the firing signal or firing stimulus to the primer and the moment of irreversible function of the explosive train, or the moment a specified condition is reached, such as a specified gas pressure in a combustion chamber
Ignition System	The aggregate of devices involved in the control and generation of the operating signal to cause the rocket or missile to function
Ignition Train	In general munitions, a succession of pyrotechnic elements arranged to cause the ignition of a charge. In fuzing systems, the deflagration train beginning with the initiator and terminating with the igniter charge
IM	Insensitive Munitions - those that reliably fulfil their performance, readiness, and operational requirements on demand, but are designed to minimize the violence of a reaction and subsequent collateral damage when subjected to unplanned heat, shock, fragment or bullet impact, electromagnetic pulse (EMP), or other unplanned stimuli.
IM Signature	The worst plausible responses of a munition to each of the following specified environments: fast heating, slow heating, bullet impact, sympathetic reaction and light fragment impact
IM Technology	Any structural or energetic material, concept or design which is an integral part of the munition itself, that can reduce the probability and violence of a munition response when subjected to an accidental or hostile stimulus
Impact Action Fuze	A fuze that is set in action by the striking of a projectile or a bomb against an object
Implosion	The definitions for this term are as follows: (1) The violent disruption or collapse of an evacuated vessel due to external pressure. (2) The effect of a hollow spherical charge of explosive, from which a concentrated shockwave impinges on any material, e.g. fissile, at the centre
Improvised Explosive Devices (IED)	Those devices placed or fabricated in an improvised manner incorporating destructive, lethal, noxious, pyrotechnic or incendiary chemicals, designed to destroy, disfigure, distract or harass. They may incorporate military stores, but are normally devised from non-military components
IME	An explosive mixture made, usually by terrorists, from common substances which are obtainable (legally or illegally) from shops, school laboratories, industrial promises, etc. (sometimes referred to as Home Made Explosives (HME))
IMS	Ion Mobility Spectrometers
IMX-101	A US explosive comprising DNAN, NQ and NTO
IMX-104	A US explosive comprising DNAN, NTO and RDX

In Line Explosive Train	An explosive train which has no physical interruption between the primary and secondary explosive elements
Incendiary Mix	A pyrotechnic composition which upon ignition rapidly converts to high temperature gases and hot particles
Incineration	The controlled burning of unwanted material to produce gases and solid residues containing little or no combustible material
Incremental Charge	An amount of propellant in a separate container, added to or taken from a propelling charge, to permit variation of the ballistic performance. (See also Augmenting Cartridge)
Independent Safety Feature	Each of several features is independent if it senses a different environmental force or condition from that sensed by the other safety features and if the integrity of the safety feature is not affected by the function or malfunction of one or more other safety features
Induced Environment	The conditions to which a material or component thereof may be exposed during its life cycle and which are directly or indirectly the result of human intervention
Inert	Not containing any explosive substance or other energetic material
Inertia Pellet	There are two definitions for the term Inertia Pellet: (1) In Fuzes, this is a mass, usually cylindrical in shape and of metal, which is used to sense the deceleration of the projectile. (2) In Fuzes, this is a free mass, usually cylindrical in shape and of metal which on impact or graze produces a sufficient force, normally transmitted through a striker, to initiate an explosive train
Ingestion	Entry into the body by eating or swallowing
Inhibitor	The definitions are: (1) An adherent layer of material applied to part of the surface of a propellant to prevent burning at that surface. (2) A substance employed to prevent or oppose chemical change in a system
Initiation	The action of a device used as the first element of an explosive train which, upon receipt of the proper impulse, causes the detonation or burning of an explosive item
Initiation System	System to initiate an explosive train or component in a munition
Initiator	The definitions for this term are: (1) A device for igniting or detonating explosives or pyrotechnics, commonly an igniter or detonator. (2) The term is also used as an abbreviation for the initiatory compositions, i.e. primary explosives, used in such devices. This usage introduces ambiguity and is best avoided.
Insensitiveness, Figure of (F of I)	A figure, determined by the Rotter Impact Test, which is a measure of the sensitiveness to impact of an explosive. It is a figure of insensitiveness because the results are calculated so that the higher the figure the more insensitive the explosive

Installed Munition	Any munition placed in a long-term fixture to the vehicle structure with or without anti-vibration mounts or isolators
Intermediary	An explosive of which the sensitiveness to initiation by impact or shock wave is intermediate between that of primary explosives and secondary explosives. The term is falling into disuse; such explosives are now classed as secondary explosives
Internal Energy	The total of all the forms of energy (translational, rotational and vibrational) in a chemical system. It is a function of temperature
Interrupter (Shutter)	A mechanical barrier in the explosive train which, when in the safe position will prevent the boost being initiated if the detonator inadvertently explodes. It is moved from the 'safe' position to the armed position by the effect of the launch environment of the weapon
Intraperitoneal Toxicity	Toxicological effects produced as a result of insertion of toxic substances directly into the abdominal cavity
Intravenous Toxicity	Toxicological effects produced as a result of injection of toxic substances directly into a vein
IPCC	Intergovernmental Panel on Climate Change – the United Nations associated body of scientists who evaluate the risk of global warming and climate change caused by the activities of mankind
IPN	Isopropyl nitrate, or more correctly propan-2-yl nitrate. A monopropellant for use in missile auxiliary power units
IRFNA	Inhibited red fuming nitric acid - red fuming nitric acid inhibited with a small percentage of of hydrofluoric acid (HF) and used as a bi-propellant oxidizer
ISO 14001	International Standard Organisation (ISO) for an Environmental Management System. Sets out the actions to be taken by a company in running an Environmental Management System and allows for an independent third party to assess (through an audit) whether a company meets the ISO14001 specification.
ISO 14040	International Standard Organisation standard which describes the principles and framework for life cycle assessment
IPN	Isopropyl nitrate - 2-propyl nitrate $(CH_3)_2$ $CHONO_2$ – used in starters for gas turbine engines
ITAR	International Traffic in Arms Regulations - a United States regulatory regime to restrict and control the export of defense and military related technologies to safeguard U.S. national security and further U.S. foreign policy objectives
ITOER	Identification and Traceability of Explosives Regulations 2010 - requires that explosives for civil uses are uniquely identified and can be traced from the production site through to their final use

J

Jet	In the context of the functioning of a shaped charge, this refers

	to the dense material part, generally metallic, cylindrical, stretched fluid, solid or in particles, moving at high velocity, coming from the charge liner
JSP	Joint Services Publication
JSP 403	MOD Handbook of Defence Range Safety
JSP 418	MOD document setting out policies and procedures for the management of Environmental Protection in Defence
JSP 482	MOD explosives regulations
JSP 520	Safety and Environmental Management of Ordnance, Munitions and Explosives over the Equipment Acquisition Cycle
JSP 862	MOD maritime explosive regulations
JWL	Jones-Wilkins-Lee, an analytical equation of state used to describe the detonation products of high explosives

K

Kistiakowsky Wilson Rules	A set of empirical rules for calculating approximately the composition of the gaseous products of a high explosive
KDNAN	Potassium dinitroacetonitrile. $K^+[O_2N=(CNO_2)CN]^-$
KDNBF	Potassium 4, 6 dinitrobenzofuroxan, a lead-free primary explosive used as a low toxicity replavement for lead azide
Kokinakis-Sperazza Model	A semi-empirical model to estimate the probability of incapacitation or medical severity of wounds by a penetrating fragment from a munition
Kyoto Protocol	United Nations treaty introduced in 1997 with the aim of reducing global warming by reducing emissions of greenhouse gases

L

L Mixture	An igniferous primary explosive composition, also known as RD 1651, comprising lead dinitroresorcinate, barium nitrate and tetrazene in the proportion 50/45/5
Lag Time	The period between first applying current to an electro explosive device and subsequent breaking of the circuit
Laser Initiation	The activation of an initiator by laser energy
LAT	Lead axotetrazole, $Pb(N_4.CN{=}NC.N_4).Pb(OH)_2$, a primary explosive
Launch	The irreversible discharging, firing, ejecting or releasing of a munition
LC_{50}	Concentration of substance which, under specified conditions, is lethal, to 50 % of those exposed. (Typical units are mg m^{-3} for a specified time)
LC_{t50}	Integrated atmospheric dosage (product of concentration and exposure time) which is lethal to 50 % of those exposed. (Typical units are mg min m^{-3})

LD_{50}	Dose of a substance which is lethal to 50 % of those exposed. (Typical units are mg, or mg per kg of body weight)
LCA	Life Cycle Assessment - a technique for assessing the environmental impact of product throughout the entire lifecycle from extraction of raw materials to disposal, often referred to as cradle to grave
LCC	Linear shaped cutting charge. A linear charge of high explosive encased in a metal tube which has a groove on one side. When detonated groove inwards against sheet metal it produces a cutting effect
LDNR	Lead salt of 2, 4-dinitroresorcinol or of 4,6-dinitroresorcinol. A primary explosive. The 2,4 type is known in the British service as “R” composition. $Pb[O_2C_6H_2(NO_2)_2]$
Lead	An intermediary secondary high explosive element or component designed to transmit a detonation reaction
Lead Azide	Lead salt of hydrazoic acid; a primary high explosive, PbN_6
Lead B-Resorcylate	A platonising ingredient in double base rocket propellants. Alternative name: lead 2,4 dihydroxybenzoate
Lead Block Test	See Explosive Power
Lead dinitroresorcinate	Lead 2,4-dinitroresorcinate – a primary explosive
Lead mononitroresorcinate	A primary explosive
Lead Styphnate	Lead salt of 2,4,6-trinitroresorcinol. A primary high explosive. $Pb(O_2C_6H(NO_2)_3].H_2O$ particularly sensitive to initiation by spark
Lead Thiocyanate	A primary high explosive. $Pb(C_6H_2O_{10}N_3Pb$
Lead Trinitrophlorogluci nate	lead 2,4-dinitroresorcinate – a primary explosive
LEEFI	Low Energy Exploding foil initiator detonators - EFI initiators which can reliably, safely and precisely operate at reduced firing voltages
Lethal Range	The range at which a fragment from a warhead has slowed down sufficiently to become sub-lethal
Life Cycle	A time-base description of the events and environments from manufacture to final expenditures or removal from the operational inventory. It includes one or more operational profiles and disposal or demilitarization
List I and II	Lists of substances in the EC Dangerous Substances Directive (74/464/EC)
Liquid Propellant	A substance or mixture of substances which is required to react in a combustion chamber in a controlled manner in order to generate propulsive force. These may be mono-propellants, bi-propellants or hybrids composed of liquids and solids
Loading Safety	The property of the ammunition and its constituent parts that enables the ammunition to be loaded into a weapon with the required level of safety
Logistic Storage	The long-term storage of items in depots, usually under

	controlled relative humidity conditions. For munitions this usually implies unarmed and in its logistic package
Logistic transportation	The transport of items to and between, and from storage depots to and from maintenance workshops
Lot	A quantity of munitions, munition components or explosives, each of which is manufactured by one manufacturer under uniform conditions and which is expected to function in a uniform manner. The lot is designated and identified by assignment of a serial number
Low Explosive	An explosive which does not detonate under normal conditions of use. The term is rarely used now because the compositions which it covers fall largely into the category of propellants
Low Order Detonation	A detonation in which the charge is completely consumed but the velocity of detonation is well below its maximum value and the effect in therefore less violent. This phenomenon is commonly associated with nitroglycerine explosives. It must be carefully distinguished from partial detonation
Lower Conditioning Temperature (LCT)	The temperature to which test items are stabilised for cold tests. This temperature is based on the climatic region that the testing nation and the using nation predict to be the worst case cold environment that the test item will encounter during storage and transportation
Lower Firing Temperature (LFT)	The temperature to which test items are stabilised for cold test firing. This temperature is based on the climatic region that the testing nation and the using nation predict to be the worst case cold environment that the test item will encounter during operations
LOVA	Low Vulnerability gun Ammunition
LOX	Liquid Oxygen
LTEL	Long Term Exposure Limit - the maximum exposure permitted over an 8-hour period
Lung Oedema	Accumulation of excessive fluid in the lunge which can lead to interference with respiration
Lyddite	An alternative name for Picric Acid

M

Mach Reflection	The interaction of a reflected portion of a shock wave with an incident (unreflected) portion. Constructive interference produces a strengthened wave called the Mach Stem. In the ideal case the Mach Stem is perpendicular to the reflecting surface
MACR	Major Accident Control Regulations - applicable to any establishment storing or otherwise handling large quantities of industrial chemicals of a hazardous nature such as explosives or petrochemicals
MAF	"Mixed amine fuel" a packageable liquid fuel for a rocket bi-propellant system

Magazine	There are three definitions for this term; (1) Any storehouse or compartment that is authorised for storage of explosives and that is maintained under 'clean conditions`. (2) A feed bin forming part of a gun. (3) The container for an intermediate charge between the initiator and the main charge
Magnadet	A high safety system of electrical initiations in which the detonator circuit in activated by magnetic induction only when a high frequency alternating current is applied to a separate circuit
Main Charge	The charge which is provided to accomplish the end result in a munition, i.e. bursting a casing to produce blast and fragmentation, splitting a canister to dispense sub missiles or producing other effects for which it may be designed
Maintainability	The ability of an item, under stated conditions of use, to be retained in or restored to a specific condition when maintenance is performed by personnel having specified skills levels under stated conditions and using prescribed procedures and resources
Mandatory Data	Test and analysis results concerning safety, suitability for service and performance of a munition or an explosives which shall be provided to determine its acceptability for military use
Mandatory Test	Test deemed essential to produce adequate data for assessing the safety and suitability for service of a munition or an explosive material being considered for military application
Mannitol Hexanitrate	A primary high explosive. $CH_2NO_3(CHNO_3)_4CH_2NO_3$
MARPOL	International Convention for the Prevention of Pollution from Ships - MARPOL is short for marine pollution
Mass Burning Rate	The rate at which a burning propellant is converted into heat and gas – measured in grams per second
Material	Any equipment, stores, packaging and supplies used by the military forces
Maximum Operating Pressure (MOP)	For cannon systems, the Extreme Service Condition Pressure (ESCP) plus three standard deviations in pressure estimated during the cannon design phase
MDC	Miniature detonating cord
Mechanite	A series of double base propellants used in engine starter cartridges
Melt-out	Removal of the energetic material from the munition envelope by applying heat to the filler causing it to melt and flow out
MEMS	Micro Electro Mechanical Systems whose applications include actuators, igniters, detonators and safety arming units
Mercury Fulminate	Mercury (II) salt of fulminic acid. $Hg(ONC)_2$. A primary high explosive
Mesonisation	The modification of the burning rate/pressure curve of a double base rocket propellant to achieve a falling burning rate over a range of pressure (a mesa or hump in the curve)
Metabolite	A product resulting from the biochemical breakdown of a

	substance after entry into the body
Methaemoglobin	Abnormal haemoglobin which has had the haem iron oxidised to the 3+ valency state
Methemoglobinemia	A condition caused by elevated levels of methemoglobin in the blood. Methemoglobin is a form of the oxygen-carrying metalloprotein haemoglobin
Methyl Centralite	Diphenyl dimethyl urea, used in gun propellants as a stabiliser/placticiser/coolant or as a surface moderant
MIDAS	Munition Items Disposition Action System – a US database system to aid the safe and environmentally acceptable disposal of munitions
Mie-Grüneisen	The Mie-Grüneisen equation of state is a relation between the pressure and the volume of a solid at a given temperature
Minol	Amonium nitrate + TNT + aluminium. Minol 1 is 42/48/10 and Minol 2 is 40/40/20. Both were naval explosives
Minolex	Minol with the addition of RDX
MIP	Molecularly imprinted polymers
Misfire	The situation where, on application of the firing pulse, the motor or propellant does not ignite.
Missile	A weapon or object to which self-contained propulsive energy is applied during flight
Mixed Acids	Variable mixtures of mixed nitric and sulphuric acids, also known as nitrating mixtures
MMH	Monomethylhydrazine – a hydrazine derivative used for rocket propulsion
Molar (or Universal) Gas Constant (R).	A constant which appears in the equation of state for a perfect gas, viz. PV = RT. Its value is the same for all gases
Molten Salt Destruction	The conversion of the organic constituents of the waste into non-hazardous substances such as carbon dioxide, nitrogen and water. Any inorganic constituent of the waste is retained by the molten salt. The destruction of the energetic materials is accomplished by introducing it together with oxidant gases into a crucible containing a molten salt such as sodium carbonate or a suitable mixture of carbonates, chlorides or sulphates of sodium, potassium, lithium and calcium
Monopropellant	A single liquid that burns in the absence of air to produce hot gas for propulsion purposes. Such propellants do not provide sufficient impulse to propel modern aerial missiles but can be used in their gas generator devices, they are also used for the underwater propulsion of torpedoes
Montreal Protocol	International treaty introduced in 1987 with the aim of phasing out the use of substances such as CFCs which were known to be responsible for depleting the Ozone layer
Mortar	A weapon system with a short barrel in proportion to its bore, rifled or smooth, for firing shells at high angles
Mortar Munition	The complete munition comprising projectile and propellant

	system to be fired from a mortar. The projectile normally comprises fuze, body filled with HE or other filling, obturator and tail fin. The propellant system normally includes a primary cartridge and augmenting charge(s)
Mott Equation	An equation to predict the way in which the metal casing of a cylindrical explosive charge will break up into fragments
MSER	The Manufacture and Storage of Explosives Regulations 2005 - now superseded by Explosives Regulations 2014
MSIAC	Munitions Safety Information Analysis Centre (NATO)
MT Fuze	Mechanical Time fuze in which the timing function is performed by a mechanical clockwork
MTV	Magnesium Teflon Viton – a composition used in infra-red decoy flares
Munition	A term used to indicate a complete device, e.g. missile, shell etc, charged with explosives, propellants, pyrotechnics, or initiating composition. Munitions may be used in connection with defence, offence, training or non-operational purposes, including mines and demolition stores. When used in an OB paper the term must be defined because of its wide meaning
Munroe Effect	A local concentration of shock wave energy produced by shaping the explosive charge
Mutagenicity	The ability to cause inheritable genetic alterations in organisms
Muzzle Velocity	The velocity of a projectile with respect to the muzzle at the instant the projectile leaves the weapon

N

Napalm	This term is defined as: (1) Powdered aluminium soap or similar compound used to gelatinise oil or gasoline for use in napalm bombs or flame throwers. (2) The resultant gelatinised substance
National Parks	The national parks of England and Wales are areas of relatively undeveloped and scenic landscape that are designated under the National Parks and Access to the Countryside Act (2016).
Natural Fragmentation	The munition case breaks up to produce fragments of a range of shapes and sizes
NC	Nitrocellulose – and ingredient of gun and rocket propellants with a chemical formula $C_6H_7(NO_2)_3O_5$
NCT	A single base propellant based on nitrocellulose (T – tubular)
NDED	Norwegian Defence Environmental Database
2 NDPA	2- nitro diphenylamine – a stabiliser for nitrate ester propellants
NENA	Nitratoethylnitramines – energetic plasticisers available as butyl-NENA, methyl-NENA and ethyl-NENA
Neonite	Propellant with a nitrogen content of 12.5% - known as “Nobels Rifle Neonites” NRN
New Explosive	The term 'new explosive' encompasses: (1) Any modification to an existing specification which defines the composition of the explosive, its material constituents or the process by which the

	composition in prepared. (2) An explosive of a type not hitherto Qualified. (3) The application of an explosive in a role (e.g. main charge filling, booster, primary, rocket motor propellant, gun propellant, illuminant, smoke pyrotechnic, etc.) for which the explosive has not already been Qualified
New Munition	A munition which differs from munitions accepted for use by NATO forces in terms of (a) design (definition in accordance with its full data package, material specifications, drawings, etc.); (b) the user's manual and other user instructions; (c) production definition (product processing, tooling, quality assurance); (d) acceptance testing; € use in a specified role (weapon systems, interface with joint elements) or (f) its life cycle profile and the resulting environmental profile
NG	See Nitorglycerine
NHTPB	Nitrated hydroxyl terminated polybutadiene – an energetic binder
NM	Nitromethane, CH_3NO_2 - capable of detonation if shocked by a good booster charge
Nitramine	The nitramine molecule is essentially an amine group ($-NH_2$) bonded to a nitro group ($-NO_2$).
Nitrate Ester	A nitrate ester is the organic functional group with the formula $RONO_2$ where R stands for any organic residue.
Nitrocellulose	Nitric esters of cellulose having a nitrogen content depending upon conditions of preparation
Nitroglycerine	Glyceryl 1,2,3-trinitrate, alternatively named propane-1,2,3-triyl trinitrate. Used as a secondary high explosive in some desensitised form, or as a propellant ingredient. $CH_2(ONO_2).CH(ONO_2).CH_2(ONO_2)$.
Nitroglycol (EGDN)	Ethyleneglycol dinitrate, a low-freezing liquid secondary HE. $(CH_2.ONO_2)_2$ Alternative name: Ethane-1,2-diyl dinitrate. In this country it is used in admixture with nitroglycerine in commercial explosives. In some other countries it is now used as a straight replacement for nitroglycerine, to which it is slightly superior in respect of performance
Nitromethane	Nitro-methane (CH_3NO_2) was an early monopropellant, also used as a bi-propellant
NMR	Nuclear Magnetic Resonance (NMR) Spectroscopy
No-Fire Threshold	The value of an electrical parameter of an EED at which its defined probability of functioning is low
No-Function Threshold	The value of a stimulus which, under specified conditions, is predicted not to cause a device or a component to function, with a stated probability
Nonel	A non-disruptive detonating cord which produces flash but little shock effect. It is used in commercial blasting operations and in rocket motor ignition systems
Non Permitted Explosive	An explosive which is not among those 'permitted' by HM Government for use in underground coal seams. It can, however, be used for any other blasting work provided it is on the Home Office List of 'authorised' explosives

Non-Renewable Resource	A resource which cannot be replenished naturally at a rate comparable to which it is being consumed. For example coal and oil
New Explosive	The term 'New Explosive' encompasses the following; (1) An explosive material not previously qualified, (2) An explosive material for which the existing specification defining its composition, its material constituents or the process by which the composition is prepared has been modified. An explosive material resulting from a change in manufacturer or manufacturing location. (3) An explosive material used in a role for which the explosive has not already been qualified, (4) An explosive material used in a role for which it has not yet been qualified
NQ	Nitroguanidine - an organic compound with the formula $(NH_2)_2CNNO_2$ used as a constituent of gun propellants
NRN	Nobels Rifle Neonites – see also Neonites
NSO	NATO Standardization Office
NTO	3-nitro-1,2,4-triazol-5-one – an explosive which is less sensitive to shock and heat thanTNT and RDX

O

Obturation	The sealing of the chamber of a gun to prevent the hot propellant gas escaping from the rear of the gun on firing
Obturator	This can be defined in three ways: (1) A small malleable cup employed in pressure recording to prevent seepage of gas. (2) A sealing device used in the breach of certain guns. (3) A sealing device on a projectile to prevent gases escaping
Octogen	German name for HMX
Octol	US name for HMX + TNT in proportion 75/25
ODS	Ozone Depleting Substances
Oedema	Accumulation of large quantities of fluid
OEL	Occupational Exposure Limit, maximum concentration levels of a toxic substance in air which, under certain conditions, is considered acceptable for the exposure of industrial workers. (OELs are set by the United Kingdom Health and Safety Executive)
OME	Ordnance, Munitions and Explosives
ONR	Two definitions – (1) UK – Office of Nuclear Regulation (2) – US – Office of naval Research
Open Burning	The burning of explosives and munitions in the external environment, without the control of resulting emissions
Open Detonation	The detonation of explosives and munitions in the external environment, without the control of resulting emissions
Open-pit Burning	The destruction of material by burning in a pit, often made of concrete, so that the material to be burned is not placed directly on the ground
Operational	The total set of all external natural and induced conditions to

Environment	which a materiel is exposed during its operational life
Operational Life	The time during which materiel may be expected to remain safe and serviceable when used under service or training conditions, when these are different from its storage conditions, but is within the envelope of its life cycle
Optional Test	Additional test not required by the standard test requirements. Optional tests are usually performed during development, for instance to determine the margins of safety and the reliability of the design
Oral Toxicity	Toxicological effects produced as a result of eating or swallowing toxic substances
Ordnance	Any munition or weapon that discharges a projectile
OSPAR	Oslo/Paris Convention for the Protection of the Marine Environment of the North-East Atlantic
Out-of-Line Explosive Train	An explosive train in which the elements containing primary explosives are held out of line or physically interrupted until the safe separation distance has been reached
Overpressure	The pressure resulting from the blast wave of an explosion. It is referred to as 'positive' when it exceeds atmospheric pressure and 'negative' when during the passage of the wave the resulting pressures are less than atmospheric pressure
Oxidation	The loss of electrons by an ion. This process is widely used to treat wastes, common oxidants being chlorine or hypochlorites, potassium permanganate and hydrogen peroxide
Oxygen Balance	For an explosive containing the usual elements carbon, hydrogen, nitrogen and oxygen, it is the percentage by weight of oxygen, positive or negative, remaining after combustion, assuming that all the carbon and hydrogen is converted into carbon dioxide and water. Effectively it is the oxygen content of the explosive in relation to the content of fuel elements
Ozone Layer	A naturally occurring layer of gas positioned 15-25 miles up in the earth’s atmosphere which protects the planet from harmful ultra violet rays from the sun

P

Partial Detonation	Ignition and burning of the confined energetic materials leads to non-violent pressure release as a result of a low strength case or venting through case closures (leading port/fuze wells, etc.). The case might rupture but does not fragment; closure covers might be expelled, and unburned or burning energetic material might be thrown about and spread the fire. Pressure venting can propel an unsecured test item, causing an additional hazard. No blast or significant fragmentation damage to the surroundings; only heat and smoke damage from the burning energetic material
Partial Ignition	An ignition from which subsequent burning fails to propagate throughout the sample. It would be more properly referred to an partial burning

PB	Poly(buta-1,3-diene), a synthetic elastomer used as a fuel/matrix in some rubbery composite rocket propellants. [-CH_2-CH-CH-CH_2-]n. See CTPB and HTPB
PBAN	Polybutadiene acrylonitrile, a copolymer of PB. Used as a fuel/maxtrix in some rubbery composite rocket propellants
PBX	Polymer Bonded Explosive
PD Fuze	Point detonating fuze – located in the noze of a projectile, designed to function as a result of impact
PDN	Propane-1,3-diyl dinitrate, otherwise trimethylene glycol dinitrate, a propellant ingredient with high explosive properties. -$CH_2ONO_2.CH_2.CH_2.ONO_2$
PE	(1) Plastic explosive, q.v. British service plastic explosives are of various compositions each denoted by a numerical suffix, e.g. PE4, PE7. (2) Penta erythritol, the parent compound of PETN
Pellet	An increment of explosive charge pressed in a tool or die to a predetermined size and density. It is assembled into ammunition in this form. The term is also sometimes used for an inertia mass in fuzes
Pentolite	An explosive comprising a mixture of PETN and TNT, usually 50/50
Percussion Cap	A cap containing a composition which produces a flash when struck. The first component of an igniferous train. Percussion caps are used in the Services for a variety of stores, including small arms cartridges, mortar bomb primary cartridges, some cannon and artillery primers, grenade fuzes, pyrotechnic stores and thermal batteries, also seat ejection and canopy jettison systems for aircraft
Percutaneous Toxicity	Toxicological effects produced as a result of penetration of substances through the skin
PERME	Propellants, Explosives and Rocket Motor Establishment
Permitted Explosive	An explosive which is specifically 'permitted' by HM Government for use in underground coal seams. Permitted explosives are characterised by a high ammonium nitrate content, low explosion temperature and low detonation velocities and are safe in flammable atmospheric conditions
PES	Potential Explosive Site - any stock of explosives, however or wherever stored (building, stack, vehicle, railway wagon, berth, transit shed etc), the explosion of which will affect an Exposed Site
PETN	Pentaerythritoltetranitrate – a high explosive used in exploder pellets and as an additive to other explosives. Chemically, it is a nitrate ester
PGDN	Propylene glycol dinitrate - a major constituent (76 %) of OTTO Fuel II used as a torpedo propellant

Phlegmatisation	The desensitisation of an explosive by mixing a soft or viscous substance with it, e.g. waxes, grease, oils, polymers. Such additives are called phlegmatisers
Photocatalytic Neutralisation	The use of a light emitting source to render an energetic material inactive or ineffective
Phytoextraction	Uptake and concentration of the contaminants from soil and water into plant biomass
Phytotransformation	Explosives are transformed as a result of the plant metabolism, leading to the formation of a less toxic product, degradation, or immobilization
Phytostimulation	Introduction of a plant that has got micro-organisms living in the root zone of the plant able to degrade the explosives.
PIB	Polyisobutene (or-butylene). [-CH_2-$C(CH_3)_2$-]. A viscous synthetic polymer used as a fuel/matrix in some plastic rocket propellants, also as a matrix in some plastic high explosive compositions
Picric Acid	2,4,6 trinitrophenol – also known as Lyddite
Picratol	US name for ammonium picrate + TNT 52/48
Plain Detonator	A demolition detonator designed to be initiated by means of safety fuze, as distinct from the electric type
Plastic Explosive	Explosive which is malleable at normal temperatures
Platonisation	A substance (certain lead or copper compounds) added to propellants to produce an alteration in the burning rate/pressure curve making the burning rate virtually independent of pressure within a given range
Plastic Propellant	A thermoplastic fuel/binder and an oxidant - ammonium perchlorate. The usual fuel/binder was polyisobutene (PIB): sometimes, with the addition of ethyl oleate as a plasticiser to improve the low temperature mechanical properties
PMMA	Polymethylmethacrylate - also known as acrylic or acrylic glass as well as by the trade names Plexiglas, Acrylite, Lucite, and Perspex, is a transparent thermoplastic
PN	(Porton Number followed by a numeral), a series of British service pyrotechnic compositions
pNMA	N-methyl-4-nitroaniline - a stabiliser for nitrate ester propellants
PNS	Peripheral Nervous System, that part of the nervous system which is not included in the CNS
POEMS	Ministry of Defence project Oriented Environmental Management System – used to identify the principal environmental impacts arising from the undertaking of activities using equipment throughout its life cycle
Polyisoprene	A synthetic polymer used as a matrix for plastic rocket propellants. Poly(2 methyl buta 1,3 diene)
Polymer Bonded Explosive (PBX)	A high explosive in which the solid ingredients e.g. the nitramines and/or ammonium perchlorate are embedded in a polymer matrix
Polymorphs	Forms of a substance chemically identical but with different crystal structures and X ray patterns
Poly-NIMMO	Poly-3-nitratomethyl-3-methyloxetane – an energetic binder

POMSTER	2.2.7 Placing on the Market and Supervision of Transfers of Explosive Regulations 1993 - mainly concerned with safety requirements for explosives and security controls on their transfer. They apply to explosives intended for use in the civil sector
POP	The POP plot, named after Alphonse Popolato, relates the distance-of-run to detonation versus initial shock pressure. It is a key characterization of shock initiation in a heterogeneous explosive
Potassium picrate	$C_6H_2KN_3O_7$; $C_6H_2(NO_2)_3OK$ - Potassium picrate is somewhat shock-sensitive. In contact with flame it deflagrates. If ignited in confined space, it will detonate.
Power	See Explosive Power
Pollution	The introduction of a substance to air, water or land that has the potential to cause harm to the environment. Oil, chemicals and litter are all examples of potential pollutants
Precautionary Principle	This means that there is a moral and sometimes legal obligation to take action if it is found that there could be a small risk that an activity could cause harm to the environment or to people.
Pre-formed Fragmentation	The munition case contains balls, cubes or rods to produce solid fragments with approximately the same characteristics
Premature Functioning	Complete or partial functioning of a munition payload after launch or emplacement at a moment or place prior to the intended fuze functioning before the intended point of operation of the fuze as foreseen by the time setting, proximity sensor function, pressure rise, etc.
Pressure of Combustion (or of Explosion)	The maximum static pressure produced when a given weight of high explosive or propellant is burned, without detonating, in a closed vessel of given volume. It should not be confused with detonation pressure which has a much higher value
Primary Charge	The intermediate charge used to augment the impulse from the primer to a magnitude sufficient to ignite the following element of the explosive train
Primary Explosive	Primary Explosives are sensitive formulations or compounds such as Lead Azide or Lead Styphnate which are used to initiate detonation or deflagration
Primary Fragments	Those fragments produced by a munition, whether the case or another component
Primer	The term Primer has the following three definitions: (1) In a gun cartridge it is the explosive device containing a cap and a charge of pyrotechnic or other flame producing material which ignites the propellant charge. (2) The term is sometimes used for the percussion cap of a small arms cartridge. This usage introduces an element of ambiguity when compared with (1) above, in which the cap in only part of the primer assembly. (3) The term is loosely used to describe any component of a disruptive explosive train which is interposed between the detonator and the main charge

Propellant	An explosive (in the broad sense) used to propel a projectile or missile, or to do other work by the expansion of high pressure gas produced by burning, e.g. for starting engines
Proximity Fuze	A fuze wherein initiation occurs by detecting the presence and/or the position of a target by means of a signal emitted by the fuze or by the target
PTFE	Polytetrafluoroethylene $(C_2F_4)n$ - a synthetic fluoropolymer of tetrafluoroethylene. The best known brand name of PTFE-based formulas is Teflon
PU	Polyurethane – used as a binder in composite propellant and other applications
Pulmonary	Relating to the lungs
PVA	Polyvinyl acetate is an aliphatic rubbery synthetic polymer with the formula $(C_4H_6O_2)_n$. It belongs to the polyvinyl esters family
PVC	Polyvinylchloride $(C_2H_3Cl)_n$ - produced by polymerization of the vinyl chloride monomer
Pyrotechnic	A substance or mixture of substances which when ignited undergoes an energetic chemical reaction at a controlled rate intended to produce on demand and in various combinations, specific time delays or quantities of heat. noise, smoke. light or IR radiation
Pyrotechnic Delay	A pyrotechnic device added to a firing system which transmits the ignition flame after a predetermined delay
Pyrotechnic train	An explosive train beginning with the igniter and terminating in a pyrotechnic or propulsive main charge
Pyromechanism	A mechanical device that is capable of releasing energy stored in a chemical composition and harnessing this energy to perform useful mechanical work or to create particular mechanical effects
Pyrophoric	liquids and solids that have the potential to spontaneously ignite in air at temperatures of 130 ° F (54 °C) or below
Pyrotechnics	Materials capable of undergoing self-contained and self-sustained exothermic chemical reactions for the production of heat, light, gas, smoke and/or sound

Q

Q	Heat of explosion - the heat liberated under adiabatic conditions
QF (Gun)	Originally stood for Quick Firing but now describes a system of rear obturation in which sealing is achieved by a cartridge case, which expands against the chamber of the gun. Ignition of the propellant is by means of a primer in the base of the cartridge case
Qualified Explosive	An explosive is qualified when it has been assessed by the National Authority and adjudged to possess properties which

	make it safe and suitable for consideration for use in a particular role (e.g. as a main charge filling, a booster, propellant, gun propellant, illuminant, pyrotechnic, etc.)
Quickness	A measure of both the pressure generated in a confined space by a propellant, of given composition and grain shape, and the rapidity with which the pressure is produced. Effectively the product of force constant and vivacity
QRA	Quantitative Risk Assessment - can be used for many explosive risk applications. It is especially useful for site risk analysis when reliance on quantity distance (QD) tables is not feasible

R

RACK-A-ROCK	A former US blasting explosive consisting of nitrobenzene and potassium chlorate. The name is still used today for a similar mixture improvised by terrorists
RADHAZ	Radio and Radar radiation hazards –the risk of inadvertent ignition of electro-explosive devices and inflammables, injury to personnel or malfunction of safety critical electronic systems resulting from exposure to electromagnetic radiation environment in the frequency range emitted by radio and radar installations
Raman	Raman (named after Sir C. V. Raman), is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified
Ramjet	A jet propulsion engine containing neither compressor nor turbine which depends for its operation on the air compression accomplished by the forward motion of its engine
Rankine–Hugoniot	The Rankine–Hugoniot conditions, also referred to as Rankine–Hugoniot jump conditions or Rankine–Hugoniot relations, describe the relationship between the states on both sides of a shock wave in a one-dimensional flow in fluids or a one-dimensional deformation in solids
RARDE	Royal Armament Research Development Establishment
Rate of Burning	This term is defined as follows: (1) The rate of regression of the burning surface of an explosive, usually a propellant grain, under given conditions of pressure and grain temperature. Sometimes referred to as the 'linear rate of burning' in the geometrical sense but not the algebraic sense. (2) The rate of consumption of a burning explosive, usually a propellant or bipropellant combination, in terms of mass per unit time
Rate of Fire	The number of rounds fired per weapon per minute or per second
RATTAM	Response to Attack of Ammunition - The "RATTAM SCALE" quantifies the characteristics of magazines and ordnance e.g. in surface ships and tanks, when subjected to small arms or

	fragment attack
REACH	European Union regulation concerning the Registration, Evaluation, Authorisation and restriction of Chemicals that came into force on 1st June 2007
RD	Research Department - a series of materials, explosive or otherwise, which may be found in British service ammunition, each member of the series having a separator numerical suffix
RDX	Research Department Explosive - RDX is the organic compound with the formula $(O_2NNCH_2)_3$. Chemically, it is classified as a nitramine
Reaction Zone Thickness	The distance between the shock front and the Chapman Jouguet surface in a detonation wave
Recovery	The process of extracting serviceable and economically repairable components and material from excess or surplus munitions
Recycling	The re-use of materials recovered from a munition
Reduced Smoke Propellants	Reduced smoke propellants use nitramines (RDX and HMX) with hydroxyl-terminated polybutadiene or polyurethane as a binder. They have no aluminium and a low AP content
Renal	Relating to the kidneys
Resorcinol	1,3 dihydroxy benzene, the parent compound of several primary explosives
Render Safe	To bring an armed munition to a non-armed condition
Resource Depletion	An economic term meaning the exhaustion of a raw material or use of a resource faster than it can be replenished
Response	An observed reaction of a test specimen to an imparted stimulus, for example, fracture, detonation, deformation, penetration, arming, etc.
Respiratory Toxicity	Toxicological effects produced as a result of absorption of substances via the lunge and respiratory tract
Response Descriptors	Classification of reactions resulting from unwanted initiation of a munition, based on the effect on the environment of the munition. The types of reactions are: propulsion and type I,II,III, IV and V
Reuse	The alternative use of a munition or its components, for instance change from operational to training use
RF Hazard (RADHAZ)	The danger of the accidental initiation of an electro explosive device by radio frequency electromagnetic radiation
Risk	The combination of the frequency, or probability, and the consequence of a mishap
Risk Analysis	The systematic use of available information to identify hazards and to estimate the risk to individuals or populations, property or the environment
Risk Assessment	The overall process of risk analysis and risk evaluation
Risk Control	Process, the purpose of which is to determine the status of each individual risk throughout a programme. The principal activities involved in this process are the drafting of specifications and risk identification, assessment, reduction and acceptance

Risk Estimation	The process used to produce a measure of the level of being analysed. Risk estimation consists of the following: frequency analysis, consequence analysis and their integration
Risk Evaluation	The process by which judgements are made on the tolerability of the risk on the basis of risk analysis and taking into account factors such as socio-economic and environmental aspects
Risk Management	The systematic application of management policies, procedures and practices to the tasks of analysing, evaluating and controlling risks
Rocket Propellant	Substance or mixture of substances which is required to burn in a controlled manner within a rocket motor producing hot gases which are vented through a nozzle to propel the munition
Rotter Impact Test	An empirical test to determine the sensitiveness of a given explosive to mechanical impact, in this case a falling weight. An important part of hazard assessment. Results are calculated as a Figure of Insensitiveness (F of I)
Round	All the parts that make up the ammunition necessary in firing one shot
RP	Red phosphorus

S

SAA	Small Arms Ammunition
Sabot	Lightweight carrier in which a sub-calibre projectile is centred to permit firing the projectile in a larger calibre weapon. The carrier fills the bore of the weapon from which the projectile is fired; it is normally discarded a short distance from the muzzle. The large area of the sabot relative to the penetrator allows the propellant gases to impart greater energy to the round in the gun
Safe And Arming Device	A mechanism whose primary function is to prevent an unintended detonation and in turn allow the explosive train of the munition to function after the munition has reached the proper point in time or space
Safe Separation	The places or area where the risks to personnel are acceptable, with regard to the intentional or accidental function of a weapon or a munition, and the protection provided
Safe Separation Distance	A minimum distance between the delivery system or launcher and the armed munition beyond which the risks of functioning of the munition to personnel and the launch platform or delivery system are acceptable
Safety and Suitability for Service (S3)	A general term used to summarise the requirements for a munition to be acceptably free from hazards and to have inherent characteristics that meet specified requirements during its agreed life cycle. It does not include operational effectiveness
Safety Barrier	Material or procedure designed to interrupt or modify a feared potential event, in order to reduce the probability or gravity of the event

Safety Critical	Characterisation of a condition, event, function, operation, process or item of a system whose proper recognition, control, performance or tolerance is essential to system safety during any phase of its life cycle
Safety Critical Function	A function in which any failure will result in a potential unacceptable risk to the user, friendly forces, the system, other materiel, third parties or the environment
Safety Critical System	A system in which a failure will result in a potential unacceptable risk to the user, friendly forces, the system, other materiel, third parties or the environment
Safety Feature	An element or combination of elements which prevent unintentional arming and unintentional detonation
Safety Fuze (Bickford Fuze)	Flexible tube for the transmission of flame in an explosive train; commonly used to provide a delay of seconds or minutes in blasting or demolition operations. It comprises a gunpowder core in a flax or jute tube covered by bitumen or PVC
SAU	Safe and Arm Unit (or Safety and Arming Unit)
Scaled Blast Parameters	The blast effects of different explosions can be compared by scaling down the measurements of distances and pressure duration times. These are divided by the cube root of the charge weight, thus comparing parameters on the basis of unit weight of explosive
SCB	Semiconductor bridges – used in initiators with improved safety characteristics; The current pulse required to function SCBs is a unique signal preventing their accidental functioning.
SDS	Safety Data Sheet
SDT	Shock to detonation transition
Sealed Vessel	A strong steel vessel in which high explosives are ignited electrically to test their explosiveness
SEAP	“Self-extinguishing at ambient pressures” – a desired characteristic of caseless ammunition
SEC	Size Exclusion Chromatography
Secondary Explosive	An explosive which can be made to detonate when initiated by a detonation wave or other shock front but which does not normally detonate when heated or ignited
Secondary Fragments	Fragments coming from the material surrounding, but not part of, an explosive device
Secure Cargo Munition	Any munition which is firmly attached to the vehicle structure with or without anti-vibration mounts or isolators, but which will be removed or launched from the vehicle at some stage
Self Destruction	Automatic destruction of an explosive charge in a munition that did not or will not complete its mission as intended
Semi-Conductor Bridge (SCB) Initiator	An electro-explosive device containing a bridge which, when subjected to a pulse of electrical energy, produces a plasma discharge initiating an explosive with which it is in contact
Semtex	A series of Czechoslovakian explosives. Often refers to Semtex E, a plastic explosive based on PETN and RDX
Sensitisation	In the context of toxicology an enhanced effect, caused by previous exposure to a substance, which is produced on re

	exposure
Sensitise	To increase the sensitiveness or the sensitivity of an explosive
Sensitiveness	A measure of the minimum level of a prescribed stimulus, relevant to an accident situation, required to ignite or initiate an energetic material. Such stimuli include, among others, impact, friction, and electric spark
Sensitivity	A measure of a prescribed stimulus required to achieve reliable functioning of an energetic material in its designed mode.
SEPA	Scottish Environment Protection Agency - Scotland's environmental regulator
Septum	An item in an explosive train usually providing environmental sealing
Service Environment	The total set of all external natural and induced conditions to which an item or a materiel is expected to be exposed throughout its service life
Service Life	The time during which materiel, in specified storage conditions and when subsequently used in its specified operational and/or training conditions, may be expected to remain safe and serviceable
Service Life Cycle	A time-based description of the events and environments an item experiences from manufacture to final expenditures or removal from the operational inventory, to include one or more mission profiles, but not disposal or demilitarisation
Set-back	The inertial forces acting upon the contents of a projectile due to its being accelerated in a gun barrel
SFG	Sulphur-less Fine Grain gunpowder composition used as a primer
SGV	Soil Guidance Value - developed by DEFRA and the Environment Agency as indicators of potentially unacceptable toxicity risk
Shaped Charge	A charge shaped so as to concentrate its explosive force in a particular direction (see Hollow Charge)
Sheet Explosive	Plastic explosive provided in a sheet form
Shell	A hollow projectile filled with HE or other material, fired from a gun, cannon, howitzer or recoilless gun. Mortar fired projectiles are called shell (US) or bomb (UK)
Shell, High Explosive Anti-Tank (HEAT)	A shell used primarily for armour penetration, incorporating a shaped charge, which on detonation causes penetration of armour plate by means of a jet of metal and gas having a highly directional effect
Shell, High Explosive Squash Head (HESH)	A shell used primarily for attack of armour. It contains a high explosive filling and a base fuze which is operated by the shell hitting the target. The shell is designed to detonate when the HE is in contact with the target. The shock wave causes the rear face of the armour to scab (US term: High Explosive Plastic)
Shock Front	A discontinuous change in the pressure and other parameters of a medium. This change is propagated at supersonic speed
Shock to	Phenomenon of the transformation of a mechanical shock into a

Detonation Transition (SDT)	detonation
Shock Wave	A shock front together with its associated phenomena. It can be transmitted through all kinds of matter and can be generated by explosive or other means
Shock Tube	A flexible plastic tube of which the internal surface is covered by a thin layer of explosive and applied as a means of transmission in an explosive train
Shutter	A safety device in an explosive train for isolating the initiating explosive
Shuttered Fuze	A fuze in which a component, usually the detonator, is held out of line in a shutter from the iniating explosive train until the fuze senses the design environment allowing it to arm
Silver Azide	Silver salt of hydrazoic acid, a primary high explosive, AgN_3
Silver Fulminate	(CNO)Ag - the highly explosive silver salt of fulminic acid
Silvered Vessel	A special type of Dewar vessel for testing the stability of nitrate ester propellants when maintained at elevated temperatures for longer periods. May also be used to assess the compatibility of the propellants with other materials
Single Base Propellant	A class of propellants comprising nitrocellulose without nitroglycerine (or equivalent), plus small amounts of stabiliser, surface coating, etc
SLA	Service Lead Azide
Slapper Detonator	See Exploding Foil Initiator (EFI)
Slurry Cast Double Base Propellant	In the slurry casting process the solid ingredients, which may include a nitramine or ammonium perchlorate in addition to granular nitrocellulose are added to a liquid plasticiser
Slurry Explosive	A type of blasting explosive developed in recent decades, with advantages of cheapness and low accident risk. It consists largely of solid ammonium nitrate suspended in a gelled, saturated, aqueous solution of same, with a wide range of possible fuels and other ingredients.
SOLAS	Safety of Life at Sea - International Maritime Organisation (IMO) Convention that requires vessels and craft to carry distress pyrotechnics on-board
Solar Radiation	The infra-red, visible and ultraviolet radiation from the sun. Solar radiation beyond these spectra is not usually considered to be relevant to munitions
Specific Heat Capacity	See Heat Capacity
Specific Impulse	The time integral of the thrust produced in a rocket motor by unit mass of propellant (or of bipropellant combination). It can also be defined as the thrust per unit mass rate of burning of the propellant. The specific impulse is, ideally, a constant for a given propellant (or combination) and is an important performance parameter
Specific Surface	The ratio of the surface area of a solid object (e.g. a gun propellant grain) to its nett volume. It is measured in cm^{-1}

SPR	Source-pathway-receptor pollution linkages concept. It describes how a contaminant can enter the environment from a source and move through the environment by air, soil or water (pathway) to a receptor
Springall Roberts Rules	A set of empirical rules indicating the composition of the gases produced by high explosives detonating under heavy confinement
SPTA	Salisbury Plain Training Area
SQEP	Suitably Qualified and Experienced Personnel
Squib	A small electro explosive device for producing a rapid evolution of a gas to power a mechanical device or for igniting a pyrotechnic
SR	Superintendent Research Composition – a pyrotechnic composition designation used at RARDE Fort Halstead
SSSI	Site of Special Scientific Interest – a piece of land given statutory protection owing to its biological (habitats and species) and/or geological interest being of national importance. An Environmental Impact Assessment is more likely to be required for planning applications proposed within or near to an SSSI.
STANAG 4170	Standard NATO Agreement - Principals and methodology for the qualification of explosive materials for military use.
Stabiliser	A substance which prevents or reduces autocatalytic decomposition of explosives
Stand-off	The distance of a shaped explosive charge from a target at the instant of detonation. In general there is an optimum value at which best performance is achieved
Statutory Instruments	Statutory Instruments, also known as SIs, are a form of legislation which allows the provisions of an Act of Parliament to be subsequently brought into force or altered without Parliament having to pass a new Act. They are also referred to as secondary, delegated or subordinate legislation
STEL	Short Term Exposure Limit - the acceptable average exposure over a short period of time, usually 15 minutes
Stemming	There are two definitions: (1) An explosive filling which has been loaded in increments. (2) Inert material such as clay or sand used to close a loaded shot hole during rock blasting
Sterilisation	A process that renders a munition permanently incapable of being initiated or activated
Stimulus	The applied energy or power such as current, voltage, mechanical impact, friction or any other physical phenomenon such as (rate of) change of current or pressure which is capable of initiating directly or indirectly an explosive event
Stimulus Level	The value of a test variable imparted to an individual item or test unit
Stoichiometry	The relationship between the relative quantities of substances taking part in a reaction or forming a compound, typically a ratio of whole integers
Storage	The deposit of munition in a covered or uncovered enclosure, awaiting transportation to or from operational theatres or direct

	use. Normally the munition is stacked in its logistic package and ideally in a controlled environment
Storage Environment	The total set of all external natural and induced conditions to which a materiel is exposed during its storage life
Storage Life	The time for which an item of supply, including explosives, given specific storage conditions, may be expected to remain serviceable and safe
Stored Energy	The latent energy within a (sub)system which, when triggered, is released to perform a function. Examples include springs under load, batteries, charges capacitors, compressed gas devices and explosive actuators
Strand Burner	A device for measuring, experimentally, the rate of regression of a length of propellant, burning endwise at a fixed pressure
Subcutaneous Toxicity	Toxicological effects produced as a result of introduction of a substance directly underneath the skin
Surface Launched Munition (SLM)	Any munition containing explosives which is launched from the ground or sea surface
Surface Moderant	An additive applied to the surface of some gun propellants to reduce the burning rate in the early stage of combustion
SX	Sheet explosive, in British service nomenclature
Sympathetic Detonation	The detonation of an explosive substance or of an explosive device as the direct result of another detonation. The term in normally used in accident situations. Strictly speaking, the term should be used for initiation by shock wave only
Sympathetic Reaction	Explosive reaction of a munition by exploding another munition adjacent to it
Synergism	Co-operative action of two or more substances such that the total physiological effect is greater than would be expected for the sum of the individual effects acting independently
System Safety	The capability of a system to avoid causing personal injury or damage to property or the external environment

T

Tactical Storage	The storage of an item for a limited period of time under field conditions. It denotes storage in ammunition depots or readying sites located adjacent to bases, in naval vessels, and, on land, deployment areas, usually without any kind of controlled environment
Tactical Transportation	Transport of items in field conditions from depot staorage to bases, naval supply vessels, deployment areas, etc. The concept includes short transport of items within and between these sites
TAGN	Triaminoguanidine nitrate, a constituent of some experimental US gun propellants
TAT	1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane – a non-energetic intermediate in the production of HMX using Dinitrogen Pentoxide as the nitrating agent

TATB	Triaminotrinitrobenzene (2,4,6-triamino-1,3,5- trinitrobenzene) – an explosive which is extremely insensitive to accidental stimuli
TATP	Triacetonetriperoxide – a white powdery solids which is extremely sensitive to shock, friction, electrostatic spark and flame
TCD	Thermal conductivity detector
T&E	Test and Evaluation
TEGDN	Triethylene glycol dinitrate - an energetic plasticiser for explosives and propellants
Temperature Of Ignition	The temperature at which an explosive ignites under specified conditions. This is affected by Heating Rate and Mass
Temperature Coefficient	The variation per °C with respect to chamber pressure or muzzle velocity
Terahertz Radiation	Terahertz radiation also known as sub-millimetre radiation and T-waves lies in the far infra-red region from 0.1 to 10 THz. Most explosives and explosive related compounds have spectral fingerprints within this range, hence the technique's use in explosive detection
Test Configuration	A detailed description of the test item state during the test, for instance package mode or unpackaged, operating or not, environmental conditions, interfaces with associated equipment, fixation and orientation on test equipment, measurement points and eventual modifications for safety (e.g. replacement of explosives with inert material)
Test Directive	In Staff Requirements this is a documented set of requirements including a requirement to conduct tests and the objectives of the tests
Test Method	A document describing the requirements for the execution of a type of test and its objectives. It comprises modes of execution, sequences, parameters, configurations, equipment, data collection and treatment, and potentially criteria for acceptance with regard to the objectives of the test
Test Plan	A document describing the tests to be executed required to meet the objectives defined in the test directive. Included are: identification and quantities of the munition to be tested, reference to or description of the test methods, the test sequences, the values of the test parameters (severities), personnel and equipment needed, procedure for disposal of explosives remainders, data collection and treatment and the criteria to meet the requirements
Tetrazene	(1-5' tetrazolyl)-3-guanyltetrazene monohydrate. A primary high explosive used as a sensitising ingredient in primary compositions
Tetryl	2,4,6-Trinitro-phenylmethylnitramine – used as a booster explosive. Also known as Composition Exploding (CE)
TFA	Trading Fund Agency - an executive agency, government department or often simply a part of a department, that enables the department to handle its own revenues and expenses

	separately from overall government finances and more like a business, as opposed to having to obtain funding from the government's legislature and feeding income back into its treasury. The UK Hydrographic Office is a TFA within MOD
Tg	Glass Transition Temperature - the temperature at which a polymer turns from a ductile material to a hard, brittle material
TGA	Thermogravimetric analysis - a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss)
Thermal Explosion	Explosion resulting from a runaway exothermic reaction in an explosive charge in a region where heat is liberated more rapidly than it can be transferred away
Thermal Time Constant	In the context of electro-explosive devices, the time taken for the bridge-wire, the film or the conducting composition to reach 63% of the equilibrium temperature when a specified constant power is applied to the terminals of the device
Thermite	Fuel oxidant mixtures comprising metal/ metal oxide combinations
Time Fuze	A fuze designed to initiate a munition at a desired time after launch, release, drop, impact or emplacement
TLB	Top Level Budgetary area within the MOD
TLC	Thin Layer Chromatography
TLV	Threshold Limit Value
TMDI	(or TDI) Trimethyl hexamethylene di-isocyanate. Used in the production of some plastic-bonded explosives
TMETN	2-methyl-2-[(nitroxy) methyl] – propane – 1,3-diyl dinitrate ester, a propellant ingredient
TNB	2,4,6-Trinitrobenzene, $C_6H_3.(NO_2)_3$, a secondary high explosive
TNC	Tetranitrocarbazole $C_{12}H_5N_5O_8$ - used in the Anti-riot Irritant CS Hand Grenade L13 as delay composition
TNT	Trinitrotoluene or more specifically 2,4,6-trinitrotoluene, is a chemical compound with the formula $C_6H_2(NO_2)_3CH_3$
TNT Equivalent	A measure of the energy released from the detonation of a nuclear weapon, or from the explosion of a given quantity of fissionable material, in terms of the amount of TNT (trinitrotoluene) which could release the same amount of energy when exploded
Torpex	Mixtures of RDX, TNT, and aluminium, used as fillings for aircraft bombs and underwater weapons: wax is also used in some of these compositions
Toxicity	Degree of poisonousness
Tracer	Pyrotechnic element enabling optical tracking of the trajectory of a projectile
Triple Base Propellant	A class of gun propellants comprising nitrocellulose, nitroglycerine and nitroguanidine (picrite), the latter ingredient providing a reduction of gun flash compared with other types of propellant

Tritonal	US name for TNT/aluminium 80/20

U

Underwater Launched Munition (ULM)	Any munition that is ejected, propelled, released, placed or otherwise launched in an underwater environment
UDMH	Unsymmetrical dimethylhydrazine, a rocket bi-propellant. It has the advantage over hydrazine that it has a much lower freezing point; -57 °C as compared with +2 °C. A mixture of hydrazine and UDMH has been used as a liquid bi-propellant fuel
Urea Nitrate	$CH_5N_3O_4$ - Urea nitrate is a fertilizer-based high explosive that has been used in improvised explosive devices in Afghanistan, Pakistan, Iraq, and various other terrorist acts elsewhere in the world
UNDEX	An underwater explosion
Unsafe Area	Surroundings of a weapon system, the trajectory of launched munitions and the areas where the munition payload could function, wherein the risks for friendly personnel and materiel are unacceptable
Upper Conditioning Temperature (UCT)	The temperature to which test items are stabilised for hot tests. This temperature is based on the climatic region that the test nation and the using nation predict to be the worst case hot environment that the test item will encounter during storage and transportation
Upper Firing Temperature (UFT)	The temperature to which test items are stabilised for hot test firing. This temperature is based on the climatic region that the test nation and the using nation predict to be the worst case hot environment that the test item will encounter during operations
UXO	Un-exploded Ordnance

V

Vasoconstrictor	Substances that induce a narrowing of the blood supply vessels
Vasodilator	Substances that induce a widening of the blood supply vessels
Velocity of Detonation	This is the speed at which a detonation wave progresses through an explosive. When, in a given system, it attains such a value that it will continue without change, it is called the stable velocity of detonation for that system
VH2	'Von Hertz' mixture for percussion caps, consisting of lead styphnate, barium nitrate, antimony sulphide, calcium silicide and lead peroxide, sensitised with tetrazene. VH4 is somewhat similar but contains no calcium silicide or lead peroxide
Vibration	A state of oscillatory motion induced in a body or mechanical system by an input of mechanical energy. This input may in

	itself be oscillatory or in the form of a shock pulse or a succession of shock pulses
Vieille's Law	Defines the relationship between the rate of regression (r) in a burning propellant and the rocket motor chamber pressure (Pc). The relationship is expressed as $r = a P_c^n$
VITON	Viton is a brand of synthetic rubber and fluoropolymer elastomer used in Magnesium Teflon Viton (MTV) infra-red decoy flares
Vivacity	The way in which a gun propellant charge, of given composition and grain dimensions, behaves in respect of its mass burning rate during combustion under adiabatic conditions. Experimental determination is necessary and employs the closed vessel
VOCs	Volatile organic compounds - contaminants such as petroleum products (e.g. jet fuel, refinery wastes, diesel, some insulation materials, and paint)
VoD	Velocity of Detonation of an explosive charge

W

Waiver	In the context of qualification of a munition, acceptance by the appropriate accredited acceptance authority of a munition which does not meet all requirements for safety
Warhead	That part of a missile, torpedo, rocket or other munition which contains either the nuclear or thermonuclear system, high explosive system, chemical or biological agents or inert materials intended to inflict damage
Washout	The use of an agent such as hot water, solvent or cryogenic dry wash to remove energetic material from a munition without destruction of the case metal
Waste	Any substance or object that the holder discards, or intends, or is required to discard. This includes waste sent for recycling even if it is sold to the recycler
Water Jet Cutting	The use of a high pressure water jet to cut a variety of materials. If abrasive is entrained into the water jet, the method is called abrasive water jet cutting
WEL	Workplace Exposure Limit – under the COSHH regulations employers have a duty to ensure that their employees are not exposed to any concentration of substance in excess of the Workplace Exposure Limits for that substance
WM	“Waltham Abbey Modified” - a propellant with a nitrogen content of 12.9% to 13.1%
WOME	Weapons, Ordnance, Munitions and Explosives
Woolwich Process	A process for the manufacture of RDX by nitrating hexamine with nitric acid
WP	White phosphorus

X

XDT	See Explosion to Detonation Transition
XRF	X-ray Fluorescence spectroscopy – used in the detection of explosives

Y

Y	(Used in detonator nomenclature), tetryl

Z

Z	(1) Used as a suffix in propellant nomenclature, (2) Used in detonator nomenclature, lead azide.
ZND	Zeldovich-von Neumann-Doering - a one-dimensional model for the process of detonation of an explosive