

CHAPTER 2

HISTORY OF EXPLOSIVES

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2 THE HISTORY OF EXPLOSIVES

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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 Lefauchaux 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 C¹⁹th 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 Eugène 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, carbamate-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, carbamate, was new and in 1940, when wartime supplies of carbamate were running low, the change had to be partly reversed. Some of the carbamate 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
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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 than 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 $+20^\circ\text{C}$ 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 than 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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