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NOTES ON PYROTECHNICS

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Chapter 1

INTRODUCTION

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WHAT IS PYROTECHNICS?

The word "Pyrotechnics" comes from the Greek and may be translated as "the art of fire". The subject is concerned with the understanding and manufacture of chemical mixtures which can burn to produce a desired effect. This desired effect can be the production of heat, or light or other electromagnetic emission, sound, motion, gas or any combination of these. It is important that the reaction is a *combustion* which propagates throughout the quantity of the pyrotechnic mixture employed. Other types of reaction, such as that between a metal and an acid which produce gas and heat, are not to be considered as pyrotechnic reactions.

TERMINOLOGY

It is well to define at this point some of the terms that will be used in the following discussion, and throughout this book.

Combustion Reaction.

An exothermic chemical reaction characterised by a moving high temperature reaction zone which separates the unreacted materials from the combustion products, and through which the pressure does not vary. It is important to note that a combustion reaction does not necessarily produce a flame.

Pyrotechnic Composition.

Any mixture of chemical reactants (essentially a fuel and an oxidising agent) capable of undergoing self-propagating combustion under the right conditions, and in the absence of air. While such mixtures will obviously burn in the presence of air, often with enhanced vigour, they should contain enough oxidising agent to burn anaerobically, although not necessarily to completion.

Because of certain similarities of application, primary explosives are sometimes included among pyrotechnic compositions. In fact, their properties are very different from those of pyrotechnics, and they will not be considered in this volume.

Ignition and Initiation.

These two terms are usually confused and used interchangeably, whereas they are in fact different processes. *Ignition* is the process of starting a combustion reaction, and involves the application of an igniferous stimulus; *initiation* is the process of starting a detonation and involves a shock stimulus. In pyrotechnics the term *ignition* is almost invariably the correct one.

Pyrotechnic Device.

Any device which contains a pyrotechnic composition. Examples include fireworks, solid rocket motors, smoke grenades and illuminating flares.

Required Effect.

This is the effect that the pyrotechnic composition is required to produce. For example, an illuminating composition is required to produce as much light as possible for the required duration, preferably spectrally matched to sunlight; a signalling flare may be required to

produce a coloured light of adequate intensity to be easily visible, and of adequate saturation to make its colour unambiguous.

USES OF PYROTECHNICS

The importance and use of pyrotechnics lies in the large amount of energy that they can contain in a small volume. For example, a compressed pellet of magnesium and sodium nitrate produces about 8500 J per gram when it burns. If the pellet has been manufactured properly, and if it is adequately protected from moisture, physical damage and high temperatures, then it will remain quiescent for many years, ready to release its energy on the application of a suitable stimulus (*e.g.* a flame).

The most obvious civilian application of pyrotechnics is in fireworks. Various pyrotechnic mixtures, each in a carefully controlled physical form, produce the various effects such as coloured lights, propulsion, crackles, pops and loud bangs which are familiar to everyone. The general principles of fireworks are similar to those of other civilian and military applications with the possible difference that fireworks are not intended to have a prolonged shelf life and are made to be fired within a short time. This allows methods of assembly, choice of materials, and design of container which may not be suitable for other purposes.

An increasingly important civilian application is the inflation of car air bags designed to protect the occupants from the effects of a crash. The protective system must react very rapidly, and most contain a pyrotechnic igniter which is fired electrically by sensors on the vehicle, and which in turn lights a pyrotechnic composition which burns rapidly to produce large quantities of pure gas to inflate the bags. Here, the attraction of pyrotechnics is the large quantity of gas which can be produced from a relatively small and light device. The safety-critical rôle of the pyrotechnic and the extreme conditions under which they are stored (*e.g.* in a sealed vehicle in the tropical sun) make the design of the compositions and their containers at least as demanding as for military applications.

An application of great significance is the development, initially by the Russians, of pyrotechnic reactions to produce a wide range of solid materials such as ceramics and intermetallics in specific shapes for purposes such as insulators for high tension power lines, friction liners, and etc.. The immense heat of the combustion reaction produces the necessary sintering under relatively light confinement.

However, most pyrotechnics are used by the military, and the first pyrotechnic compositions and devices were developed for warfare. Modern military pyrotechnic devices include signalling, illuminating and tracking flares, smokes to obscure a target from observation, and decoys to protect aircraft and ships from the attentions of heat seeking missiles.

BRIEF HISTORY OF PYROTECHNICS

This is a huge subject which can be considered only in broadest outline. Even now, the practice of pyrotechnics relies greatly on experience and rules of thumb rather than on detailed quantitative understanding of the phenomena that are produced. This is largely due to the complexity of the heat transfer process by which the pyrotechnic process propagates, and its sensitivity to the physical and chemical properties of the ingredients and to the

ambient environment. The physics of detonation, which is largely a physical event, has been well established for many decades. Even our present insight into the chemistry and physics of pyrotechnic reactions extends back scarcely 50 years, and in the general absence of quantitative predictive models, much pyrotechnics formulation and design is pragmatic when not outright trial and error.

Pyrotechnics has a long history, much of which is actually the history of gunpowder.

Although naturally occurring fuels such as wood have been used for many millennia as sources of heat for cooking and warmth, it would seem that the Chinese were the first to develop what might be properly called a combustion technology. Thus, Temple (1986, page 78) records that before the third century BC the Chinese were using natural gas, and that Ch'ang Ch'ü described the use of natural gas, possibly including the use of bamboo pipes to lead it to a distance, in his book *Records of the Country South of Mount Hua* written in 347. Temple (1986, page 98) also records a description dating to 950 by T'ao Ku in his *Records of the Unworldly and the Strange* of the use of pine wood sticks impregnated with sulphur to make them more easily flammable.

The development by the Chinese of the technology of pyrotechnics and gunpowder has been documented by Needham. It is recorded that they first used fire in warfare as early as the 11th century BC using naturally occurring combustible materials, and subsequently they appear to have been the first to have deliberately produced mixtures that we would recognise as pyrotechnic. The earliest were slow burning mixtures of organic fuel and naturally occurring nitrates which were used for the production of noxious smokes from mixtures which often contained animal dung as fuel and toxic minerals. An illustrative example of a discouraging smoke is quoted by Temple (page 216) and given in Table 1-1. This mixture is not pyrotechnic because it contains no oxidising agent and therefore relies on atmospheric oxygen to burn. Had combustion been complete, then the specific origin of the organic fuels would have been irrelevant, as they would have contributed only carbon dioxide, water, and minor quantities of oxides of nitrogen, sulphur etc., to the final effect. One may assume however that, under whatever conditions the device containing these ingredients would have been deployed, combustion would have been incomplete, and that more or less irritating or toxic products would have been released in the smoke. The arsenic compounds would under any conditions, at adequate temperature, have produced toxic volatile materials.

Later, slow burning gunpowder-like mixtures were developed which were pressed into tubes held on poles and lit before advancing with them on the enemy (fire lances). Fire arrows (presumably normal arrows carrying incendiary charges) were reported by 969AD. Subsequently, these formulations appear to have developed into propellants (by adjusting the ratio of the ingredients for faster, more energetic combustion) and finally into gunpowder that could be said to explode. The discovery of gunpowder-like formulations pre-dates its description by Quing Xu Zi in 808 AD, the earliest known recipes were published in 1044 AD, and gunpowder was in large scale manufacture in China by the middle of the 11th century. Projected exploding grenades were in use probably before the 13th century.

Ingredient	parts
human excrement, dried, powdered and very fine	240
Wolfsbane	8
aconite	8
croton oil	8
soap-bean pods	8
arsenious oxide	8
arsenic sulphide	8
cantharides beetle (*Mylabris cinnnnchorii*)	4
Ashes	16
Tung oil	16

Table 1-1 Early Chinese Noxious Smoke Formulation (Temple)

Gunpowder was introduced to Europe in the 13th century, either from the Mongols or the Arabs, and was investigated by, amongst others, the English Franciscan monk Roger Bacon (c.1220 – 1292) who gave a description of its manufacture (1242) but was unaware of its origin. His recipe was quite a way from the optimum for an explosive, but it would have been an energetic propellant. It was used as a military propellant from the 14th century, and was used exclusively for military purposes until the 17th century when its use in mining was reported in Hungary.

An advantage of gunpowder as a gun propellant was that it could be manufactured in different grain sizes which could be adapted to the weapon. Early cannon were not very strong, and a slow pressure rise was essential to prevent (too frequent) bursts. However, the combustion products of gunpowder are corrosive and at least 50% is solid which limits the propulsive force and produces heavy obscuration on the battlefield. Gunpowder as a gun propellant was gradually replaced by smokeless powders (based on nitrocellulose) from the 1860s. It still has its uses as an igniter (it lights very easily and it produces an excellent igniferous mixture of flame and hot and reactive gases and particles), and as a propellant in short barrelled launchers (such as for smoke grenades) in which the low pressure and great leakage make more modern propellants unsuitable. It is also quite cheap.

For most of its history pyrotechnics has relied on naturally occurring products as fuels (petroleum, pitch, charcoal) and on naturally occurring nitrates (originally sodium nitrate $NaNO_3$ from dung and urine, and later potassium nitrate KNO_3 prepared from it).

Nitrates occur naturally as the result of the action of certain bacteria on organic matter in the soil, and have been known since antiquity. Most nitrates are soluble in water, and solid deposits occur largely in the dry regions of the world. The sodium nitrate deposits in Chile are particularly famous, and led to the common name for the salt of *Chile saltpetre*. Less commonly, calcium nitrate (*wall nitre*) is found, particularly on walls of cattle barns and middens. Both these materials are hygroscopic (take up moisture from the air) and early formulations using them were unsatisfactory. The effect of this on the development of gunpowder (Buchanan, 1996) is discussed in a later chapter.

In *ca.*1675 Hennig Brand in Hamburg prepared white phosphorus by the reduction of urine, being the first scientist ever to isolate an element from one of its compounds. He kept his process secret, and white phosphorus was isolated independently by Robert Boyle in 1680. This paved the way much later for the development of the match industry, although the

material, which burns spontaneously in air and cannot be mixed safely with solid oxidisers, is hardly a true pyrotechnic ingredient.

In 1786 Berthollet showed that the result of passing chlorine water into a solution of potassium hydroxide was potassium chlorate $KClO_3$. The reaction was investigated by Gay Lussac in 1842 who improved the yield by using higher temperatures. Subsequently the material was produced commercially by the electrolysis of brine (sodium chloride solution) and precipitation with potassium chloride.

Potassium chlorate is a much more powerful oxidising agent than potassium nitrate, and it allowed the preparation of much more energetic pyrotechnic mixtures. Its low decomposition temperature, and the chlorine which it contains, permits the production of particularly beautifully coloured flames which led to an increase in the popularity of fireworks. Now, however, the explosive hazards of mixtures containing chlorates have led to their virtual abandonment in fireworks, to the detriment of displays.

In 1805 Chancel invented the first commercial pyrotechnic match in which a mixture of potassium chlorate and sugar inflamed on contact with sulphuric acid (still a potent recipe as a starter for clandestine incendiarism).

Over the past two centuries, the increasing capability of the chemical industry has produced a huge range of potential pyrotechnic ingredients.

It is not surprising that very few of the elemental pyrotechnic fuels occur free in nature. Magnesium, which is the pyrotechnic fuel *par excellence* (or would be if it did not corrode so readily) was first isolated by Davy in 1808 and was available in modest quantities from the 1830s. It burns brilliantly in air, and is the standard fuel for energetic compositions, particularly those which are required to produce intense light for visual illumination. Aluminium was isolated by Wohler in 1827 but was not available in industrial quantities until the late 1880s. It is very energetic, but its tenacious oxide coating (which prevents its ready corrosion and makes it so useful for structural purposes) renders it a sluggish pyrotechnic fuel unless in a very violent mixture such as flash powder. The "newer" metals titanium and zirconium also burn vigorously, and are used in igniter formulations in small devices. Zirconium was isolated by Berzelius in 1824 and is now used in large quantities in the construction of nuclear reactors because it has a very low neutron capture cross-section. Titanium was first isolated by Nilson and Pettersson in 1887, but was not available in more than experimental quantities until 1946. Titanium and zirconium are particularly hazardous because of the ease with which the powdered metals ignite and explode in air.

Boron was isolated by Davy, Gay-Lussac and Thenard in 1808. Boron compounds are used extensively in industry (in enamels, and glasses, water softeners) but the main use of the element is probably in pyrotechnics, principally in igniter and delay compositions. Silicon was isolated by Berzelius in 1824. Its compounds are very widely used in industry (silicones, carborundum, etc.,) and the element is used in electronics (very pure) and in pyrotechnics principally in igniter compositions.

All manner of oxidants are now available including metallic oxides (strontium peroxide, barium peroxide for example) which react with energetic metallic fuels to produce much heat and little gas.

The major effort in pyrotechnics was undoubtedly in the two World Wars when so many of the presently used formulations originated. There was a huge demand for illumination: visual observation required intense flares which could burn for minutes and the development of aerial photography demanded intense and very brief flashes which could

allow sharp nocturnal photography of the ground using a slow shutter; ammunition required tracer for visual observation. Counters to acoustic torpedoes were developed using pyrotechnics which produced gas and noise. Smoke grenades were required to screen troops and vehicles from visual observation.

Since then, the scale of pyrotechnic development has dwindled, unfortunately at a time when improving instrumentation and mathematical tools offer remarkable ways of examining the complex physical and chemical phenomena exhibited by pyrotechnics.

Most of the work on the propagation of pyrotechnic reactions has been published since World War II, and little serious fundamental understanding was possible before theories of the reactivity of solids were elaborated to the extent that they could be applied to very energetic reactions. In 1948 Spice and Staveley reported the existence of pre-ignition reactions which occur in advance of the combustion wave, and many papers have been written on specific aspects of pyrotechnic propagation. Nevertheless, it is still impracticable to calculate from first principles an adequately precise burning rate of a practical pyrotechnic system.

However, if the scale of the activity has declined, the subtlety of the requirement continues to increase, particularly in the area of emission and screening of electromagnetic radiation. The proliferation of heat seeking missiles and thermal imagers requires devices which produce smokes impenetrable in the infrared and flares emitting in the infrared. Current smoke systems are obsolescent because they are effective only in the visual, and new systems are being procured which are effective in both regions. The next wish is to include the millimetric wave region so that one device could protect against surveillance or attack using the naked eye, thermal imager or radar. The next generation of battlefield illuminant would ideally be a flare which emits insufficient in the visual to assist the naked eye, but which produces a sufficient intensity in the infrared to allow clear observation through a personal thermal imager.

And gunpowder will still be used.

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Chapter 2

BASIC PRINCIPLES - THERMOCHEMISTRY

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INTRODUCTION

The basis of pyrotechnics is a combustion reaction which can be made to take place between two or more ingredients in a pyrotechnic mixture. This reaction produces heat as the mixture of reactants is converted into a mixture of solid, liquid or gaseous reaction products. Part of this heat is used to produce the pyrotechnics special effect ; part of the heat is necessary for the reaction to propagate through the mixture.

This chapter considers the basic thermochemistry needed to calculate the heat change during a reaction, and how the heat produced varies with the characteristics of the ingredients and their ratio in the mixture. It covers the basic concepts of heat of formation of a chemical, heat of chemical reaction, exothermicity and adiabatic reaction temperature and shows how these quantities may be derived for some simple and more complex mixtures.

HEAT, WORK AND ENERGY

The energy of a system may be defined as its capacity for doing work. The most obvious forms of energy in common experience are potential energy and kinetic energy of objects, but other forms such as electrical and chemical are inescapable.

The concept that the energy of any *closed system* (*i.e.,* an isolated system with no exchange of any sort with the outside) is constant is enshrined in the First Law of Thermodynamics as a fundamental tenet of physics. If the system is not closed, but does work on an external system, than its energy decreases ; conversely, if the external system does work on it, then its energy increases ; and in both cases the total energy of the two interacting systems remains constant.

If a system receives a quantity of heat, Q, and also performs a quantity of work W, we can define a quantity, E, the internal, or intrinsic energy of the system such that $\Delta E = Q - W$. That is, the change in the internal energy of the system depends only on the total heat change and total work done. It does not depend on the order or on the number of stages in which the changes occur.

If the system does no external work (*e.g.,* consider a quantity of gas heated inside a rigid and hermetically sealed container), then the heat added at constant volume goes only to increase the internal energy of the system. $\Delta E = \Delta Q_v$. If the gas is free to expand against the external atmospheric pressure, then the heat is added at constant pressure and $\Delta E = \Delta Q_p - P\Delta V$. If we define a quantity H the *enthalpy* such that $H = E + PV$ then at constant pressure $\Delta H = \Delta Q_p$.

The *specific heat*, c of a material is defined as the energy necessary to change its temperature by one degree. We may therefore define $c_v = (\partial E / \partial T)_v$ as the specific heat at constant volume, and $c_p = (\partial H / \partial T)_P$ as the specific heat at constant pressure. In the pressure range in which we are interested, the difference between these quantities is significant only for gases.

Combustion reactions are usually sufficiently slowly to allow the conditions to approximate to constant pressure, and the heat change of interest is the enthalpy change. Detonation reactions occur very fast, and the conditions approximate better to constant volume.

ATOMIC AND MOLECULAR MASS

As far as chemistry is concerned, an atom consist of a positively charged *nucleus* surrounded by negatively charged electrons. The nucleus consists of positively charged *protons* and neutral *neutrons* each of mass approximately 1.66×10^{-27} kg. The electron has a mass of approximately 9.11×10^{-31} kg, and its charge, approximately -1.6×10^{-19} C, is exactly equal and opposite to that of a proton.

The chemistry of an atom is essentially a matter of the energy and distribution of its electrons, and is therefore defined by the number of protons in the nucleus (the *atomic number*) which must equal the number of electrons in the neutral atom. The *mass number* of the atom is the total of protons plus neutrons. So, hydrogen has one proton only (atomic number = 1, mass number = 1), while helium has 2 protons and 2 neutrons (atomic number = 2, mass number = 4). Each different element therefore has a different number of protons. Some elements however may possess different *isotopes* which have different numbers of neutrons. For example, hydrogen always has one proton but may have 1 neutron (hydrogen), 2 neutrons (deuterium) or 3 neutrons (tritium). These may be written ${}_1^1H$, ${}_1^2H$, ${}_1^3H$ although the subscript 1 is redundant if the chemical formula is given. In most cases the chemical difference between isotopes is slight and due only to slight changes in the mass of the nucleus ; only for hydrogen with its light nucleus is the chemical difference between isotopes at all obvious.

The *atomic mass* of an element is closely related to its mass number, but differs from it for two reasons. Firstly, the element may be a mixture of isotopes ; secondly, the binding energy released or absorbed when neutrons and protons combine to form a nucleus is sufficient to cause a measurable change in the mass of the system.

The atomic masses of elements were originally determined by careful measurement of the masses of elements which combined during chemical reactions. They were therefore relative masses, and were quoted quite reasonably relative to the mass of the lightest element, hydrogen, as 1. Later, for greater practical convenience they were related to oxygen as 16, and most recently and yet more precisely, to the carbon isotope of mass number 12, as 12. The molecular mass of a compound is simply the total mass of all the atoms it contains in a molecule.

The chemical unit of quantity is the *mole* or *mol*. A mole of an element, or a compound is the mass of that element or compound which has the same number of atoms or molecules respectively as there are atoms in 12 g of ${}^{12}C$. In theory, but seldom in practice, one may define a mole of anything, *e.g.* pints of (the same) beer.

ENERGY OF CHEMICAL REACTION

We may determine by measurement in the laboratory the masses of reactants A and B which produce a product Z. If the molecular masses of A and B are known, than we may calculate from the reacting masses the number of moles involved, which is a more convenient concept to deal with.

If the reaction is between a moles of fuel and b moles of oxidant :

a Fuel + b Oxidant = products ; energy change = ΔH

The mixture that satisfies this equation without there being an excess of either reactant is called the *stoichiometric* mixture for that reaction. Let us write the energy change during

that reaction as $\Delta H = \Delta H_{stoich}$. For this mixture the heat output per unit mass is :

$$q = \frac{\Delta H_{stoich}}{a \cdot M_{fuel} + b \cdot M_{oxidant}}$$

where M_{fuel}, $M_{oxidant}$ are the molecular masses of the fuel and oxidant respectively

To calculate the energy released during reaction we must know the energy associated with the individual reactants and products. It may be useful to begin with a mechanical analogue. A ball on a table top falling to the floor releases its potential energy to the environment as the heat and noise of impact. This may be compared to an *exothermic* (heat producing) chemical reaction in which energy is released (primarily as heat) because the energy of the products (stationary ball on floor) is less than the energy of the reactants (stationary ball on table). A ball on a table top rising to the ceiling requires an input of energy from an external source to increase its potential energy. This may be compared to an *endothermic* (heat absorbing) chemical reaction in which the products contain more energy than the reactants, and energy (heat) is absorbed from the environment to make up the difference.

We are concerned here with differences of energy, not with the absolute energy of the ball, reactants or products. In the mechanical analogue, it is easy to see that the energy changes may be calculated with reference to the final height relative to the table or the floor, either of which is less cumbersome than referring all distances to the centre of the earth at which the "true" zero of potential energy occurs.

In a chemical system we follow the energy change of each chemical element and we take as zero the energy of each element in its standard state – defined to be its most stable form at 25°C and at one atmosphere pressure. Some elements can exist in more than one form at 25°C and one atmosphere. Carbon can exist in two crystalline forms (diamond and graphite) and in an amorphous form ; of these the most stable (lowest energy) is diamond. Such differences are trivial compared with the energy release of any self-respecting pyrotechnic reaction.

A fundamental characteristic of any compound is its *standard enthalpy of formation* defined as the enthalpy change when a mole of the compound is made from its elements, all reactants and products being in their standard states. For example, the standard enthalpy of formation of water is the energy change of the reaction :

H_2 (gas, 25°C, 1 atm.) + $0.5O_2$ (gas, 25°C, 1 atm.) = H_2O (liquid, 25°C, 1 atm.)

$\Delta H = \Delta H_f$

The energy released (or absorbed) by the reaction is the total energy of the products minus the total energy of the reactants.

Heat of reaction $\Delta H = \Sigma \Delta H_f$ (products) - $\Sigma \Delta H_f$ (reactants)

where ΔH_f is the enthalpy of formation of an ingredient or product, and the summation is carried out over all reactants and products.

Heats of formation of compounds are tabulated in the literature. A selection relevant for our purposes is given in Annex A. It must be understood that the more negative the heat of formation (the more energy lost to the system when the compound is formed) the more stable the compound is likely to be ; such compounds with negative heats of formation are called *exothermic* compounds. Conversely, compounds with positive heats of formation

(*endothermic* compounds) contain more energy than their separate elements and are likely to be relatively less stable.

It is seldom possible to synthesise compounds directly from the elements, so that the heat of formation can seldom be measured directly. However, it is usually possible to calculate it by more roundabout methods. A common method of calculating the heat of formation of a fuel is from the *heat of combustion* which is often available experimentally. See Example 2-1.

Example 2-1

Calculate the heat of formation of butane (Calor gas) C_4H_{10}.

We require the heat of the (impracticable) reaction :

$$4C\ (\text{crystalline}) + 5H_2\ (\text{gas}) = C_4H_{10}\ (\text{gas})$$

We know (from tables) the heats of combustion of carbon, hydrogen and butane :

$C\ (cr) + O_2\ (g) = CO_2\ (g)$	$\Delta H = -393.5$ kJ
$H_2\ (g) + 0.5O_2\ (g) = H_2O\ (l)$	$\Delta H = -285.8$ kJ
$C_4H_{10}\ (g) + 6.5O_2\ (g) = 4CO_2\ (g) + 5H_2O\ (l)$	$\Delta H = -2877.0$ kJ

Multiply the first two equations by the required factors, reverse the third, and add them all together to produce the required equation for the formation of butane from the elements :

$4C\ (cr) + 4O_2\ (g)$	$= 4CO_2\ (g)$	$\Delta H = 4 \times (-393.5) = -1574$ kJ
$5H_2\ (g) + 2.5O_2\ (g)$	$= 5H_2O\ (l)$	$\Delta H = 5 \times (-285.8) = -1429$ kJ
$4CO_2\ (g) + 5H_2O\ (l)$	$= C_4H_{10}\ (g) + 6.5O_2\ (g)$	$\Delta H = +2877$ kJ
$4C\ (cr) + 5H_2\ (g)$	$= C_4H_{10}\ (g)$	$\Delta H_f = -126$ kJ

The heat of formation of butane is therefore -126 kJ mole^{-1}.

It can be shown from thermodynamics that for a reaction to proceed spontaneously the change in the *Gibbs free energy*, ΔG must be negative. The change in Gibbs free energy is related to the enthalpy change by the equation

$$\Delta G = \Delta H - T\Delta S$$

where T is the (absolute) temperature of the reaction, and ΔS is the change in *entropy* which is related to the disorder of the system. Therefore, a spontaneous reaction is favoured by a negative ΔH (an exothermic reaction) and a positive entropy change. If the reactants and products are solids, the entropy change is close to zero ; if solids react to produce liquid or gas, then the entropy change is positive. Therefore, for most pyrotechnic systems the reaction will proceed spontaneously if it is exothermic ($\Delta H < 0$).

Note however that the *rate* at which the reaction proceeds at constant temperature is not necessarily related to its exothermicity. It is, however, fundamentally related to the *activation energy* for the reaction which is discussed later. However, as all the reactions with which we are concerned increase in rate as the temperature rises, exothermic reactions tend in practice to increase the temperature of the system, and therefore proceed faster.

The types of reaction used in pyrotechnics are *fuel - oxidant* reactions : that is, they are chemical reactions between a fuel and an oxidising agent (which is usually a source of

oxygen, but may be a source of another powerful oxidising agent such as fluorine). They are also *combustion reactions* : they propagate through the solid or liquid phase by means of a combustion wave which may or may not produce flame.

The enthalpy of reaction is calculated from the reaction equation and is quoted in Joules (J). To calculate the heat of reaction it is necessary to know what the reaction products are, so that a realistic chemical equation can be written. Often it is not obvious what the major reaction products might be, and a certain amount of intuition or experimental evidence may have to be used. It must be remembered that the products to be considered must be those which are formed at the temperature of the combustion reaction, perhaps several thousand degrees Celsius. Computer programs exist to help in the choice.

A further characteristic of great practical importance is the energy released per gram of reacting mixture – the *exothermicity*, q usually given in kJ kg^{-1}.

The mixture containing the exact quantities of reactants described by the equation is called the *stoichiometric* mixture. Every other mixture contains either excess fuel or excess oxidant and has a lower exothermicity because the heat producing mixture is diluted with the excess ingredient. Measurement of the heats produced by a range of ingredients ratios therefore gives useful information on the chemistry of the reaction.

For a simple binary reaction of the type fuel + oxidant = products we would expect to observe a variation in the exothermicity q as shown in Figure 2-1.

If we assume that the fuel and the oxidant do not decompose by themselves, then the heat of reaction for the pure fuel or pure oxidant is zero. As the amount of fuel increases the measured heat of reaction per unit mass of the mixture (q) increases until it reaches a maximum at the stoichiometric ratio, above which it decreases again to zero at pure fuel. The position of maximum exothermicity therefore gives the composition at stoichiometry.

It is often instructive to plot Q, the heat of reaction per mole of oxidant present in the mixture, against the amount of fuel. In the fuel lean mixture Q increases with increasing fuel content to the point of stoichiometry and then remains constant. If a plateau is not reached, then one may assume that more than one competing reaction is occurring with different stoichiometric ratios of fuel and oxidant.

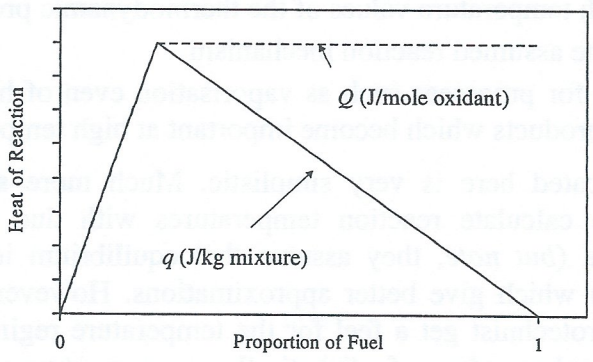


Figure 2-1 Exothermicity of simple mixture

TEMPERATURE OF REACTION

Knowing the heat of reaction one may in principle estimate the combustion temperature from the following equation :

$$q = \sum_i \int_{T_1}^{T_2} c_i dT + \sum_i L_i$$

where c_i, L_i are the specific heat and latent heat of phase transition at constant pressure of component *i,* and T_1, T_2 are the initial and combustion temperatures.

The use of this equation requires many assumptions about specific heats and latent heats of phase changes over the temperature range up to that of the combustion temperature, and about the amount of heat lost from the reaction zone. Two extreme alternative simplifications are possible with the assumptions that :

i) the reaction takes place effectively instantaneously at the ignition temperature ;

ii) the reaction does not take place until the maximum temperature has been reached.

The first assumption implies that the heat from the reaction goes almost entirely into heating the products, which are formed at relatively low temperature. The second assumption implies that the energy is used to heat the reactants to high temperature. Neither is likely to be strictly correct. If performed adequately, and interpreted with caution the calculated temperature is a useful upper limit estimate of the maximum achievable temperature assuming no heat loss from the system - the *adiabatic reaction temperature*. A simple example for a non-pyrotechnic reaction, the combustion of the stoichiometric mixture of the hydrocarbon butane and oxygen is given in Example 2-2.

The example considered gives as its "best" result a value markedly higher than that actually measured. This deviation becomes even more extreme when calculating the temperatures of energetic pyrotechnic systems. The reasons for the difference are easy to list, but often difficult to quantify. They include :

- heat losses from the system by convection, conduction and radiation
- errors in the high temperature values of the thermodynamic properties
- inadequacy of the assumed reaction mechanism
- failure to allow for processes such as vaporisation even of high melting solids and dissociation of products which become important at high temperatures

The calculation indicated here is very simplistic. Much more sophisticated computer programmes exist to calculate reaction temperatures with due consideration of high temperature equilibria (*but note*, they assume that equilibrium is reached, and do not consider the kinetics) which give better approximations. However, simple estimates are useful to help the pyrotechnist get a feel for the temperature regime and the factors that influence it. While absolute values of adiabatic flame temperature are likely to be severely in error, the change in temperature resulting from a deliberate variation such as change of metal fuel, is likely to offer a pyrotechnic insight.

Example 2-2

Calculate the combustion temperature of butane C_4H_{10} in air.

The reaction is : $C_4H_{10}(g) + 6.5O_2(g) = 4CO_2(g) + 5H_2O(l)$ $\quad \Delta H = -2859.6$ kJ

Given :

	Heat capacity (J $mol^{-1}K^{-1}$)			Heat of vaporisation (kJ mol^{-1})
	298K	373K	3000K	398K
$H_2O(l)$		75.4	75.9	40.897
$H_2O(g)$		34.1	55.6	
$CO_2(g)$	36.6		61.4	

The heat required to raise the temperature of the system to the *adiabatic flame temperature* T_{ab} is calculated for the following processes using the information indicated :

Heat $H_2O(l)$ from 298K to 373K	temperature rise, specific heat of $H_2O(l)$
Convert $H_2O(l)$ to $H_2O(g)$ at 373K	heat of vaporisation of $H_2O(l)$
Heat $H_2O(g)$ from 373K to T_{ad}	temperature rise, specific heat of $H_2O(g)$
Heat $CO_2(g)$ from 373K to T_{ad}	temperature rise, specific heat of $CO_2(g)$

The first two calculations are simple, the last two may be carried out by trial and error until all the available heat has been accounted for, or more satisfactorily with the aid of a spread sheet.

The results below, of which the first two are reproducible from the information presented above, indicate errors that result from certain simplifications. The first calculation (A) assumes constant specific heat (c_p) using a low temperature value ; the second (B) recognises the increase in c_p with temperature and assumes a constant, mean value ; the third (C) uses an experimentally determined expression for c_p as a function of temperature, and calculates the heat change as its integral with respect to T.

	Calculation Method		
	A	B	C
Preocess :	Heat required (kJ)		
Heat $H_2O(l)$ from 298K to 373K	28	28	28
Convert $H_2O(l)$ to $H_2O(g)$ at 373K	205	205	205
Heat $H_2O(g)$ from 373K to T_{ad}	1406	1424	1445
Heat $CO_2(g)$ from 373K to T_{ad}	1210	1183	1182
		T_{ad} (K)	
	8631	6407	5825

Note that the low temperature phenomena are hardly affected by the different assumptions.

The measured flame temperature of this mixture is nearer ## K

It is difficult to make good measurements of the temperature of pyrotechnic combustion. The environment is very aggressive, and the temperature of the hotter systems is higher than thermocouples can stand. Heat losses through thermocouple wires can be important and induce large errors, so the finest (and naturally the most delicate) should be used. Shidlovsky reports the effect of the diameter of the wire of a thermocouple on the measured combustion temperature of a smoke composition containing rhodamine dye (no further details given, Table 2-1).

diameter of wires	(mm)	0.5	0.2	0.1
maximum measured reaction temperature	(°C)	338	697	837

Table 2-1 Effect of Thermocouple on Measured Temperature

High combustion temperature is favoured by :

- high heat of reaction
- low volatility and high melting point of reactants and products
- high thermal stability of products (low dissociation)
- low heat capacity

Consequently, high temperature is also favoured by high pressure which suppresses volatilisation and dissociation.

This is a very important consideration in pyrotechnics, because different pyrotechnic effects are achieved optimally at different temperatures.

So, illuminating compositions are required to produce the highest intensity of white radiation and therefore should achieve as high a temperature as feasible because the luminous flux is proportional to the fourth power of the absolute temperature. Consequently, a metal fuel and sodium nitrate are the favoured reactants which give as products magnesium oxide m.p. 2852°C, b.p. 3600°C, the very stable gas nitrogen, and potassium oxide which is a disadvantage because it decomposes at low temperature. Compositions producing coloured lights should not burn as hot as illuminating compositions to reduce the amount of white radiation from the hot particles which dilutes the required colour from the metal salt. Consequently they contain lower proportions of metal, and increased amounts of organic compounds. Efficient production of a coloured smoke by the volatilisation of an organic dye is achieved at a temperature high enough to produce rapid vaporisation, but not so high that the dye is largely carbonised, which requires perhaps the lowest temperatures usually encountered in pyrotechnics.

On the basis of earlier measurements, Shidlovsky categorised the maximum flame temperature for various classes of composition (Table 2-2).

Composition Type	Maximum Flame Temperature (°C)
photo-illuminating	2500 - 3500
illuminating and tracer	2000 - 2500
incendiary (with oxidiser)	2000 - 3500
solid rocket fuel	2000 - 2900
night signal flare	1200 - 2000
smoke composition	400 - 1200

Table 2-2 Typical Flame Temperatures for Different Applications (Shidlovsky)

This categorisation is supported by later measurements, for example by Haynes using chromel-alumel thermocouples of the combustion temperatures of some US coloured smoke compositions based on sulphur / potassium perchlorate burning in M18 grenades (from about 440° to about 780°C, the measured differences not readily related to the differences in formulation) and by Pan Gongpei et al., using tungsten - rhenium thermocouples of the red flare composition magnesium / strontium nitrate / ammonium nitrate / calcium resinate (2100 – 2200°C, the temperature increasing with increasing magnesium content.

A useful comparison of techniques applied to hot reactions is given by Merzhanov, together with optical measurements of the extreme temperatures achieved by condensed phase reactions (Table 2-3).

	Measurement method		
	thermocouple	micro-thermocouple	optical
	Combustion Temperature (K)		
Hf + C	3,650		
Zr + 2B	3,240		
Ti + C	3,070		
Ti + B	2,500	2,570	2,500
Hf + 2B	3,000	2,920	2,880
5Ti + 3Si	2,350	2,270	2,360

Table 2-3 Measured Temperatures of Solid State Reactions (Merzhanov)

CALCULATION OF PYROTECHNIC MIXTURES

INTRODUCTION

The most basic assumption, and it is a bold one, is that we can write an adequate equation for the reaction under consideration. It must be remembered that we really need to write the equation for the reaction(s) proceeding at the temperature of combustion, perhaps 1500°C. That is not common experience.

Modern thermodynamic codes can predict the thermodynamically stable mix of products at any temperature, and such calculations may help in deciding the best equations to choose as the basis for a formulation exercise. The exothermicity curves can provide great assistance, but require that considerable experimental information is available in advance.

Oxidation of metals is usually fairly straightforward. Oxidation of organic compounds is reasonably straightforward, although it should be remembered that both carbon monoxide and carbon dioxide are possible products. The major uncertainty is the decomposition of the oxidising agent, and here often questionable assumptions must be made. Other reactions such as the formation of borates, chromates *etc.*, and dissociation of products at high temperature may occur and lead to considerable deviations from the experimental results.

In this section we give examples of simple calculations on the basis of "reasonable" stoichiometry, and compare the results where possible with experiment. Note that the stoichiometric mixture releases the most heat per gram of mixture, and is therefore the most efficient mixture for pyrotechnic purposes.

OXYGEN BALANCE

While the behaviour of a pyrotechnic mixture is critically dependent upon the ratio of fuel and oxidant, *oxygen balance* is seldom explicitly considered in pyrotechnics, although it is the base for rationalising much of the behaviour of high explosives and propellants.

The oxygen balance of a mixture is the additional quantity of oxygen required for complete oxidation (*negative* oxygen balance), or left over when complete oxidation has been achieved (*positive* oxygen balance). In more usual pyrotechnics parlance, a negative oxygen balance corresponds to a *fuel rich* mixture, and a positive oxygen balance to a *fuel lean* mixture. As we will see, most pyrotechnic mixtures are fuel rich, very few (perhaps only oxygen generators) are oxidant rich.

As an example, consider boron (fuel), potassium nitrate (oxidant) and their mixtures. We write the equations for the oxidation of boron, and for the decomposition of potassium nitrate as follows :

$$2B + 3[O] = B_2O_3$$

$$2KNO_3 = K_2O + N_2 + 5[O]$$

We see that 2 x 10.8 = 21.6 kg boron require 3 x 16 = 48 kg oxygen for complete combustion. The oxygen balance of pure boron is therefore -48/(21.6 + 48) = -0.69 (or -69%). The oxygen balance of potassium nitrate is +5 x 16/(2 x 101.1) = +0.40 (or +40%).

The stoichiometric reaction between these ingredients may be written :

$$10B + 6KNO_3 = 5B_2O_3 + 3K_2O + 3N_2$$

This mixture contains 15.1% boron, and 84.9% potassium nitrate and has zero oxygen balance.

A typical practical mixture contains 30% boron and is used as a vigorous igniter composition. This is obviously fuel rich. From above 1 kg potassium nitrate oxidises 0.177 kg boron. One kilogram of this mixture therefore contains (0.300 – 0.7 x 0.117) = 0.128 kg boron in excess of what can be oxidised by the potassium nitrate. This requires 48/21.6 x 0.128 = 0.28 kg oxygen for complete oxidation. The oxygen balance of the mixture with 30% fuel is therefore –28/1.28 = -21.9%.

CALCULATION OF BINARY MIXTURES

INTRODUCTION

If there is no experimental evidence, chemical intuition, backed up if possible with some thermodynamic calculations is required. It is advisable to start with the simplest reasonable equation, and this may be an adequate starting point for experimental work. Once experimental information is available (variation of temperature, exothermicity or burning rate with ingredients ratio, and preferably some chemical analysis of products) it is possible to start to elaborate.

EXAMPLES OF BINARY MIXTURES

MAGNESIUM AND SODIUM NITRATE

The complete reaction to form the usual oxide of sodium may be written :

$$5Mg + 2NaNO_3 = 5MgO + Na_2O + N_2$$

The heat of reaction may be calculated using the heats of formation from the Annex remembering that the standard heat of formation of an element is zero.

ΔH_{form} (Na_2O) = -418.0 kJ, ΔH_{form} (MgO) = -601.2 kJ, ΔH_{form} ($NaNO_3$) = -468 kJ.

The heat of reaction is therefore $\Delta H = (-418.0 - 5\times601.2) - (-2\times468.0) = -2488$ kJ , and $q = 8535$ kJ kg^{-1}.

At stoichiometry (41.7% Mg) we may calculate $Q = 8535\times85\div0.583 = 1244$ kJ mol^{-1}

Calculate the exothermicity for an 80% magnesium mixture using the above equation. 1.915 g Mg must be added to one gram of the stoichiometric mixture to give an 80% fuel content. For this mixture, therefore, q = 8540/2.915 = 2930 kJ kg^{-1}.

Experimental values were obtained by Singh et al., for the heat of reaction over a range of compositions. These are shown in Figure 2-2 and compared with the above values. The q and Q values are in reasonable agreement with experiment near the assumed stoichiometry (8364 kJ and 1185 kJ kg^{-1} respectively at 40% magnesium) but at higher fuel content calculated q is markedly lower than experimental, and experimental Q rises steadily with increasing fuel content suggesting the further reactions are taking place, perhaps further reduction in the presence of excess fuel.

A possible modification to the reaction scheme above is the formation of elemental sodium rather than sodium oxide by further reduction with the excess fuel.

$$6Mg + 2NaNO_3 = 6MgO + 2Na + N_2(g) \qquad \Delta H = -2671 \text{ kJ},\ q = 8458 \text{ kJ kg}^{-1}.$$

Magnesium content at stoichiometry is 46.2%, and $Q = 1336$ kJ mol^{-1}.

The formation of an 80% fuel mixture requires the addition of 1.69 g magnesium per gram of stoichiometric mixture. For this mixture, therefore, $q = 8458/2.69 = 3144$ J g^{-1}. This is an improvement on the above result, but still low compared with experiment.

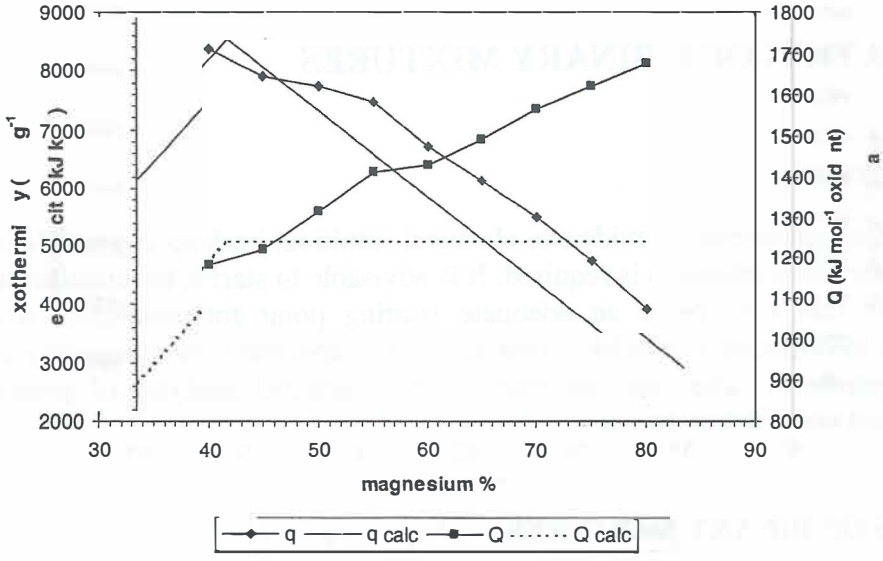


Figure 2-2 Measured and calculated exothermicity of magnesium – sodium nitrate

An additional possible reaction is the formation of magnesium nitride from excess magnesium and nitrogen :

$$3Mg + N_2(g) = Mg_3N_2 \qquad \Delta H = -460.7 \text{ kJ}$$

This reaction has 72.2% magnesium at stoichiometry, and produces 16.45 kJ per gram nitrogen.

Assuming that at high fuel content the last two equations prevail – *i.e.,* the products are magnesium oxide, magnesium nitride, sodium and excess magnesium, we may calculate for the mixture of 80% magnesium :

From the formation of MgO, Na and N_2, as shown above, $q = 3144$ kJ kg^{-1},

From the reaction of excess Mg with the 28/(2 x 85) x 0.2 = 0.0329 g nitrogen produced from 0.2 g sodium nitrate, $q = 16.45 \times 0.0329 = 541$ kJ kg^{-1}.

The total heat produced is therefore 3687 J g^{-1} which is about 7% below the measured value of 3944 kJ kg^{-1}, and probably within experimental error.

The above analysis is supported by the authors' report that when the magnesium content is below 55% the products were sodium oxide Na_2O, magnesium oxide MgO, and excess magnesium. At 70 - 80% magnesium the products were sodium, magnesium oxide, magnesium nitride and excess magnesium.

BORON + BARIUM CHROMATE

Boron and barium chromate mixtures have been used for many years as delay compositions. A reasonable attempt at a reaction stoichiometry is

$$2B + 2BaCrO_4 = 2BaO + Cr_2O_3 + B_2O_3 \qquad \Delta H = -627 \text{ kJ}, q = 1186 \text{ kJ kg}^{-1}$$

This equation requires 4.1% boron and Q = 313 kJ mol^{-1}. Comparing this with measurements by Charsley et al., in Figure 2-3 we see that while these values are not too far adrift from measurements near the assumed stoichiometry, other reactions occur at higher boron concentrations to increase the exothermicity considerably, and move the maximum to the region of 15% boron. X-ray analysis of combustion residues showed the presence of a barium borate and chromium boride, indicating that reactions such as the following must be of significance :

$5B + 2BaCrO_4 = 2BaB_2O_4 + CrB_2$ (14.6% boron)

This example indicates the problems that arise with materials such as boron which can react in various ways with metals.

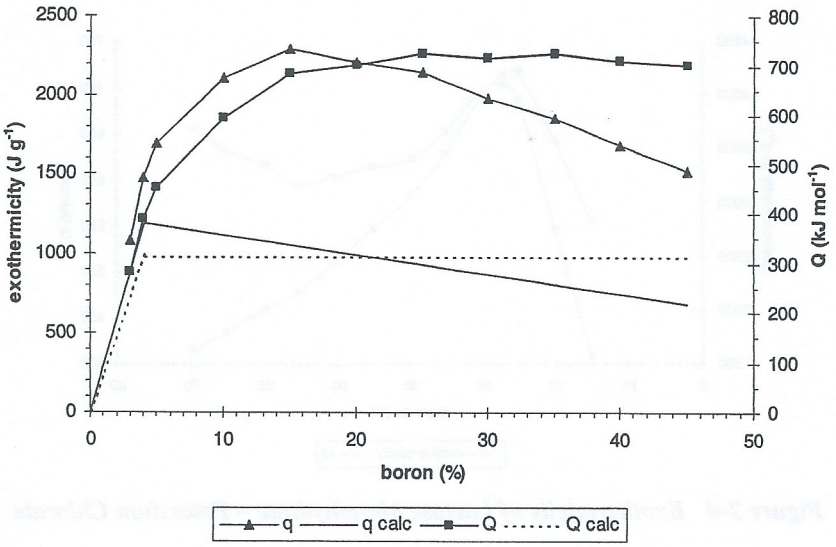


Figure 2-3 Measured exothermicity of boron – barium chromate

LACTOSE MONOHYDRATE – POTASSIUM CHLORATE

Consider the reaction between lactose and potassium chlorate, which is used to volatilise dyes and other smoke-producing molecules.

The oxidation of lactose to form carbon dioxide and carbon monoxide respectively may be written as follows depending on whether there is adequate oxygen for complete oxidation of the carbon :

$$C_{12}H_{22}O_{11}.H_2O + 12O_2 = 12CO_2 + 12H_2O$$

$$C_{12}H_{22}O_{11}.H_2O + 6O_2 = 12CO + 12H_2O$$

The corresponding complete pyrotechnic reactions may be written

$$C_{12}H_{22}O_{11}.H_2O + 8KClO_3 = 8KCl + 12CO_2 + 12H_2O \quad 27\% \text{ fuel}$$

$$C_{12}H_{22}O_{11}.H_2O + 4KClO_3 = 4KCl + 12CO + 12H_2O \quad 42\% \text{ fuel}$$

It may be expected that the former reaction will be predominant at low fuel content, but that the latter may become important at high fuel content.

The thermochemistry of this reaction has been studied by Scanes and Martin who found maximum exothermicity to occur near 26% fuel (Figure 2-4) as expected from the first equation. The value of Q however decreased markedly at higher fuel content indicating the occurrence of other reactions. Chemical analysis of the reaction products by Griffiths and Oliver revealed carbon dioxide, carbon monoxide, water and hydrogen in fuel rich mixtures. The authors considered that some of the excess lactose charred to form carbon, and that this reacted with water to form carbon monoxide and hydrogen (the *water gas* reaction).

$$C_{12}H_{22}O_{11}.H_2O = 12C + 12H_2O$$

$$C + H_2O = CO + H_2$$

The latter reaction, once of great commercial importance, proceeds rapidly above about 500°C and in high yield above about 900°C.

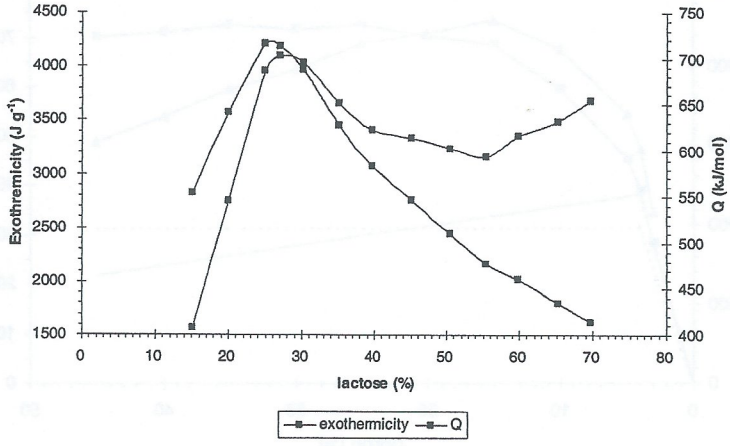


Figure 2-4 Exothermicity of Lactose Monohydrate – Potassium Chlorate

More detail

Overall, however, the study shows that the simple reaction is a good description for the purposes of pyrotechnic formulation.

TERNARY MIXTURES

The basic assumption (Shidlovsky) is that the system can be split into two binary mixtures which react independently. This is a dubious assumption, but it provides a starting point for formulation. There are very few adequate thermal studies of ternary systems.

The simplest reason for having a ternary mixture is that the binary mixture requires a binder to allow the manufacture of pellets or candles. Most binders are organic compounds and can therefore act as fuels. It is usually desirable to minimise the amount of binder in a composition, and experience shows that adequate effects can usually be achieved at about

the 4% level unless one or more of the ingredients is particularly fine, when more binder becomes necessary to coat the larger available surface.

It is also necessary to coat reactive metals to prevent them corroding, and again a few percent of the third ingredient is advisable.

Let us therefore consider a tracer priming composition consisting of magnesium, barium peroxide and acaroid resin as protecting agent and binder. The ideal is a mixture burning as hot as reasonable (*i.e.* near stoichiometry) and producing minimal volatile material (*i.e.* little organic binder and near stoichiometry).

$$Mg + BaO_2 = MgO + BaO \qquad \Delta H = -520.5 \text{ kJ}, q = 2688 \text{ kJ kg}^{-1}$$

This mixture contains 12.6% magnesium.

Assuming acaroid resin has the following formula, the reaction with barium peroxide is

$$C_{42}H_{43}O_{10} + 95.5BaO_2 = 95.5BaO + 42CO_2(g) + 21.5H_2O$$

and the stoichiometric mixture contains 4.2% resin

Assuming that 2% resin is adequate for the purpose the stoichiometric mixture is 12.3% magnesium, 85.7% barium peroxide and 2.0% resin.

A second reason for using a ternary system is to extend the range of burning rates that may be achieved by using various mixtures of fuels with the same oxidising agent, or of a single fuel with mixed oxidants.

SUMMARY

The propagation of a pyrotechnic reaction is normally described in terms of layer to layer burning. The rate of propagation is difficult to calculate and depends on the chemistry, the ingredients ratio, the physical properties of the ingredients, the temperature and pressure of the system, and the geometry and thermal characteristics of the container. The exothermicity (heat generated per unit mass) of the mixture must be matched to the intended purpose. Metals are used for highest temperatures (say 2000°C and above) and gassy, organic fuels for low temperatures (say 1000°C and below).

The burning rate of a composition can be affected by the chemical and physical characteristics of the ingredients (chemical nature, particle size, particle shape, presence of impurities or defects), the ratio of the ingredients, the characteristics of the combustion products, the method of filling (compaction load), and the dimensions of the column and the ambient temperature and pressure.

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Chapter 3

BASIC PRINCIPLES – PROPAGATION OF COMBUSTION

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INTRODUCTION

The previous chapter laid the foundations for an understanding of the basic thermochemistry of pyrotechnic reactions. Here, we consider the way in which that energy allows propagation of reaction through the mass of the reactants, and the factors that influence the rate at which the combustion wave travels.

QUALITATIVE CONSIDERATIONS

Consider a long column of a pyrotechnic mixture compressed into a metal tube, all parts being originally at room temperature (Figure 3-1a). When heat (say, radiant heat) is applied at one end of the column, the temperature of the composition at the end of the column rises until the temperature of ignition of the mixture (under those conditions) is achieved throughout the first layer of the column. At this temperature the mixture starts to react and generates heat, some of which passes into the next layer of unreacted composition and raises its temperature until it ignites in turn and provides heat to the next layer of the column (Figure 3-1b).

In this way the reaction zone moves into the column of unreacted composition leaving behind it the mixture of combustion products which may stay at least partly in place, or may fly away from the reaction zone depending on their physical properties. If the chemical reaction generates enough heat to ensure that adjacent layers of reactants reach ignition temperature, then the propagation of reaction becomes self-sustaining, and the column burns from end to end.

Obviously, the energy from the reaction zone does not all pass into the unreacted reactants: some goes into the walls of the container and some is carried away by the combustion products. If the container is a thermal conductor, some preheating of the reactants will occur.

It was first pointed out by Spice and Staveley (1948) that the combustion reaction is not the only reaction of importance. At temperatures below the ignition temperature of the mixture *pre-ignition* reactions can occur which consume some of the reactants, pre-heat unreacted layers, and perhaps have a considerable effect on the rate of the subsequent reaction. Obviously ready propagation is favoured by a low ignition temperature and by a high exothermicity. During WWII McLain proposed a "propagation index" as a method of assessing the suitability of a candidate as a delay composition which must sustain combustion in a long narrow tube:

$$\text{P.I.} = (\text{Heat of Reaction})/(\text{Temperature of Ignition})$$

The higher the value, the better the composition should propagate (McLain Chapter 5). This is particularly important for slow burning compositions, particularly those in narrow channels where heat losses are more significant. However, other factors including the physical form of the combustion products are also of great importance. For example, viscous slags retain heat near the combustion zone, while gases tend to remove it.

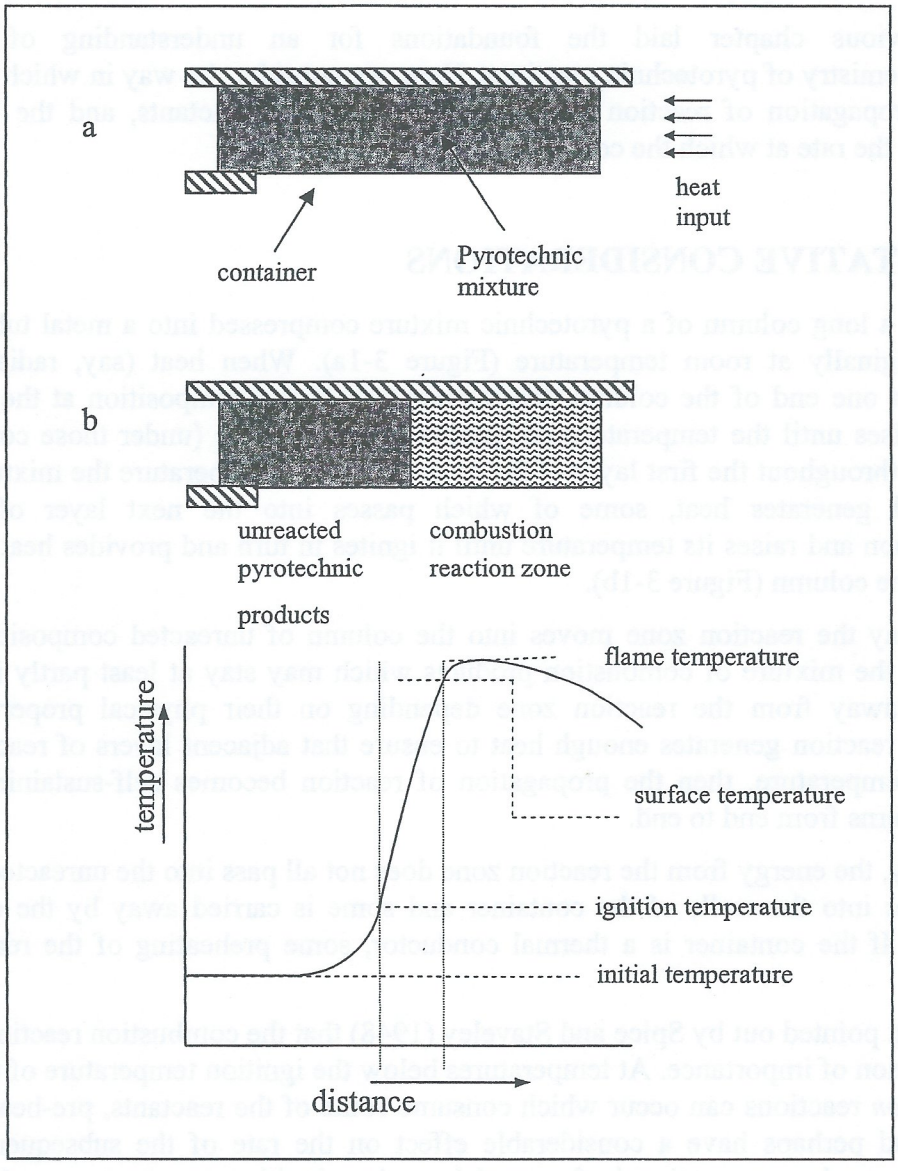


Figure 3-1 Propagation of Pyrotechnic Reaction

Within limits, ignition can be achieved by applying heat slowly for a long time, or rapidly for a short time. However, if the heat flux is too low, too much heat is wasted, and if it is high but for too short a duration, an inadequate quantity of the acceptor composition starts to react. The practical consequence is that it is desirable that the burning rates of compositions in the ignition train do not differ too greatly; the mismatch that can be tolerated depends on the compositions and the design.

CHEMICAL KINETICS

A fundamental point about pyrotechnic mixtures and all energetic materials is that they are thermodynamically *unstable*. They can react to produce products which contain less energy than the starting mixture, and the excess energy is released as heat. At normal temperatures this reaction proceeds so slowly that the mixture may be stored for long periods without deterioration. The mixture must be heated to a sufficient temperature for the reaction to proceed at a noticeable rate. This process is illustrated in Figure 3-2. Before the reaction can proceed, a relatively small amount of energy (the *activation* energy ΔE^*) has to be supplied by the environment. In the mechanical analogue of Section 2.2 this corresponds to the small amount of energy necessary to roll the ball against friction until it drops off the table. In a chemical system this energy is largely associated with the breaking of chemical bonds. Then, the reaction can proceed and release energy (ΔH).

The propagation of the reaction depends on the rate at which successive layers of reactants can be heated to the ignition temperature by the heat transferred from the burning front.

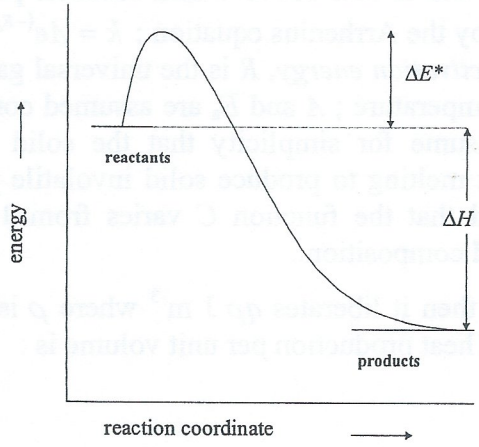


Figure 3-2 Energy Change in a Reaction

SIMPLE COMBUSTION MODEL

HEAT CONDUCTION EQUATION

The basic pyrotechnic characteristic is the burning rate of the mixture. We need to understand how different mixtures can burn at different rates, and how that rate is affected by changes in the chemistry of the mixture, and by external influences such as temperature and confinement. That is, we need a model for the combustion process which has as inputs the various measurable properties of the pyrotechnic mixture, and has as output the rate of propagation.

Considerations involving conservation of energy lead to the standard equation for conductive heat flow in a medium :

$$\lambda \nabla^2 T + \frac{dq}{dt} = \rho c_p \frac{\partial T}{\partial t}$$

where T is the temperature, λ the thermal conductivity, q the heat generated per unit volume within the medium, ρ the density, and c_P the specific heat at constant pressure. Solution of this equation gives the temperature – time history throughout the medium.

APPLICATION TO PYROTECHNICS

In our case, *dq/dt* results from a chemical reaction, or several reactions in competition or in sequence, which release or absorb heat.

The rate of a chemical reaction may be written in general : rate = $k\,C^n$

where k is the *rate constant* for the reaction, C a function of the concentration of the reactants, and n a constant.

We will assume that there exists a particular temperature T_{ign} (the *ignition temperature*) below which no reaction occurs, and at and above which reaction proceeds with a rate constant which may be described by the Arrhenius equation : $k = Ae^{(-E_a/RT)}$ *where* A is the *pre-exponential factor*, E_a is the *activation energy*, R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the absolute temperature ; A and E_a are assumed constant, independent of temperature. We will also assume for simplicity that the solid ingredients of the pyrotechnic mixture react without melting to produce solid involatile products, that only one chemical reaction occurs and that the function C varies from 1 for the unreacted mixture to 0 for completely reacted composition..

If this reaction liberates q J kg^{-1}, then it liberates $q\rho$ J m^{-3} where ρ is the density of the mixture in kg m^{-3}. Then the rate of heat production per unit volume is :

$$\frac{dq}{dt} = q\rho C^n A e^{(-E_a/RT)}$$

So, the equation that we seek to solve is:

$$\lambda \nabla^2 T + q\rho C^n A e^{(-E_a/RT)} = \rho c_p \frac{\partial T}{\partial t}$$

With suitable software, this equation may readily be solved within the limitations imposed by the crudeness of the assumptions, and the accuracy of the values of the various properties.

Figure 3-3 shows the general characteristics of a combustion propagating through a cylindrical column surrounded by a non-reacting container. The curved lines are isotherms.

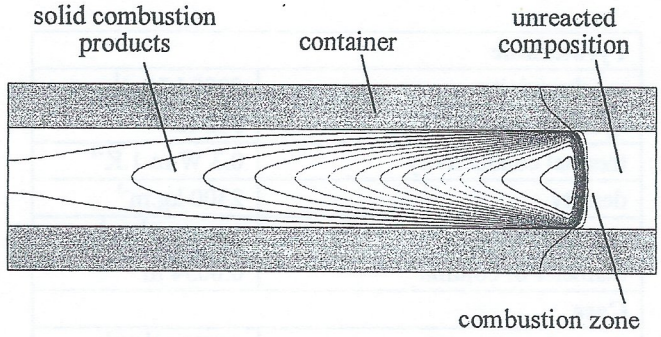


Figure 3-3 Propagation of combustion in a cylindrical column

It should be noted that, in the system shown, preheating of the unreacted mixture occurs only over a narrow region, and the burning front is convex to the reactants because of heat loss to the wall. If we plot a particular moment the temperature along the central axis as a function of distance (Figure 3-4), we obtain the general shape of the *combustion wave* which sweeps along the column. The speed of the combustion wave is the burning rate of the composition in this system.

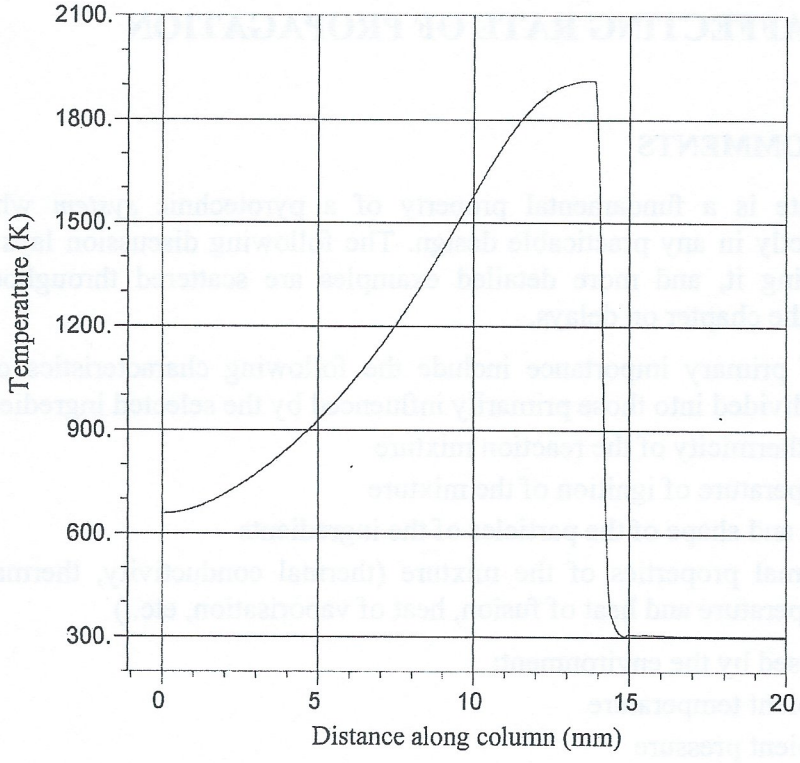


Figure 3-4 Combustion wave in pyrotechnic column

In this particular example, the temperature rises from ambient (300 K) to 1900 K within 1 mm of column length.

We are now in a position to examine the effect on the burning rate of the various parameters which define the composition and the environment. The following discussion uses the results from the simple model to indicate qualitatively the types of changes that are observed in real systems. Unless otherwise indicated, the modelled system is a cylinder of gasless pyrotechnic enclosed in a conducting metal case. Details are:

Pyrotechnic	
exothermicity	9000 $kJ.kg^{-1}$
ignition temperature	502 K
thermal conductivity	0.3 W.m-1.K^{-1}
density	2300 $kg.m^{-3}$
specific heat	540 $J.kg^{-1}.K^{-1}$
diameter of column	0.0034 m
Case	
thermal conductivity	40 $W.m^{-1}.K^{-1}$
density	7900 $kg.m^{-3}$
specific heat	540 $J.kg^{-1}.K^{-1}$
wall thickness	0.0015 m

Table 3-1 Details of modelled system

It must be remembered that in this model heat transfer is by conduction only.

FACTORS AFFECTING RATE OF PROPAGATION

GENERAL COMMENTS

Propagation rate is a fundamental property of a pyrotechnic *system* which must be managed correctly in any practicable design. The following discussion lays a foundation for understanding it, and more detailed examples are scattered throughout this book, particularly in the chapter on delays.

The factors of primary importance include the following characteristics of the system which may be divided into those primarily influenced by the selected ingredients:

- exothermicity of the reaction mixture
- temperature of ignition of the mixture
- size and shape of the particles of the ingredients
- thermal properties of the mixture (thermal conductivity, thermal diffusivity, temperature and heat of fusion, heat of vaporisation, etc..)

and those imposed by the environment:

- ambient temperature
- ambient pressure
- characteristics of the container (confinement, heat loss, etc..)

These variables are discussed in some detail below.

EFFECT OF TEMPERATURE

Pyrotechnics burn more slowly at low temperature than at higher temperatures, and the burning rates of the same system at two different temperatures can usually be related approximately by an equation of the form:

$$r_1 = r_0 \exp(bT_1/T_0)$$

where r_1, r_0 are the burning rates at absolute temperatures T_1, T_0, and b is a constant for the system. This equation has the form of the Arrhenius equation used to describe the temperature dependence of the rate of elementary chemical reactions.

The reason for this can be seen from consideration of the energy – reaction co-ordinate picture of Chapter 2. In order to move from the reactants to the products it is necessary to pass over the energy hump ΔE^*. The more reactant that can achieve the necessary energy, the greater will be the rate of conversion – *i.e.*, the greater will be the reaction rate. The higher the initial temperature of the reactants, the more easy is it to achieve the required activation energy. According to quantum mechanics, the relative concentration of the same species in two different energy levels is given by

$$\frac{c_1}{c_0} = e^{-(E_1 - E_0)/kT}$$

where c_1, c_0 are the equilibrium concentrations, E_1, E_0 are the energies of the two states, k is the Bolzmann constant, T is the absolute temperature.

However, the Arrhenius type equation is not an exact description of the temperature dependence of the burning rate of real systems for several reasons, even if the chemistry of the combustion process is unchanged over the temperature range. One of these is the existence of the ignition temperature below which the reaction does not proceed: the lower the temperature of the unburned composition, the greater the amount of heat required to raise it to the ignition temperature. Another is balance between self heating and heat loss from the system during combustion. Both these considerations lead to a burning rate higher in practice than expected by extrapolation from lower temperature.

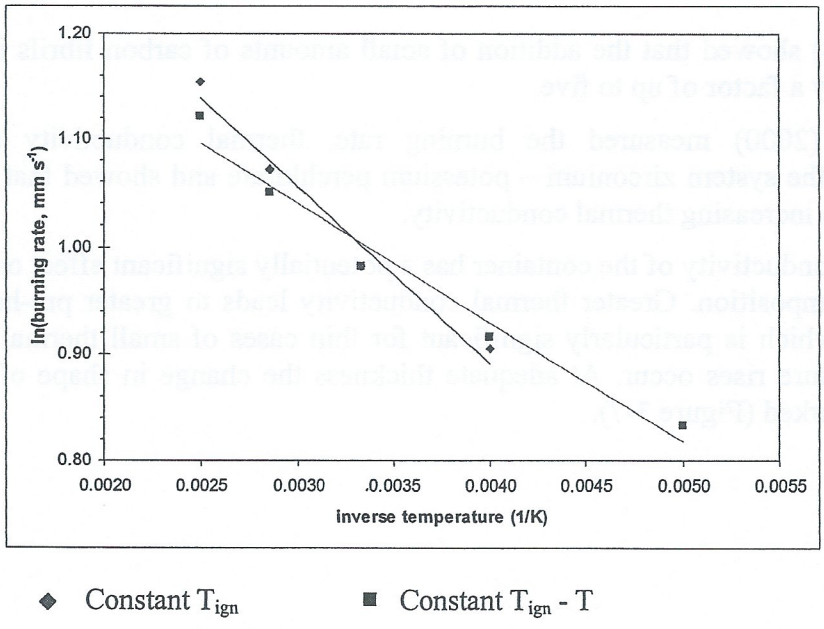


Figure 3-5 Calculated temperature dependence of burning rate

THERMAL PROPERTIES OF COMPOSITION AND CONTAINER

The heat flow from the combustion zone is obviously affected by the thermal conductivity of the column of reactants and of the surrounding medium, and by their thermal masses. Considering the composition: the greater the thermal conductivity the more heat flows into it, and the smaller the thermal gradient; the greater the heat capacity, the smaller the temperature rise. Considering the container: a high thermal conductivity combined with a small heat capacity may give rise to additional pre-heating of the composition at the walls, and high thermal conductivity combined with large thermal mass will tend to take much heat from the composition.

The effect of thermal conductivity of the composition on the equilibrium burning rate is modelled in Figure 3-6.

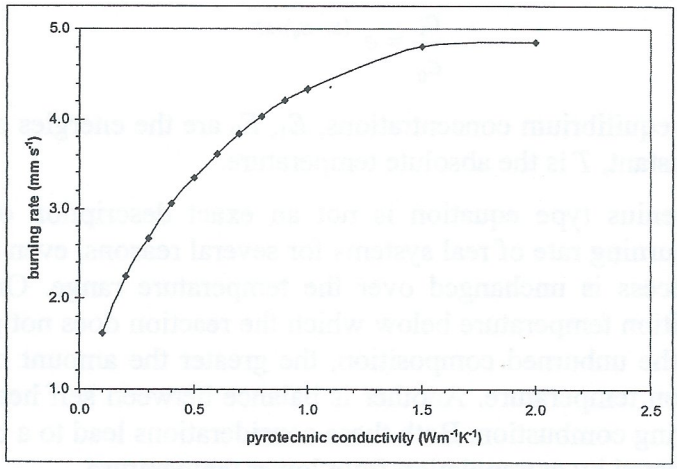


Figure 3-6 Effect of thermal conductivity of composition on burning rate

Nielson (1995) showed that the addition of small amounts of carbon fibrils increased the burning rate by a factor of up to five.

Sarawadekar (2000) measured the burning rate, thermal conductivity and thermal diffusivity of the system zirconium – potassium perchlorate and showed that burning rate increased with increasing thermal conductivity.

The thermal conductivity of the container has a potentially significant effect on the burning rate of the composition. Greater thermal conductivity leads to greater pre-heating of the composition which is particularly significant for thin cases of small thermal mass where large temperature rises occur. At adequate thickness the change in shape of the burning front is not marked (Figure 3-7).

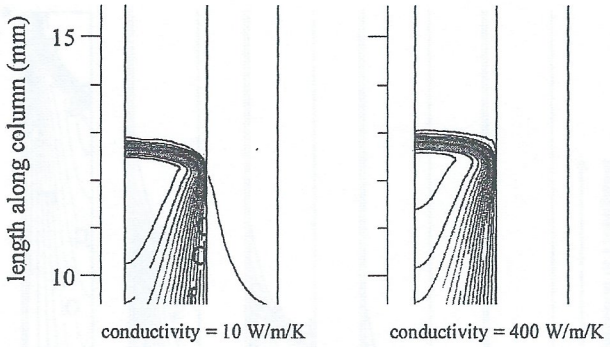


Figure 3-7 Effect of conductivity of thick case on shape of combustion front

The dramatic effect of a sufficiently thin case is shown in Figure 3-8 and in Figure 3-9. Immediately after ignition, before preheating can occur, the flame front is concave to the unreacted mixture as shown in the column on the left. As combustion progresses pre-heating along the container walls changes the shape of the front. If the heat loss is insufficient (as at the end of the column) the composition at the wall is raised to ignition point and radial burning occurs. The greater the thermal conductivity of the case, the sooner these phenomena occur. If the case is sufficiently thick, and the thermal mass correspondingly greater, the combustion front remains concave and radial burning does not occur.

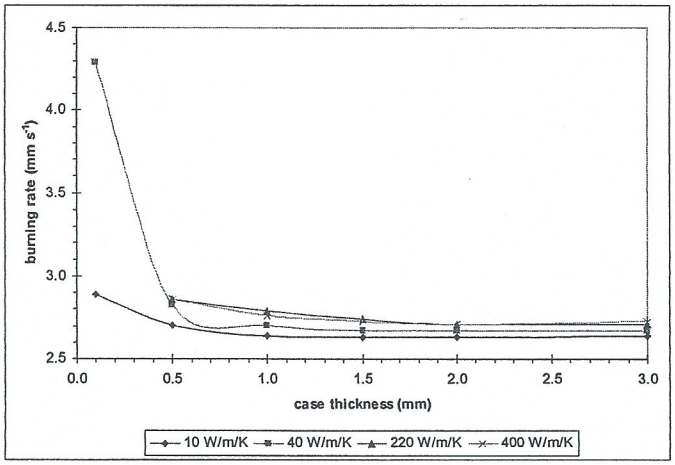


Figure 3-8 Effect of case thickness on burning rate

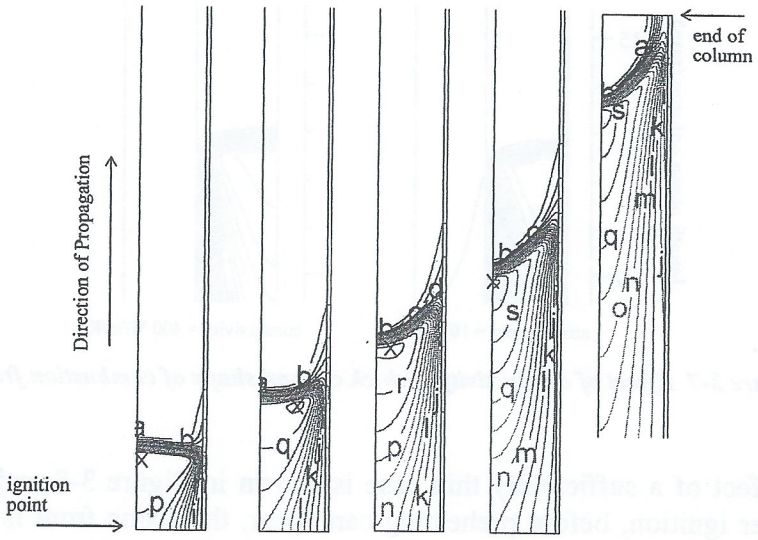


Figure 3-9 Effect of thin case on shape of burning front

This change of shape of the burning front may be associated with an increase in the burning rate.

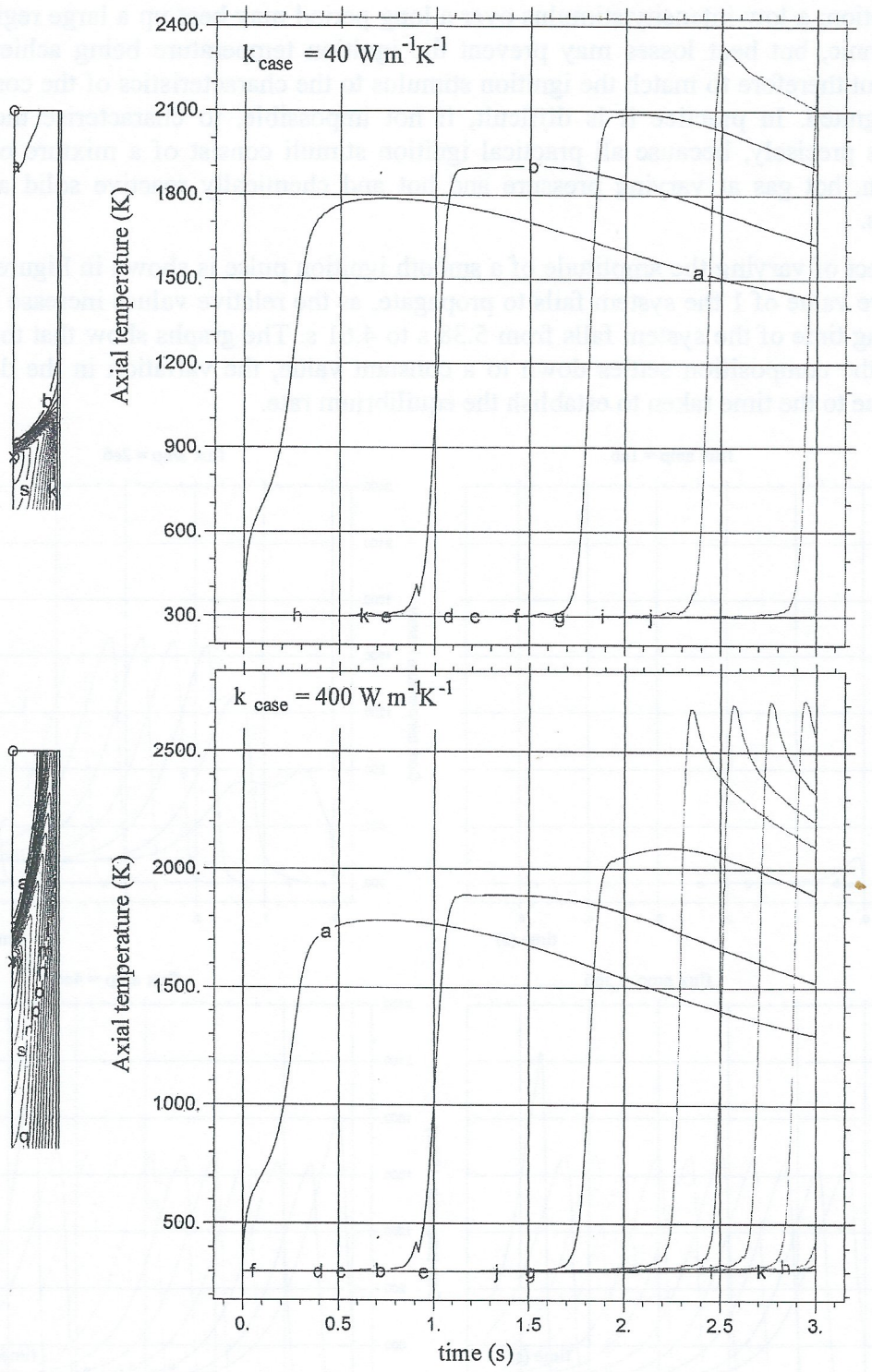


Figure 3-10 Effect of thin case on combustion wave

IGNITION STIMULUS

It is not just the amount of energy that is delivered to the pyrotechnic surface that is important, but the time over which it is delivered. A stimulus of very high intensity and short duration may ignite an inadequate amount of composition to allow subsequent

propagation; a low intensity stimulus over a long period may heat up a large region of the pyrotechnic, but heat losses may prevent the ignition temperature being achieved. It is important therefore to match the ignition stimulus to the characteristics of the composition to be ignited. In practice it is difficult, if not impossible, to characterise the ignition stimulus precisely, because all practical ignition stimuli consist of a mixture of thermal radiation, hot gas at varying pressure and hot and chemically reactive solid and liquid particles.

The effect of varying the amplitude of a smooth ignition pulse is shown in Figure 3-11. At a relative value of 1 the system fails to propagate, as the relative values increase from 2 to 4 burning time of the system falls from 5.38 s to 4.61 s. The graphs show that the burning rate of the composition settles down to a constant value, the variation in the delay time being due to the time taken to establish the equilibrium rate.

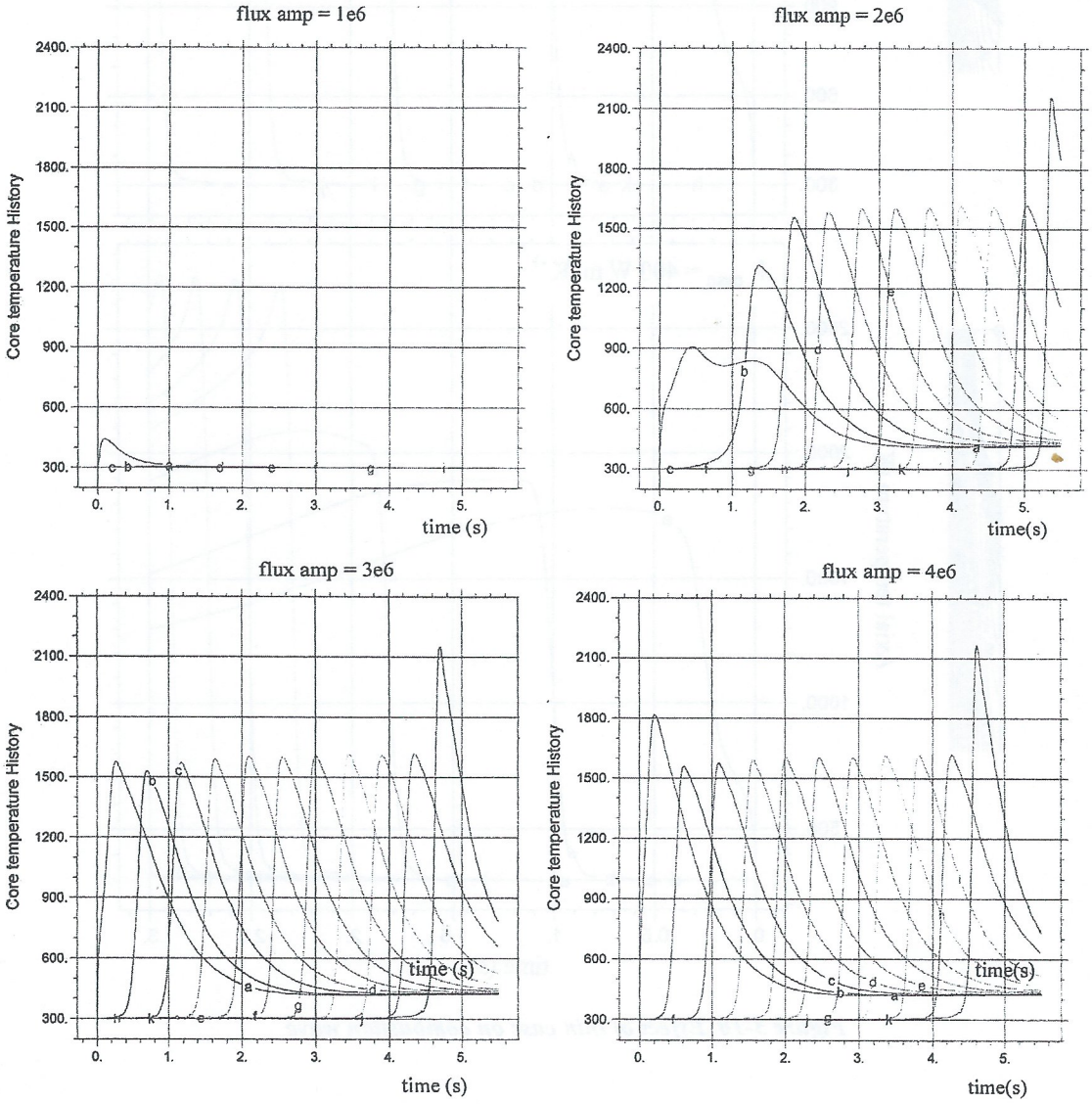


Figure 3-11 Effect of ignition pulse amplitude on combustion wave

EFFECT OF AMBIENT PRESSURE

Volatile reactants, volatile products, and involatile dispersed products remove energy from the reaction front. Involatile products which remain as slags retain heat near the reaction zone. Reactions involving volatile ingredients, or exothermically reacting intermediates occurring away from the reaction zone can add energy back into it primarily by radiation. If the combustion products are volatile then the contribution should be sensitive to the gas pressure; if the products are involatile, then the gas pressure should have relatively little effect. Reality, as usual, lies between the two extremes.

The pressure dependence of burning rate generally follows Vieille's law:

$$r = \beta p^{\alpha}$$

where r is the burning rate at pressure p, and α and β are constants for the particular system.

In general, the more gassy the system, the greater is the value of α (the greater the sensitivity to pressure). If measurements are taken over a sufficiently wide range of pressures, it may be found that the dependence is best described by two straight lines intersecting at the pressure below which conduction effects are more important than radiation. For gunpowder, $\alpha \approx 0.67$.

EFFECT OF CONSOLIDATION PRESSURE

The effect of consolidation pressure may also be marked, but is more complex. If the combustion reaction is truly solid phase (i.e., no melting in the combustion zone) then increase in consolidation should allow better contact between the reactants, and the reaction rate should increase. If the reaction is not solid phase, then the effect is less predictable. The decrease in porosity may prevent hot gas permeating the reactants and so reduce the burning rate. Possibly the energy balance between different phases may change. In most cases it is the linear burning rate (mm s^{-1}) of the composition, which is of interest to the designer, but the mass consumption rate (g s^{-1}) is also of importance because that is a measure of the power output from the device. Many compositions have a lower linear burning rate at higher compaction loads, but the mass consumption rate decreases by less, or may even increase because of the increase in density of the column.

It is unwise to attempt to predict the effect of consolidation on a new composition, because small changes in ingredients ratios, and perhaps also of particle size can change the behaviour markedly.

Figure 3-12 shows that for SR41 (B/Si/KNO_3 20/10/70) the burning rate (solid marker) and the mass consumption rate (hollow marker) decrease with increasing pressure, while for SR42 (B/Si/KNO_3 5/33/62) they both increase. Similar differences are found for B/$BaCrO_4$. For 5% boron the burning rate decreases and the mass consumption rate remains effectively constant; for 10% boron (further from stoichiometry) the mass consumption rate rises. This could be due to the greater compressibility of the 10% mix, or to a lower dependence of its burning rate on pressure.

Except for pyrotechnic delays (Chapter 3) the effect of compaction on burning rate is usually of secondary importance, and the compaction load is adjusted to give optimum mechanical properties. Attention must also be paid to the ease of ignition, which often decreases at high loads because the surface is smoother and less porous.

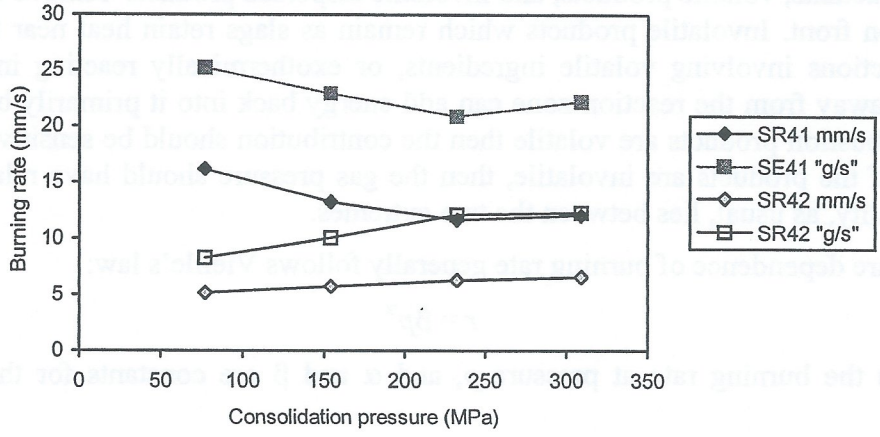


Figure 3-12 Effect of Consolidation on Two Priming Compositions

The complexity of the dependence of burning rate on consolidation pressure was noted in Chapter 2. A further example, of specific relevance to delays is given by the boron - lead monoxide system, which is used for very short delays in commercial detonators for the mining industry. At all the consolidation pressures reported (Figure 3-13) the burning rate curve peaks near 6% boron, and the reported exothermicity (not shown) peak near 10%. This is an unusual system in which the maximum burning rate seems to occur at a lower proportion of fuel than the maximum exothermicity. The simplest reaction requires 8.8% boron for stoichiometry:

$$2B + 3PbO = B_2O_3 + Pb \qquad \Delta H = -617 \text{ kJ}, \quad q = -895 \text{ kJ kg}^{-1}$$

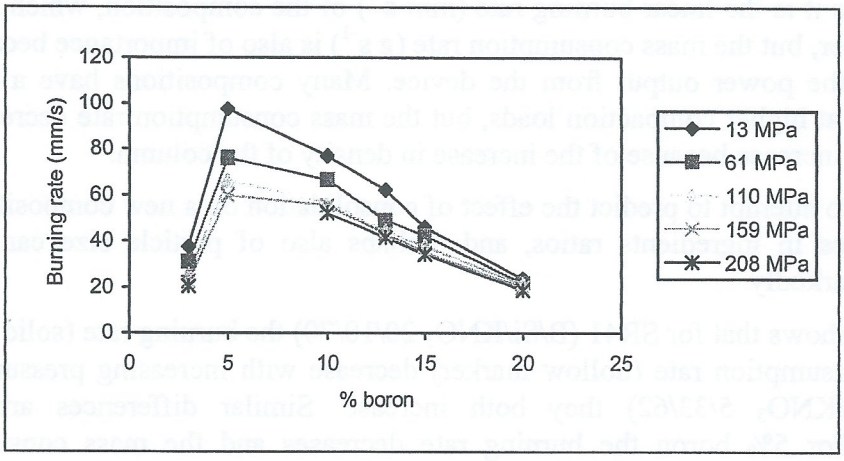


Figure 3-13 Effect of Consolidation on B – PbO [1]

The figure shows that the "stoichiometric" mixes tend to be more sensitive to compaction load than the very fuel rich or 9very oxidant rich mixtures. The reason is not at all clear.

[1] J Goodfield. Reaction energetics and mechanism in the lead monoxide-boron system. *Proc. 14th Intl. Pyro. Seminar 453 (1989)*

The designer of pyrotechnic delays must ensure that the variables of the consolidation process in manufacture do not have an unacceptable effect on the burning time of the delay, and also note that highly compressed compositions are more difficult to ignite when highly compacted than when lightly pressed.

EFFECT OF IGNITION TEMPERATURE

The ignition temperature cannot readily be predicted. For example, the effect on the measured ignition temperature of a tracer priming composition (magnesium, barium peroxide, acaroid resin) of varying the sample size and heating rate is shown in Figure 3-14 (Barton, 1982).

In simple mixtures the ignition temperature may be related to the melting point of an ingredient, or to a phase change in the oxidant, but it is often much lower than any obvious change in the ingredients. The rate at which the reaction propagates depends on the ingredients used and their particle size and shape, on the thermal properties and diameter of the column, on the thermal properties of the container, and on the temperature and ambient pressure of the column.

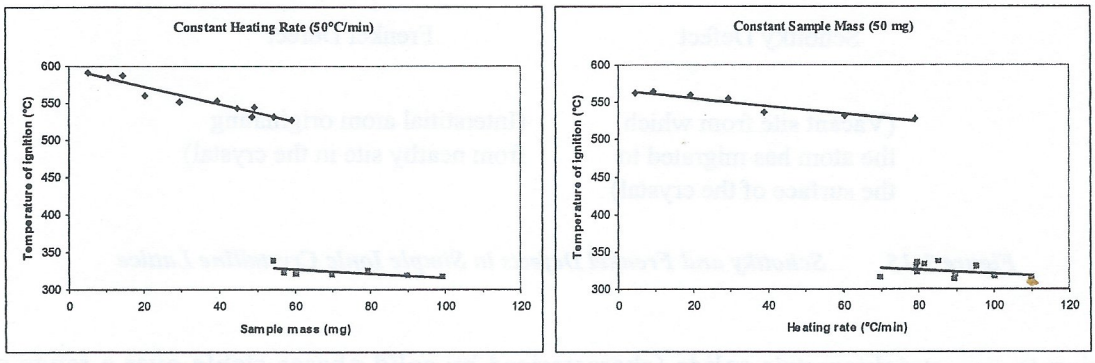


Figure 3-14 Variation of temperature of ignition with experimental conditions

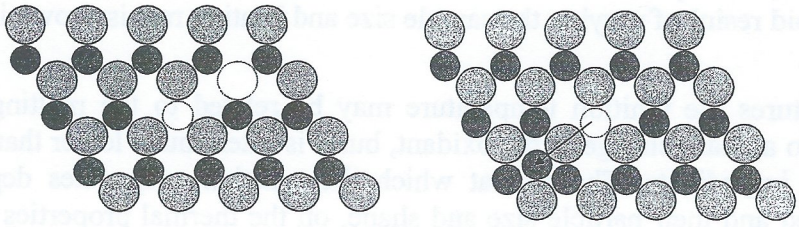
EFFECT OF INGREDIENTS

The chemical nature of the ingredients has a profound effect on the rate of propagation of a chemical reaction for many reasons. It is impossible to cover this topic in the detail necessary for a full understanding of why specific combinations of chemicals are selected for particular purposes, and there is, as yet, no satisfactory, comprehensive systematisation of the subject. However, some general principles are discussed below.

For any chemical reaction to occur between two elements or compounds it is necessary for there to be intimate contact between them or at least between one of them and decomposition products of the other. Intimacy of contact is promoted by the melting of one or more ingredients, or by permeation through the mixture of the gaseous decomposition products of one or more ingredients. However, some reactions are known to occur entirely in the solid phase, and any factor that can promote the reactivity of a solid is likely to promote the ease with which a pyrotechnic reaction can be established. In the solid phase, reactivity depends on the mobility of the ions which form the material. It has been known for many years, and has been more recently emphasised for pyrotechnic reactions by

McLain, that reactivity can be increased by the presence of defects in the solid. The subject is an extensive one but is worth exploring briefly.

Consider first *stoichiometric* crystalline solids (characterised by a solid phase which is stable over only a very narrow range of composition). At all temperatures above absolute zero (-273.2°C) atoms are in motion and it may be expected that they may become displaced from their correct (*i.e.*, minimum energy) positions in a crystal lattice. Two principle types of such defect occur in a crystalline lattice (Figure 3-15); neither of these defects leads to departure from stoichiometry.



Ionic Crystal AX

Schottky Defect	Frenkel Defect
(Vacant site from which the atom has migrated to the surface of the crystal)	(Interstitial atom originating from nearby site in the crystal)

Figure 3-15 Schottky and Frenkel Defects in Simple Ionic Crystalline Lattice

Turning to *non-stoichiometric* solids (characterised by solid phases stable over a range of compositions), it is possible to modify the reactivity by incorporating as trace impurities tiny concentrations of other atoms bearing different electrical charges from the atoms they replace in the lattice.

A simple example (Wells, p164) is that of sodium chloride (common salt) heated in an atmosphere of sodium vapour. A small amount of sodium diffuses into the lattice making the material non-stoichiometric. There is not enough chlorine to fill all the anion (negative ion) sites in the lattice (a deficit of about 1 in 10^4) which become occupied by electrons. These electrons are much more mobile than either sodium or chloride ions, and the treated material becomes a more ready conductor of electricity. This is the case for the important class of materials called *semi-conductors* which are insulators when pure, but for which the electrical properties may be profoundly modified by the incorporation of traces of impurity.

For a non-stoichiometric binary compound (consisting of two elements), there are four possible lattice defects (Figure 3-16) which are:

Type I	$MX_{1-x}(e)_x$	electron in anion vacancy
Type II	$M_{1+x}X(e)_x$	interstitial metal atom and electron in vicinity
Type III	$(+)_xM_{1-x}X$	vacant metal site and positive charge in vicinity
Type IV	$(+)_xMX_{1+x}$	interstitial anion and positive charge in vicinity

In types I and II there is a stoichiometric excess of metal due in I to an absence of some X^- ions and in II to interstitial M^+ ions; both conduct electricity by movement of electrons (*n*-type semiconductor). In types III and IV there is a stoichiometric excess of non-metal, and there is an excess of positive charge in the region of each defect (*p*-type semiconductor).

Because the probability of forming defects increases with increasing temperature, the electrical conductivity of semi-conductors *increases* with increasing temperature.

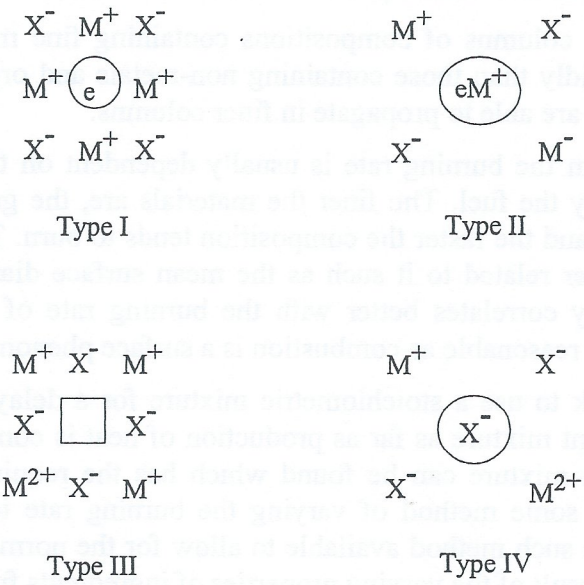


Figure 3-16 Defects in Non-Stoichiometric Binary Compounds

McLain (Chapter 3) has pursued the semi-conductor analogy to investigate the reactivity of pyrotechnic mixtures. He notes that formally oxidation is a loss of electrons, and reduction is a gain of electrons. Therefore, an oxidiser is an electron acceptor, and a reductant is an electron donor. One may therefore predict that the reactivity of an oxidiser may be increased by *p*-doping it, and that of a reductant by *n*-doping it. He quotes the reaction:

$$3NiO + 2B = B_2O_3 + 3Ni \qquad \Delta H = 523 \text{ kJ}, \quad q = 2120 \text{ kJ kg}^{-1}$$

Nickel oxide *p*-doped with lithium oxide (Li_2O) is more reactive than nickel oxide undoped or *n*-doped with chromium(III) oxide (Cr_2O_3).

While traces of impurities may be important, other chemical and physical properties usually have dominant effects.

For example, many metallic and metalloid fuels are covered with an oxide coat. The extent to which this protects the underlying material varies widely. Iron is badly protected because its common oxide (hydrated iron(III) oxide - rust) has a lower density than iron, and the layers tend to buckle and lift from the surface as they thicken. Aluminium has a particularly tenacious oxide layer that greatly reduces its reactivity. Titanium and zirconium are similar. Before combustion can take place, it is necessary to make the metal accessible by removing the oxide, or by allowing the underlying metal to diffuse through it at high temperature. Other energetic fuels such as boron and silicon burn sluggishly because the oxides that form melt at the temperature of the reaction to form viscous glasses which protect the fuel from further rapid reaction. Boron reacts to produce a polymeric

oxide and does not release the full energy expected if it formed the fully oxidised product boron(III) oxide, B_2O_3.

An effect of particular importance is that of the particle size of the ingredients, particularly the fuel. The finer the materials are, the greater the surface area available for reaction, and the faster the composition tends to burn. The specific surface of the fuel (or a parameter related to it such as the mean surface diameter obtained by the Fisher method) usually correlates better with the burning rate of the composition than mean diameter. This is reasonable as combustion is a surface phenomenon.

In general, compacted columns of compositions containing fine metal powders as fuels tend to burn more rapidly than those containing non-metals and organic fuels. They also tend to burn hotter and are able to propagate in finer columns.

In any chemical system the burning rate is usually dependent on the particle size of the ingredients, particularly the fuel. The finer the materials are, the greater the surface area available for reaction, and the faster the composition tends to burn. The specific surface of the fuel (or a parameter related to it such as the mean surface diameter obtained by the Fisher method) usually correlates better with the burning rate of the composition than mean diameter. This is reasonable as combustion is a surface phenomenon.

Ideally one would seek to use a stoichiometric mixture for a delay composition because that is the most efficient mixture as far as production of heat is concerned. However, it is unlikely that any such mixture can be found which has the required burning rate for a particular design, and some method of varying the burning rate is necessary. It is also desirable to have some such method available to allow for the normal variation in burning rate experienced as a result of the varying properties of ingredients from batch to batch.

A standard method is to add to a binary mixture a third ingredient which is either inert, or which can act as a fuel or oxidant, but which is less reactive than the other fuel or oxidant present. For example, mixtures of boron (B) and bismuth(III) oxide (Bi_2O_3) burn over a wide range of compositions, but with maximum burning rate near 10% boron (fuel rich). Mixtures of boron and chromium(III) oxide (Cr_2O_3) react exothermically, but too slowly to sustain combustion on their own.

$2B + Bi_2O_3 = B_2O_3 + 2Bi$	ΔH = -698 kJ mole-1	4.4% boron
$2B + Cr_2O_3 = B_2O_3 + 2Cr$	ΔH = -132 kJ mole-1	12.5% boron

In the ternary system, however, the more energetic reaction provides enough heat to allow the less energetic to take place as well, so both oxidants react with the boron, and a wide range of burning rates can be established over a wide range of compositions. The burning rates of a range of compositions containing 10% boron in which the bismuth(III) oxide is prpgressively replaced by chromium(III) oxide are shown in Figure 3-17.

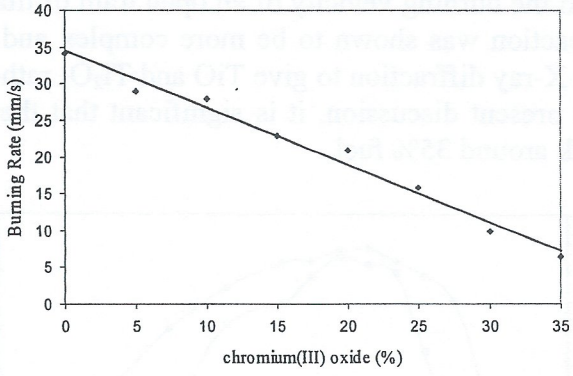


Figure 3-17 Burning rate of boron (10%) - bismuth(III) oxide - chromium(III) oxide

Another example is the use of organic fuels with the mixed oxidants potassium nitrate and barium nitrate to produce delay compositions with burning rates intermediate between those of the fuel – potassium nitrate (fast) and fuel – barium nitrate (slow).

A standard US delay composition uses nickel and zirconium as a pair of fuels to modify the burning rate. To reduce corrosion, the metals are usually added as a powdered alloy.

EFFECT OF INGREDIENTS RATIO

The variation of exothermicity with ingredients ratio has been discussed earlier. A graph of burning rate against fuel content of a binary system usually passes through a maximum, and it was first reported by Spice and Staveley (1948), and it is generally observed in consolidated systems, that the composition of maximum burning rate has more fuel than the mixture of maximum exothermicity. This is usually attributed to the fact that the thermal conductivity of the fuel is usually greater than that of the oxidant.

It is of interest to consider three systems with metal fuels which have been burned as loose, unconfined trains. Bernard (1980) measured zirconium – potassium perchlorate, Berger (2000) zirconium – manganese dioxide, and Berger (2001) titanium – manganese dioxide.

$2Zr + KClO_4 = 2ZrO_2 + KCl$ $\quad \Delta H = -2201$ kJ, $q = 6858$ J g^{-1}

Stoichiometry is at 56.8% zirconium

$Zr + MnO_2 = ZrO_2 + Mn$ $\quad \Delta H = -577.4$ kJ, $q = 3242$ J g^{-1}

Stoichiometry is at 51.2% Zr.

$Ti + MnO_2 = TiO_2 + Mn$ $\quad \Delta H = -424.7$ kJ, $q = 3151$ J g^{-1}

Stoichiometry is at 35.5% Ti.

In each case the maximum propagation rate was found near or on the fuel lean side of the composition of maximum exothermicity, which corresponded to that calculated above. In addition, Durgapal (1988) measured zirconium – potassium perchlorate as a compacted column and found that the burning rate was still increasing as the fuel content rose towards 90%.

Berger (2001) measured the burning velocity of an open train of titanium - manganese(IV) oxide. However, the reaction was shown to be more complex and the mixture with 30% titanium was shown by X-ray diffraction to give TiO and Ti_2O_3 rather than TiO_2. However, for the purpose of this present discussion, it is significant that the exothermicity and the burning rate curves peak around 35% fuel.

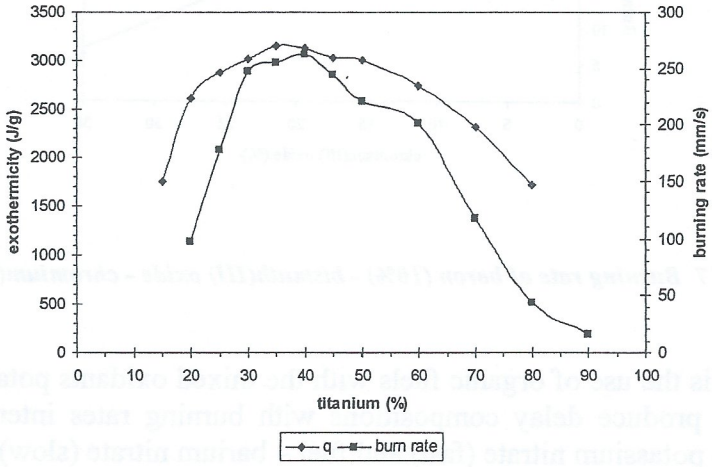


Figure 3-18: Exothermicity and burning rate of titanium – manganese dioxide

Unfortunately there seem to be no measurements published on the exothermicity and burning rate curves for fuels of low thermal conductivity such as organic compounds. The exothermicity curve has been discussed earlier, and we have the practical experience that the stoichiometric mixture is too fast burning for use in smoke compositions (see Chapter ##) and that the slower 50% mixture is used. One would expect that the burning rate curve would peak near the composition of maximum exothermicity.

Spice (1949) measured the burning rate of sulphur – barium peroxide, and Zebree (1963) measured an extraordinary number of burning rates in the system selenium – tellurium - barium peroxide (Figure 3-19 – note that the sulphur system was measured under different conditions, particle sizes are not defined, and so the absolute values of the burning rates of the three systems should not be critically compared.).

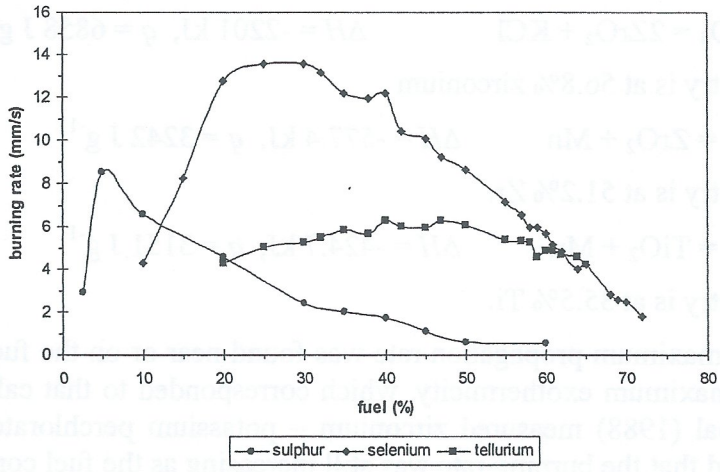


Figure 3-19: Burning rate of sulphur, selenium, tellurium with barium peroxide

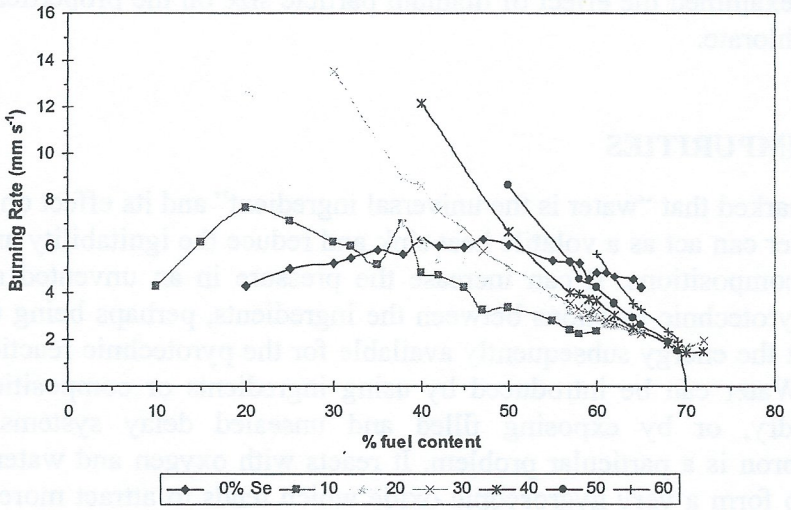


Figure 3-20: Burning rate of selenium – tellurium – barium peroxide

Writing the simplest equations:

$S + 2BaO_2 = SO_2 + 2BaO$ $\quad \Delta H = -135.3$ kJ, $q = 365$ J g^{-1}; 8.6% S

$Se + 2BaO_2 = SeO_2 + 2BaO$ $\quad \Delta H = -63.8$ kJ, $q = 152$ J g^{-1}; 18.9% Se

$Te + 2BaO_2 = TeO_2 + 2BaO$ $\quad \Delta H = -169.1$ kJ, $q = 347$ J g^{-1}; 27.3% Te

EFFECT OF INGREDIENTS SIZE AND SHAPE

The effect of the size and shape of the particle is of great importance for the practice of pyrotechnics.

Combustion occurs on the surface of particles, so the greater the specific surface (total surface area per unit mass, or per unit volume), the greater rate of mass consumption can be achieved. Further, particles that have sharp edges are more easy to ignite than those with rounded edges.

Although particle size is important in the design of pyrotechnic compositions, it is normally controlled only in a very simple way by milling and by sieving. It is general, practical experience that burning rate correlates better with a measure of specific surface (*e.g.*, Fisher mean surface diameter) than with any simple measure of actual size.

Beyens (1985) related the morphology of barium peroxide particles to the behaviour of its mixtures with magnesium as an igniter for tracers, the ingredient varying from "round and small" to "laminated and large". Practical limits were placed on the proportions of both types of particle, although the reason was not identified. Possible this is more to do with the effect of particle morphology on compaction rather than on the combustion?

Engelen (2001) examined the effect of the particle size of potassium nitrate on the combustion of a nitroguanidine – potassium nitrate composition.

Hancox (2001) examined the effect of particle size of strontium perchlorate on the burning rate of red flares.

Erickson (1989) examined the effect of particle size distribution on the ignition temperature of titanium pyrotechnics.

Berger (1996) examined the effect of titanium particle size on the properties of titanium – potassium perchlorate.

EFFECT OF IMPURITIES

It has been remarked that "water is the universal ingredient" and its effect on delays is very important. Water can act as a volatile heat sink and reduce the ignitability and the burning rate of delay compositions. It can increase the pressure in an unvented system. It can promote non-pyrotechnic reactions between the ingredients, perhaps being used up in the process, so that the energy subsequently available for the pyrotechnic reaction is less than it should be. Water can be introduced by using ingredients or compositions which are insufficiently dry, or by exposing filled and unsealed delay systems to a humid atmosphere. Boron is a particular problem. It reacts with oxygen and water (but scarcely with dry air) to form a very hygroscopic oxide which tends to attract more moisture into the system to form more oxide if air is present. The amount of free boron in the mixture therefore decreases on storage. The consequence is either a failure to ignite, or an increased delay time.

SUMMARY

The propagation of a pyrotechnic reaction is normally described in terms of layer to layer burning. The rate of propagation is difficult to calculate and depends on the chemistry, the ingredients ratio, the physical properties of the ingredients, the temperature and pressure of the system, and the geometry and thermal characteristics of the container. The exothermicity (heat generated per unit mass) of the mixture must be matched to the intended purpose. Metals are used for highest temperatures (say 2000°C and above) and gassy, organic fuels for low temperatures (say 1000°C and below).

The burning rate of a composition can be affected by the chemical and physical characteristics of the ingredients (chemical nature, particle size, particle shape, presence of impurities or defects), the ratio of the ingredients, the characteristics of the combustion products, the method of filling (compaction load), and the dimensions of the column and the ambient temperature and pressure.

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Chapter 4

INTRODUCTION TO PYROTECHNIC DESIGN

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INTRODUCTION

IGNITION TRANSFER

The correct functioning of any pyrotechnic system relies on the propagation of a combustion wave from one place to another, usually at a predefined rate. For good practical reasons more than one pyrotechnic composition is usually involved. It may be that the composition necessary to produce the special effect is difficult to ignite except by the heat generated by an adjacent pyrotechnic mixture which does not itself contribute otherwise to the effect. Some tracer compositions are not sufficiently robust mechanically to survive the conditions in the breech, but must be protected by a layer of a second composition which can do so. Sometimes it is necessary to interpose a column of a pyrotechnic mixture to produce a time delay between the initial ignition stimulus and its arrival at the payload producing the special effect. A typical pyrotechnic device may consist of several pyrotechnic compositions. The path along which the ignition stimulus travels is called the *pyrotechnic train*, or the *ignition train*, and the process by which the ignition stimulus is transferred between compositions is called *ignition transfer*.

A major part of the design of pyrotechnic munitions is to ensure an ignition transfer process robust to the design environment of the store.

Ignition transfer is a complex process involving more than one mechanism. Radiation, flame, hot burning particles, reactive particles and hot gases are usually all involved. Very seldom does ignition involve a "pure" stimulus.

It is essential that at the design stage the pyrotechnic train be considered in its entirety as a sub-system of the munition, and its interface with the complete system adequately understood. All too often the munitions designer fails to appreciate the effect that the metalwork in the system (heat sink, vent holes, varying degrees of confinement) can have on the reliability of ignition transfer.

Two examples are presented below. In each case the complete process is discussed with reference to the figure, and is summarised in the accompanying table.

Consider first the Raufoss MPI round, an HE round containing no primary explosives (Figure 4-1, Table 4-1)

The cap (not shown) in the base of the cartridge case provides a small, vigorous ignition stimulus which ignites a small primer which pressurises the cartridge case and ignites the propellant. The heat, flame and burning particles of the propellant ignite the priming of the tracer at the same time that the increasing pressure is accelerating the round up the barrel. The mechanical properties of the pressed priming (a low gas composition) are such that it neither cracks nor erodes under the conditions in the breech. The priming is alight and burning when the round leaves the barrel and the ambient pressure drops rapidly to somewhat below atmospheric. The priming continues to burn until the combustion zone reaches the interface with the main trace composition which then ignites under conditions of high spin, but of reasonably constant pressure. The tracer burns, emitting a red light, until either the round impacts a target and is destroyed, or until the tracer is nearly burned out.

If the shell hits a target within the expected time, the round functions from the fuze. This impact fuze is unusual in that it contains no primary explosive, and relies on the ignition by the impact of the pyrotechnic composition in it to start a combustion chain which leads through the ignition of the incendiary composition to the subsequent ignition of the HE which burns to detonation.

If the shell does not encounter a target the tracer burns until the heat transmitted from its combustion through the base of the shell ignites the destructor which contains a pressed explosive composition in contact with the main HE filling of the shell. This ignites the filling which burns to detonation

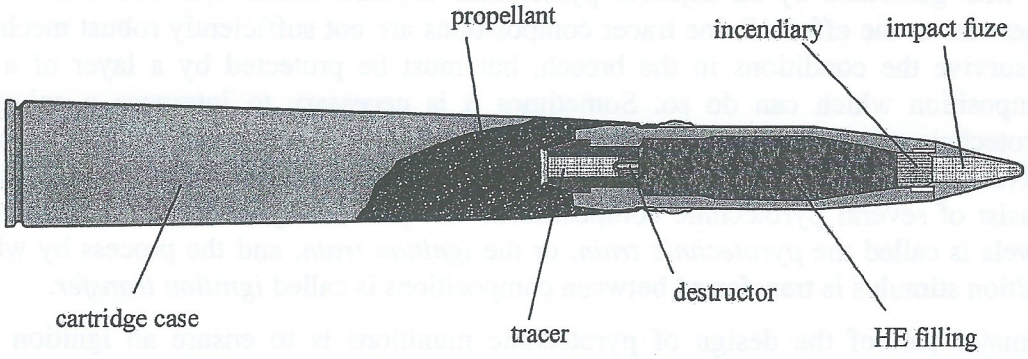


Figure 4-1 Raufoss 40mm Round

Component	Function
cap	converts electrical or percussion energy to flash output to ignite gun primer.
gun primer	pressurises cartridge case and ignites propellant.
propellant	accelerates shell; flame, burning particles and hot gases ignite tracer priming.
tracer priming composition	survives pressure and erosion in breech, continues burning through pressure drop to sub-atmospheric on muzzle exit, ignites main trace composition.
main trace composition	burns at high spin rate at adequate intensity for adequate time; ignites destructor.
destructor	generates enough heat to cause HE filling to explode if no target has been encountered.
impact fuze	pyrotechnic composition burns rapidly on impact with solid target, ignites incendiary charge.
incendiary composition	burns fiercely to provide incendiary effect and also ignite HE charge.
HE	ignites either from destructor or from front end incendiary charge, and explodes.

Table 4-1 Ignition Train in Medium Calibre Tracer Round

Consider second a simple hand thrown smoke grenade (Figure 4-2, Table 4-2). This is a cheap device ignited by a percussion cap which ignites a pyrotechnic delay. This delay is important because it ensures that no smoke is generated near the user (particularly useful if the smoke contains CS), but also prevents any smoke trail which could indicate the position of the thrower. The smoke composition itself would ignite unreliably from the brief and rather weak output from the delay, so primed cambric is used which readily ignites, and burns vigorously for sufficiently long to provide good ignition transfer to it. The pressure drop on venting is not great, but must be considered in the design and reduced to the lowest level compatible with good sealing of the grenade. The equilibrium pressure inside the grenade during burning must not be so high that the grenade can move on the ground under the force of the escaping combustion products.

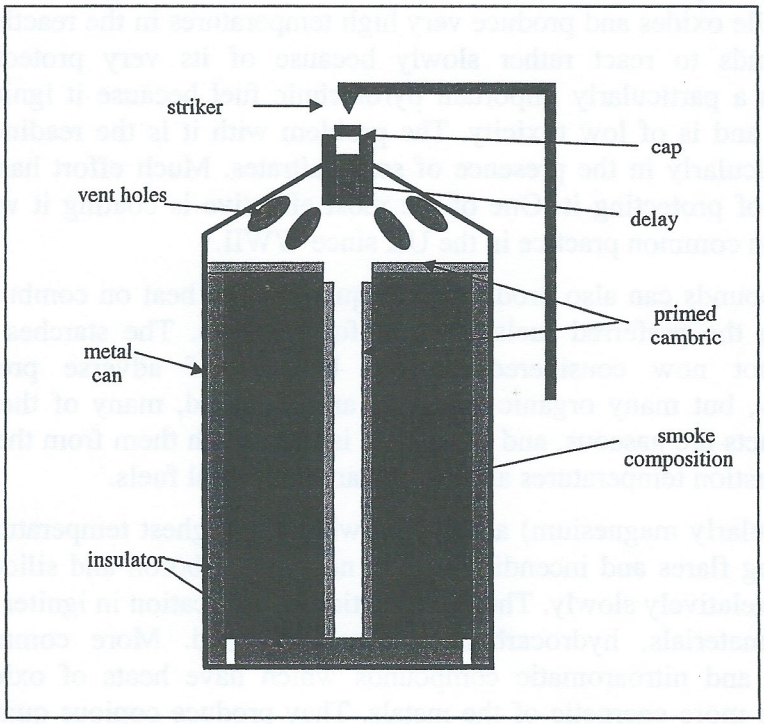


Figure 4-2 Hand Thrown Smoke Grenade

Component	Function
cap	convert percussion energy to flash output to ignite delay.
pyrotechnic delay	burn at design rate, survive impact of grenade with ground, ignite primed cambric.
primed cambric	pressurise grenade, ignite smoke composition, blow clear vent holes.
smoke composition	burn at design rate without extinction or flaming.

Table 4-2 Ignition Train in Hand Thrown Smoke Grenade

SELECTION OF INGREDIENTS

A useful way of comparing potential fuels is the examination of their heats of combustion in oxygen. Because space is usually limited in a pyrotechnic device, the heat per unit mass, or the heat per unit volume are useful parameters.

Some elements of interest because of their good heats of oxidation must be excluded for other reasons. Beryllium is too toxic, and lithium is too reactive to be of practical interest. Boron does not react immediately to B_2O_3 but initially forms less stable, glassy lower oxides and the heat in the reaction zone is less than the table above indicates. It provides, nevertheless, plenty of heat and is widely used. Aluminium, magnesium and titanium form stable, involatile oxides and produce very high temperatures in the reaction zone, although aluminium tends to react rather slowly because of its very protective oxide layer. Magnesium is a particularly important pyrotechnic fuel because it ignites readily, burns energetically, and is of low toxicity. The problem with it is the readiness with which it corrodes, particularly in the presence of some nitrates. Much effort has been devoted to finding ways of protecting it. One of the most effective is coating it with acaroid resin, which has been common practice in the UK since WWII.

Organic compounds can also produce large quantities of heat on combustion, and natural products were the preferred fuels in older formulations. The starches and sugars used earlier are not now considered suitable because of adverse properties such as hygroscopicity, but many organic materials are still used, many of them synthetic. The reaction products are gaseous, and much heat is taken with them from the reaction zone so that the combustion temperatures are lower than with metal fuels.

Metals (particularly magnesium) are chosen when the highest temperatures are required - for illuminating flares and incendiaries. The non-metals boron and silicon produce much heat but react relatively slowly. They find particular application in igniter compositions. Of the organic materials, hydrocarbons are seldom used. More commonly found are carbohydrates and nitroaromatic compounds which have heats of oxidation noticeably lower than the more energetic of the metals. They produce copious quantities of gas and have relatively low combustion temperatures. They are used particularly in smoke compositions where high temperature is not desirable, and in slow burning delays.

Generally speaking, the oxidant must decompose before the oxygen becomes available for reaction. The approximate decomposition temperatures and heats of decomposition of some common oxidants are given in Annex A. However, the exact route of decomposition can vary with the reaction conditions, so these figures are only indicative.

Most oxidants decompose endothermically (with the absorption of heat) and this heat is abstracted from the reaction zone and moderates the reaction. Note, however, that *chlorates*, and to a lesser extent *perchlorates*, decompose exothermically - the very act of decomposition pumps heat into the reaction zone. The heat of decomposition also increases with increasing temperature. This is one reason why chlorates are so particularly dangerous in pyrotechnic mixtures, and why an ignition of compositions containing them leads easily to a particularly violent event. Note that sodium chlorate (seldom used because of its hygroscopicity) has a higher heat of decomposition than potassium chlorate, and is likely to be more hazardous.

It should be remembered that even metal oxides which are not usually considered as oxidising agents can act as a source of oxygen to fuels with higher heats of oxidation, particularly at high temperatures.

SUMMARY

The propagation of a pyrotechnic reaction is normally described in terms of layer to layer burning. The rate of propagation is difficult to calculate and depends on the chemistry, the ingredients ratio, the physical properties of the ingredients, the temperature and pressure of the system, and the geometry and thermal characteristics of the container. The exothermicity (heat generated per unit mass) of the mixture must be matched to the intended purpose. Metals are used for highest temperatures (say 2000°C and above) and gassy, organic fuels for low temperatures (say 1000°C and below).

The burning rate of a composition can be affected by the chemical and physical characteristics of the ingredients (chemical nature, particle size, particle shape, presence of impurities or defects), the ratio of the ingredients, the characteristics of the combustion products, the method of filling (compaction load), and the dimensions of the column and the ambient temperature and pressure.

LIGHT AND IR EMITTING MUNITIONS

ILLUMINATING AND MARKER ROUNDS

An example of an illuminating artillery shell is shown in Figure 4-3. The illuminating assembly consists of a pressed flare candle (magnesium, sodium nitrate, binder) suitably primed and fastened by a metal strip to the parachute. The fuze is set to function at a particular time, it flashes onto a burster charge which pressurises the inside of the shell sufficiently to shear the pins at the back end of the round, and also ignites the priming on the flare candle. The payload is ejected parachute first and the flare burns suspended beneath it as it drifts downwards.

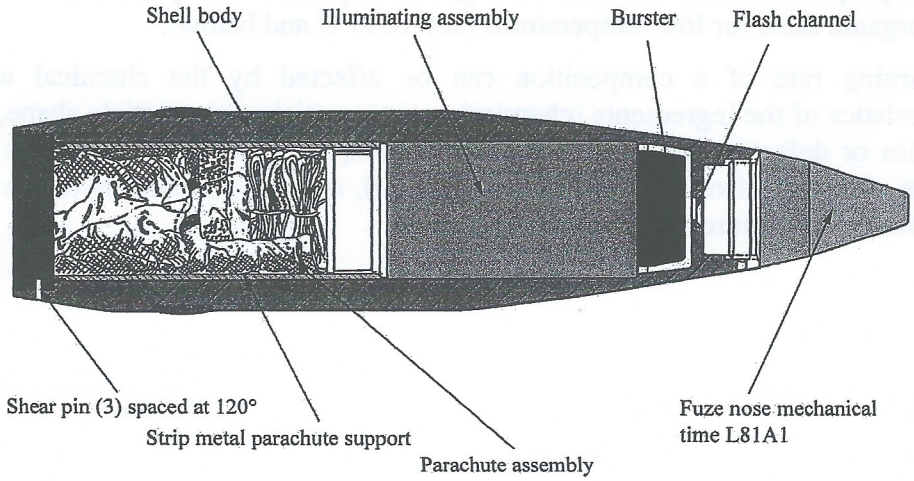


Figure 4-3 : 105mm L43A1 Fd Illuminating Shell

The ignition train must survive the rapid ignition followed by depressurisation and passage into a very fast wind stream. The flare burns subsequently in relatively slow air.

Another example is the illuminating round for the 51 mm mortar (Figure 4-4). Here the ignition train and the deployment sequence are more complex because of the overall engineering constraints of the system. There is no nose fuze, and the ignition stimulus comes ultimately from the combustion of the propellant charge. The shape of the bomb requires that the payload be ejected from the nose, while the aerodynamic requirement is for the illuminating candle to be positioned at the rear. The payload therefore ejects forward, parachute first, and the sub-system must swing around in free flight without getting entangled.

The ignition transfer sequence in one version of the bomb is : the output from the propulsion cartridge ignites the priming of a slow (organic fuel) delay which burns during the flight of the bomb. This ignites in turn an output composition which spits onto the pressed SR43 (boron / potassium nitrate) igniter composition pellet which ignites the sheets of SRE794 elastic priming. This burns vigorously, ignites the end of the SRE798 candle and internally pressurises the bomb sufficiently to force the crimped front end off the body. The parachute deploys, drags the payload out of the container, and it burns from the top down suspended from the parachute by a chain attached to the central steel tube which passes through the candle.

The conical shape of the body makes it impossible to press the flare as a conventional pellet, and the flare composition is a curable, tamp consolidated composition, This limits the achievable intensity because a high proportion of binder is necessary to give the required rheological properties, but this is adequate for the relatively low deployment height of the bomb.

In the more recent version of the design, ignition is transferred from the back to front by means of a length of fastcord, the forward end of which is sandwiched between the flare candle and the disc of priming composition.

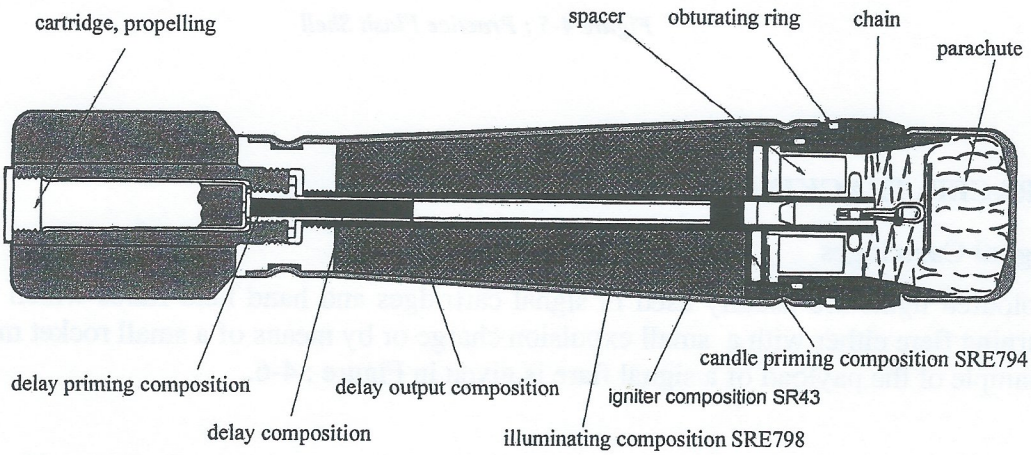


Figure 4-4 : 51mm Illuminating Bomb

In any flare it is essential that the mechanical properties of the payload are adequate to survive launch. In the cases described above the candles ignite under confinement, and a cracked payload would generate a much greater rate of pressure rise than an uncracked one with the possibility of a violent burst, or even an explosion. The composition must also be capable of burning without ejecting fragments.

Practice Flash Shell

It is a common requirement to provide a visual signature for the observation of the fall of an inert practice round. One solution is to include at the nose of the shell a pellet of high explosive (usually PETN) mixed with a dye to provide a readily observed puff of smoke, and perhaps a persistent stain on the ground.

A more convenient device is the flash indicator which is simply a container of a vigorous, high temperature composition (magnesium and potassium nitrate, for example) initiated as the shell impacts. In the designs shown, the initiating device is essentially a base mounted, quick acting fuze. To produce the necessary intensity from a small device the composition is filled as a loose powder which burns very rapidly producing a short, brilliant flash. Two examples are shown in Figure 4-5.

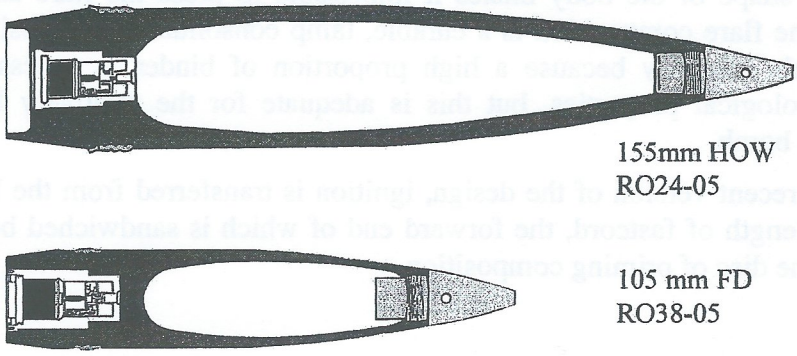


Figure 4-5 : Practice Flash Shell

TRACER, TRACKING AND SIGNAL FLARES

Signal Cartridges

Coloured lights are usually used in signal cartridges and hand held flares which propel a burning flare either with a small expulsion charge or by means of a small rocket motor. An example of the payload of a signal flare is given in Figure : 4-6.

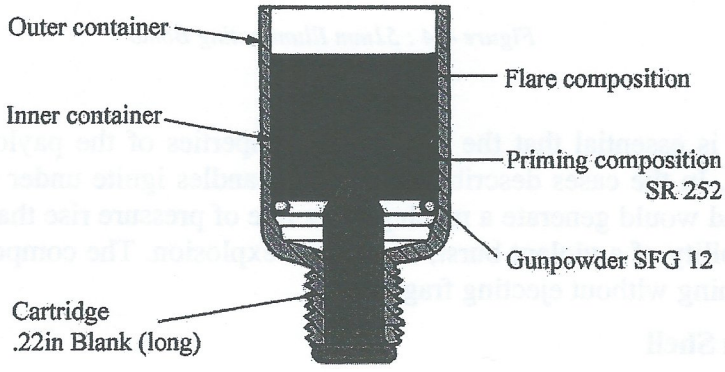


Figure : 4-6 Signal Cartridge 16mm Mk 3

A mechanical striker ignites the blank cartridge which ignites in turn a layer of gunpowder pressed as the outer increment onto the payload. This expels the pellet at sufficient velocity to achieve the required altitude and transfers ignition to the next stage, a pressed layer of SR252 (potassium nitrate, charcoal and silicon) which burns more slowly than gunpowder, and in which the hot, slowly burning silicon is an excellent medium for ignition transfer. The ignition front reaches the flare composition during flight so that the light is emitted in the upper reaches of the trajectory where it is most readily observed. In some designs the flare pellet is coated with a priming as a lacquer.

A hand-held, rocket-launched, parachute flare is shown in Figure 4-7. Here, the output from the rocket motor ignites the gunpowder charge which removes the rocket case and ignites the flare. Internal details of a hand-held rocket flare are shown in Figure 4-8. The sand provides the necessary ballast without increasing the explosive content of the device.

It is usually required, for any of these devices, that full intensity is achieved near apogee, and that the candle burns to extinction before returning to the ground.

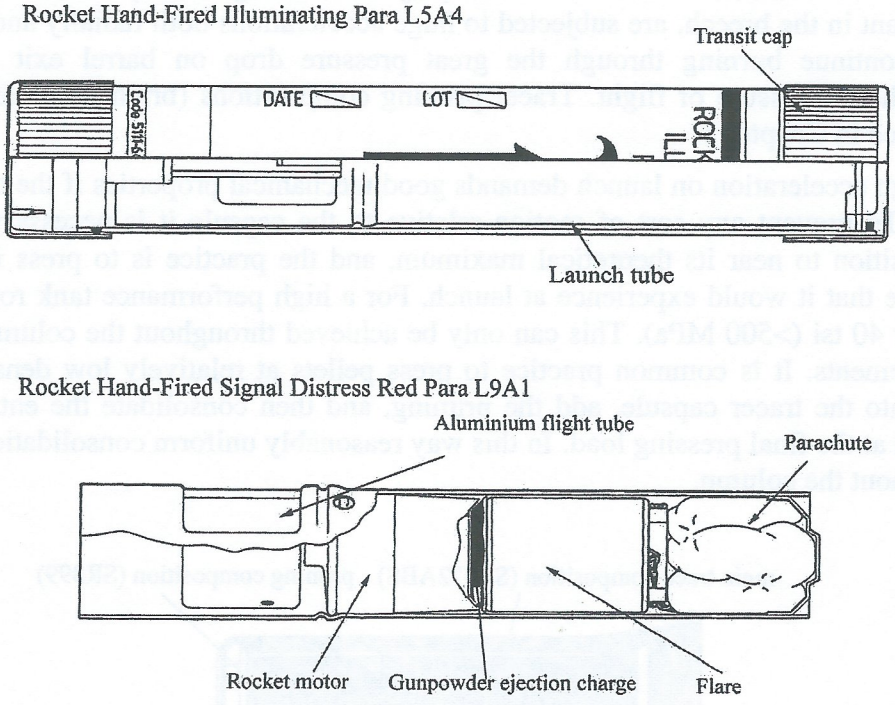


Figure 4-7 Rocket Hand-Fired Flares

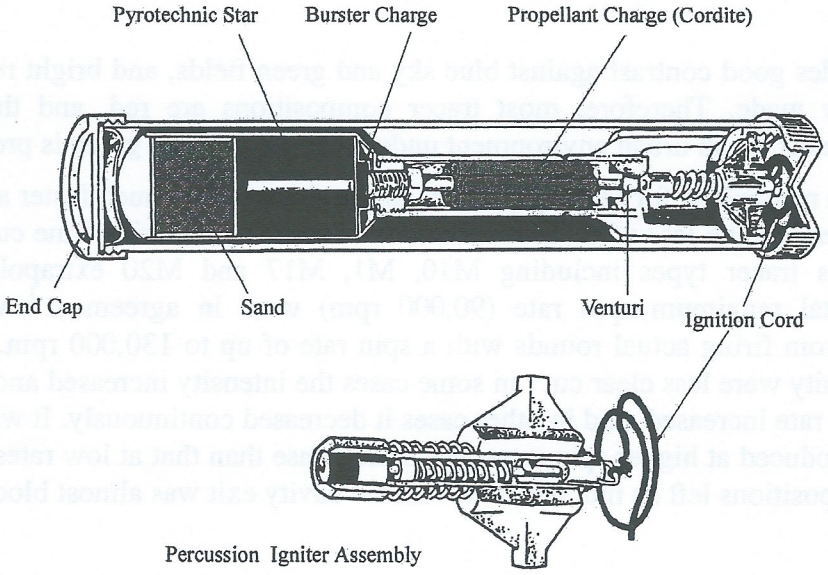


Figure 4-8 Rocket Hand-Fired Flare

Tracer

The requirement is to produce a small flare which can operate in a very severe environment and be visible at distances of perhaps miles, day or night. Tracer are required for projectiles of all calibres from small arms ammunition (say, 5.56 mm) to 120 mm antitank rounds. They are all mounted in the rear of the projectile, are ignited by the combustion of the propellant in the breech, are subjected to huge accelerations both radially and linearly, and must continue burning through the great pressure drop on barrel exit and the sub-atmospheric pressure of flight. Tracer priming compositions (bright and dark) have been discussed in Chapter 5.

The high acceleration on launch demands good mechanical properties if the tracer is not to crack. To prevent any sort of motion relative to the capsule it is necessary to press the composition to near its theoretical maximum, and the practice is to press it at the same pressure that it would experience at launch. For a high performance tank round, this may be over 40 tsi (>500 MPa). This can only be achieved throughout the column by pressing in increments. It is common practice to press pellets at relatively low density, assemble them into the tracer capsule, add the priming, and then consolidate the entire assembled column at the final pressing load. In this way reasonably uniform consolidation is achieved throughout the column.

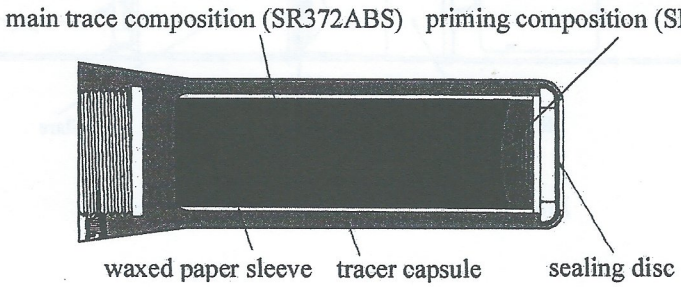


Figure 4-9 *Typical Tank Ammunition Tracer*

Red provides good contrast against blue sky and green fields, and bright red compositions are readily made. Therefore, most tracer compositions are red, and therefore contain strontium salts. In an urban environment under sodium lighting, green is preferable.

It has been recognised for many years that compositions burn much faster and that the light intensity tends to be less when spun than when stationary. Burning time curves for several small arms tracer types including M10, M1, M17 and M20 extrapolated above the experimental maximum spin rate (90,000 rpm) were in agreement [1] with the results obtained from firing actual rounds with a spin rate of up to 130,000 rpm. The results for light intensity were less clear cut : in some cases the intensity increased and then decreased as the spin rate increased, and in other cases it decreased continuously. It was observed that the slag produced at higher spin rates was more dense than that at low rates, and noted that some compositions left so much residue that the cavity exit was almost blocked.

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[1] R S Shulman. Factors affecting small arms tracer burning. *Frankford Arsenal Report FA-R-1287 (1955)*

Puchalski[2] investigated the performance of three binary mixtures (fuel lean, stoichiometric and fuel rich) of magnesium and strontium nitrate. He found that the burning rate and the luminosity increased with increasing spin rate, and that mixtures with more magnesium burned faster and had greater luminosity. He postulated that the hot slag centrifuged to the periphery of the cavity and conducted more heat into the edge of the pellet than down the centre, and that the burning surface therefore became convex to the combustion products, and the enlarged surface allowed a greater rate of combustion. Radiographs of spinning tracer (RARDE) have confirmed that postulate [3]. The intensity of the trace therefore depends not only on the burning rate, but on the aperture available through the slag to the burning surface.

Largely because of the effect of spin on burning rate, different compositions are required for small arms and tank ammunition. Two typical formulations are given in Table 4-3.

	Small Arms	Tank	Purpose
magnesium	28.6	38.0	fuel
strontium nitrate	50.4	42.8	oxidant
strontium peroxide	4.8		oxidant
beeswax		4.8	binder
boiled linseed oil	11.4		magnesium coating, binder
chlorinated rubber		4.8	light enhancer (chlorine carrier)
talc	4.8		flow agent, bulk density controller
shellac		4.8	magnesium coating
magnesium carbonate		4.8	anti-caking agent

Table 4-3 Typical Tracer Compositions

Tracking flares are often included in the base of a guided missile to allow tracking either by eye or electronically. A basic requirement is for a composition which burns with sufficient intensity for a sufficient duration under conditions of near zero spin. Some trackers use the specific emission from potassium which peaks in the near infrared (see **Error! Reference source not found.**)

INFRARED DECOYS AND "BLACK ILLUMINANTS"

Infrared flares for the protection of aircraft against heat seeking missiles are standardised on the available flare dispensers. The most common sizes are $1'' \times 1'' \times 1''$ (a "118" flare), and $1'' \times 2'' \times 8''$ (a "218" flare), although some are cylindrical. A 218 flare, burning for about 4 seconds, radiates at some 500 kW, a useful portion of it in the missile seeker bands.

A standard configuration (the US MJU-8/B, outer dimensions 36 mm diameter by 127 mm length) is shown in Figure 4-10.

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[2] W J Puchalski. The effect of angular velocity and composition on pyrotechnic performance. *Frankford Arsenal Report AD/A-003 246 (1974)*

[3] T J Barton and M J Bibby. Studies of factors affecting tracer performance. *Proc. 7th Intl. Pyro. Seminar, Vail, Colorado, USA 51 - 63 (1980)*

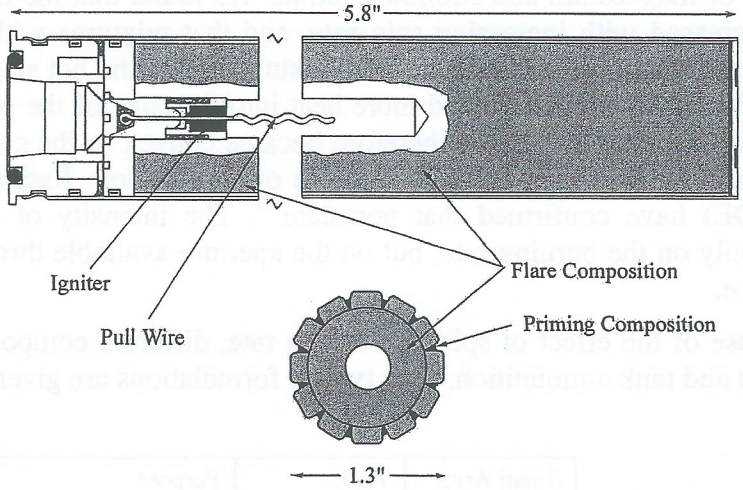


Figure 4-10 : MJU-8/B Decoy Flare

The flare is housed in a light aluminium case furnished with an electrical igniter and an expulsion charge. On ejection from the dispenser the captive pull wire (coated with red phosphorus in a varnish) is drawn through an ignition composition (lead dioxide, boron, binder) which ignites the priming composition (potassium perchlorate, charcoal, dextrin, binder) on the flare (magnesium, PTFE, Viton). The flare priming composition has better flame spreading properties than the flare composition, and is pasted into longitudinal grooves on the surface of the flare. The number of grooves and their geometry are very important because they control the rate at which the flame spreads over the surface, and therefore the rise time of the infrared radiation.

Although the case is light, it must be robust enough to keep the flare intact during ejection into a high speed wind stream and the ignition process. If the flare becomes detached to early from the igniter, ignition will not be established, or at best a delay may be introduced so that the flare rises to decoy intensity too far from the aircraft.

DESIGN OF SMOKE MUNITIONS

SMOKE POTS

These munitions are intended to provide screens of relatively long duration with a relatively slow build up of effective smoke. They are usually placed by hand, and are not in general required to survive severe mechanical shocks. Most tactical smoke pots contain HC mixtures, but for training purposes low toxic sublimation smokes based on cinnamic acid or terephthalic acid are used. The devices are essentially metal cans into which the pelleted composition is inserted. A typical example is shown in Figure 4-11. The generator shown is 200 mm in diameter and 300 mm high.

All such smoke generators are electrically ignited, and the match usually spits onto a sheet of primed cambric or some similar material. The smoke effuses through a perforated disk and baffle plate which aids in smooth generation and hides any flame. The cardboard liner is important to prevent the metal container from overheating to the extent that it may become a fire hazard, or even melt.

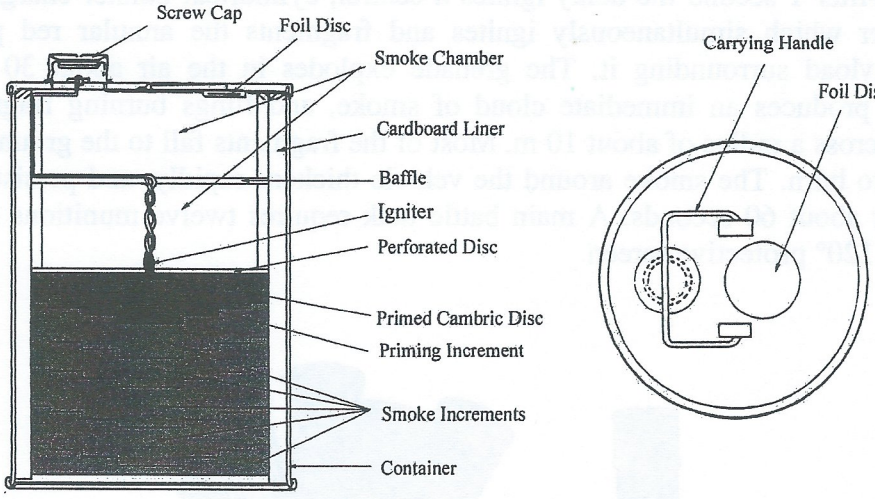


Figure 4-11 : Typical Smoke Generator

AFV SCREENING GRENADES

The classic AFV screening grenade is the British 66 mm L8 used in one form or another around the world. Its purpose is to provide the vehicle commander, on manual command, with a visual screen of approximately 60 second duration across an arc of 120° (Figure 4-12). This allows for some unobserved manoeuvre or disembarkation, and is effective against man-in-the-loop attack. Within these limitations, it functions well and reliably.

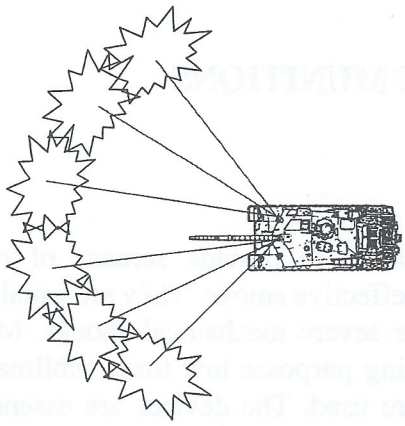


Figure 4-12 : Deployment of Smoke from a Vehicle

The external appearance of the grenade and one of the several launchers are shown in Figure 4-13. The design is simple, as is essential for a system required to be cheap.

A cross-section of the grenade is shown in Figure 4-14. An electric fuzehead in the base of the munition ignites a gunpowder charge which simultaneously ejects the grenade from the launcher at about 30 m s^{-1} and ignites a pressed gunpowder delay in the base of the grenade. After 1 second the delay ignites a central, cylindrical burster charge of granular gunpowder which simultaneously ignites and fragments the annular red phosphorus / binder payload surrounding it. The grenade explodes in the air about 30 m from the launcher, produces an immediate cloud of smoke, and flings burning fragments of the payload across a radius of about 10 m. Most of the fragments fall to the ground where they continue to burn. The smoke around the vehicle thickens rapidly, and persists as a visual screen for about 60 seconds. A main battle tank requires twelve munitions in a salvo to provide a 120° protective screen.



Figure 4-13 : L8 Grenade and Discharger

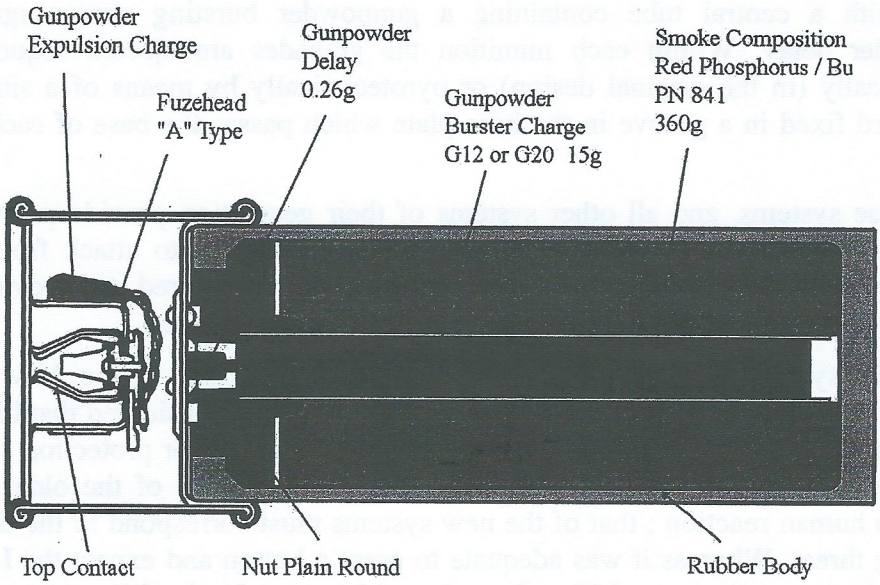


Figure 4-14 : L8 AFV Screening Grenade

Gunpowder is the preferred propellant for the L8 grenade because it is more effective than other propellants in a short barrelled, poorly obturated system such as the L8 in its launcher. It is a dirty propellant, however, and it is necessary to clean the discharger regularly.

The limitations of the L8 (and other similar grenades containing only phosphorus and binder) are :

- effective only in the visual (there are indications that an infrared screen persists for perhaps a second after the burst due to the initial radiation and to the initial high intensity of smoke along the direct line of sight) ;
- as long as the vehicle remains within the screen the commander is more blind than the hostile observer with the naked eye ;
- the smoke is anchored to the ground, and the vehicle is at the mercy of adverse winds : it cannot move against the wind without exposing itself ;
- the phosphorus grenade is incendiary : it has a large safety trace in the presence of infantry.

The system which first successfully provided an AFV with a good infrared screen was the Vehicle Infra-Red Screening Smoke (VIRSS) System invented by CDE Porton, and developed by Royal Ordnance. The concept is simple and ingenious. Instead of the single salvo of twelve large L8 grenades, twenty successive salvoes are fired at 1½ second intervals of eight or twelve small grenades containing red phosphorus payloads designed to burn entirely in the air. This constant replenishment achieves three things. Firstly, the concentration of smoke on the required line of sight is maintained at a high level ; secondly, the cloud remains warm ; thirdly, the position of the screen is less affected by wind, and can move with the vehicle. The result of high concentration and emission is to produce a very effective reduction of target contrast to an observer with a sophisticated thermal imager.

The VIRSS system consists of a set (usually eight) of munitions each containing twenty sub-munitions arranged like milk bottles in a crate. Each sub-munition consists of a plastic

bottle with a central tube containing a gunpowder bursting charge ignited from a gunpowder delay. Within each munition the grenades are ejected sequentially either electronically (in the original design) or pyrotechnically by means of a single length of delay cord fixed in a groove in the base plate which passes the base of each munition in turn.

Both these systems, and all other systems of their generation provide protection against near horizontal attack, but can leave the vehicle vulnerable to attack from above. The VIRSS-type regenerative system could readily be configured to provide additional protection, whereas a single shot device such as the L8 could not.

The earlier systems were conceived at a time when protection of the AFV relied on the firm thumb of the commander on the firing button when he considered that his vehicle was under threat. More recently, requirements are being finalised for protection systems which react autonomously to an incoming threat. The reaction time of the older systems was geared to human reaction ; that of the new systems must correspond to the timeline of the incoming threat. Whereas it was adequate to press a button and expect the L8 to function 1 second later at a distance of 30 m from the vehicle, and for the full screen to be available perhaps a few seconds later, the new requirements are more likely to require full screen in less than a second from launch at, say, 50+ metres from the vehicle. Also, as the system is launched to counter a specific incoming threat, it is desirable that the screen clear as soon as that threat has been countered, so a duration of several seconds rather than a minute is more likely.

All new systems are required to screen in the infrared as well as in the visible, and the addition of a millimetric capability to defeat surveillance and targeting radar is most desirable. No single payload can provide all this protection and multiple payloads are provided, with an unavoidable increase in required volume. A typical grenade might contain a red phosphorus payload to cover the visible and the infrared, a metal flake payload to increase the infrared effectiveness, and a chaff payload to cover the millimetric region. No material capable of broad band cover is in sight.

The performance requirements typical of a modern infrared screening grenade are outlined in Table 4-4.

Certain metal powders are effective obscurants in the infrared if dispersed as fine flake, although the visual effectiveness is low, and screening grenades using brass are in service. Such powders cannot be generated pyrotechnically, and payloads of particles of suitable size are dispersed explosively or pyrotechnically from L8-like grenades. Problems include the toxicity and adverse environmental impact of brass, its tendency to contaminate optical surfaces of the platform, and the severe wind dependence of the size and position of the cloud.

Atmospheric Conditions	
Cross wind speed	3 m s^{-1} – 8 m s^{-1}
Relative Humidity	50% - 80%
Position of sun	above or behind observer
Atmospheric visual range	> 10 km
Pasquill stability categories	A - D
Geometric	
Horizontal angular coverage	110°
Projection distance from vehicle	25 m minimum
Cloud height above ground level	8 m essential 10 m desirable
Temporal	
Time to effective screen	3 s essential 2 s desirable
Obscuration times	
Visual (0.4 – 0.7 μm)	30 s essential 45 s desirable
Infrared (0.7 – 14.0 μm)	20 s essential 30 s desirable
Critical window time	1 s

Table 4-4 : Obscurant Screen Characteristics

TUBE-LAUNCHED SMOKE ROUNDS

Mortar Ammunition

The 81mm smoke bomb currently in service with the British Army is essentially an HE bomb body filled with white phosphorus and fitted with a simple exploder to act as a bursting charge (Figure 4-15). It is filled through the base by pouring in molten white phosphorus (melting point 44°C) under water. On functioning, the bomb body splits and the molten phosphorus is sprayed over a large area and burns spontaneously in the air. The time to effective screen is short, and the duration of smoke is about 1 minute, but pillaring of the smoke due to convection currents can be severe. Such a design is very volume efficient because all the payload volume can be used for smoke composition with minimal parasitic hardware.

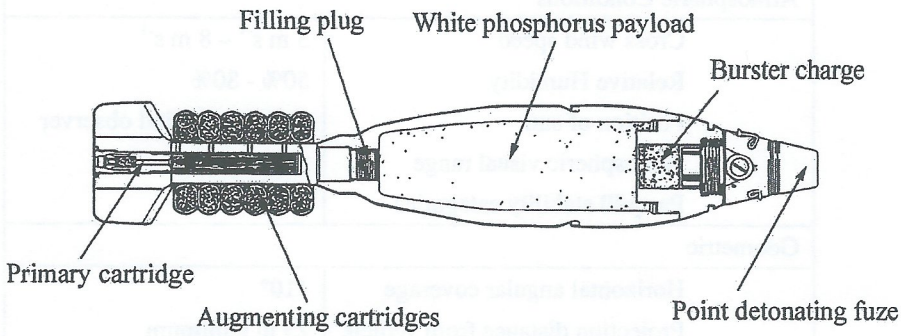


Figure 4-15 : 81 mm White Phosphorus Smoke Bomb L42

The white phosphorus round is not, strictly, a pyrotechnic device because there is no ignition transfer chain in the system.

Perhaps the simplest pyrotechnic design is that of the 51mm smoke bomb shown in Figure 4-16. The primary cartridge flashes through a narrow channel in the tail and ignites a pyrotechnic delay which in turn ignites discs of igniting composition in contact with the base of the smoke composition. The smoke composition burns, and the smoke is emitted through the hole left by the burnt out delay and through the vent holes in the tail.

Because the shape of the bomb does not allow the use of a conventional pressed pellet, the candle is filled by tamping the composition into place. PN 800 does not burn reliably as a loose pellet, but it burns readily inside a container such as the bomb case after impact with the ground.

The pyrotechnic delay prevents the production of a smoke trail in the sky which would help to pinpoint the firing position. The first observable smoke is produced about 4 s after launch when the igniting composition functions. Smoke is produced for approximately 1½ minutes.

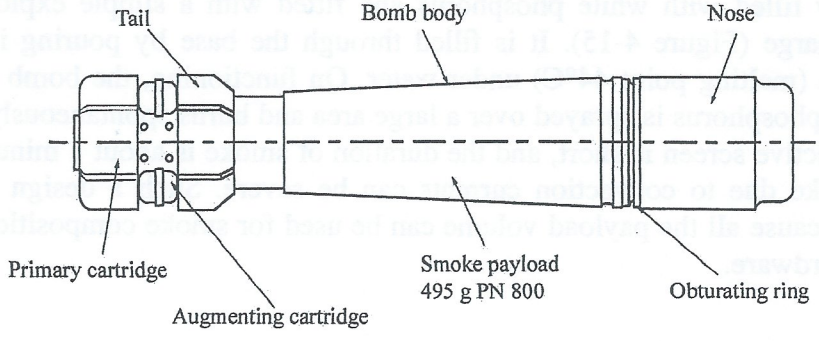


Figure 4-16 : 51 mm Smoke Bomb L15 Mk A1

More modern smoke rounds contain compositions based on red phosphorus. A typical design for an 81 mm mortar bomb is shown in Figure 4-17. The payload consists of layers of pressed pellets which are assembled three to a layer with a central cylindrical hole along the entire length of the payload. On functioning, a propellant charge in the nose of the bomb ignites the pellets, pressurises the bomb to rupture the pins, and ejects the pellets which fall burning to the ground. It is of course necessary to use a parallel sided bomb.

The use of pellets allows a rapid production of useful smoke because the surface area available for combustion is large. To ensure that the payload survives launch without crushing (which might cause premature ignition) the pellets are manufactured by pressing at a load approximating to that which they would experience on launch corresponding to an acceleration of some 10,000 g.

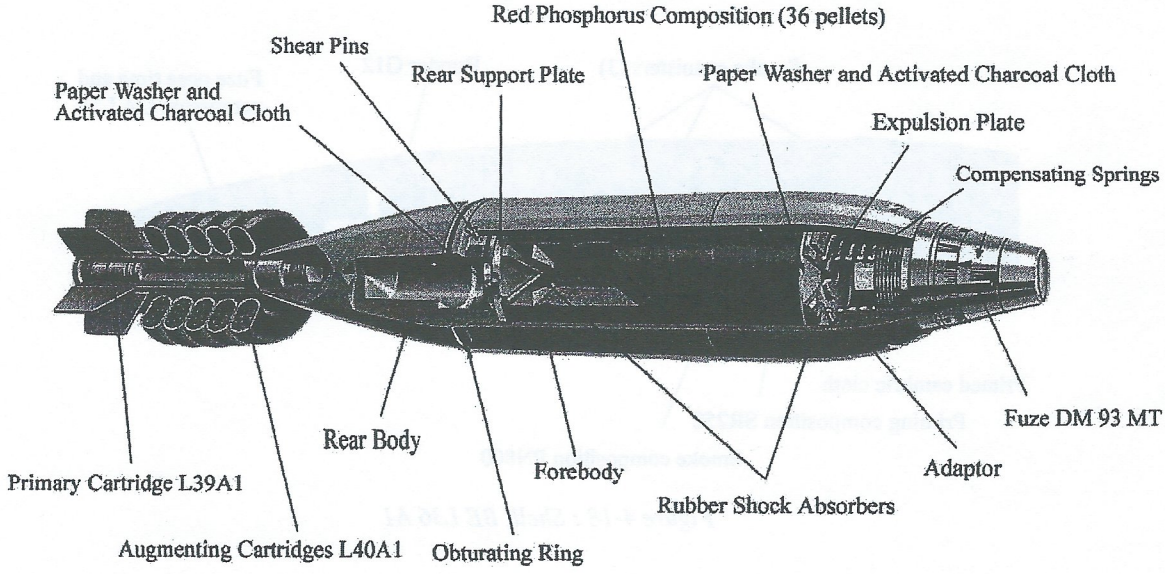


Figure 4-17 : Red Phosphorus Smoke Bomb RO 04-04

A larger amount of binder may be required to provide pellets of the necessary mechanical strength, and this reduces the amount or red phosphorus, and slows down the burning rate. The burning rate is usually increased by the addition of a small amount of an energetic fuel/oxidant mixture. The pyrotechnic designer therefore has control over the characteristics of the smoke production in several ways. The rate and duration of smoke production depends on the size and shape of the pellet and on the burning rate of the composition both of which can be varied independently. Too large a pellet and too slow a composition gives a poor screen of high persistence. Too fast a composition may generate so much heat that convection leads to pillaring.

The height of burst governs the spread of pellets and hence the basic geometry of the screen. Given optimum size and burning rate and adequate spread of pellets, sufficient concentration to give excellent visual and good infrared effect can be achieved.

Artillery Ammunition

Most in-service artillery smoke rounds are base ejection HC types in spite of its toxicity, environmental impact and ineffectiveness in the infrared. Typical is the 105 mm FD L36A1 shown in Figure 4-18. Its payload consists of a set of annular smoke pots containing PN 800 primed on the inner annular face with SR 252. When the fuze functions, it flashes onto a gunpowder burster charge in the nose which ignites the smoke pots on their inner faces, pressurises the shell case, ruptures the rear shear pins and ejects the smoke pots. The smoke pots fall burning and a slow build up of grey smoke occurs from the ground.

Royal Ordnance demonstrated a very effective 155 mm round as probably the first effective infrared round of that calibre. Like the 81mm mortar, its payload consisted of a pile of pellets of red phosphorus composition. However, because of the increased setback

force (higher acceleration and longer payload height) and the high spin acceleration, internal furniture was necessary to protect the payload. While the pyrotechnic designer may wish to fill all available space with composition to maximise the effect on the target, adherence to the external ballistics requirements of the JBMOU requires that extra metal must be included to achieve the necessary mass and mass distribution.

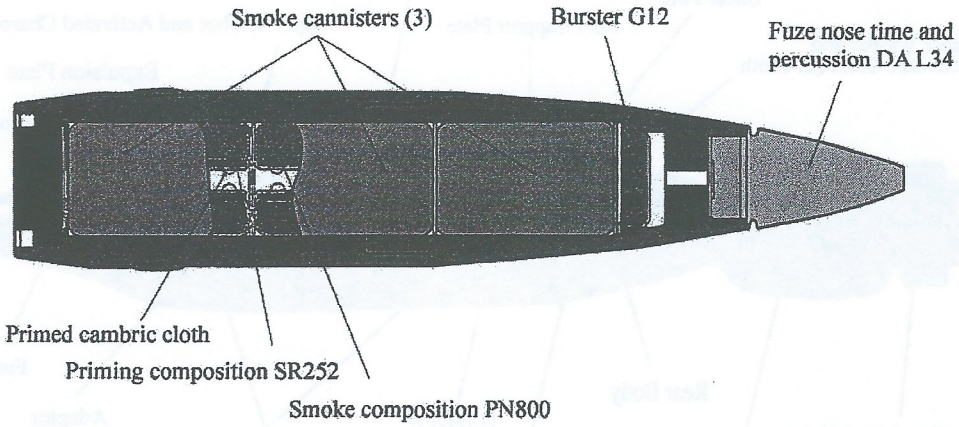


Figure 4-18 : Shell, BE L36 A1

TUBE-LAUNCHED GRENADES

The L8 is an example of a tube launched grenade. Another type is the L28 grenade which contains a number of pellets of a low toxicity smoke composition which can be spread over a wide area to produce a large, low density smoke screen. The design problem is to ignite a number of pellets from a single ignition source, and the solution in this grenade is of a very labour intensive sort. Each cylindrical pellet is annular, and a length of quickmatch is looped through the hole and tied on the outside. The pellets are packed inside a rubber body so that there are many flash paths throughout the payload from the gunpowder capsule which ignites and disperses them. The method of manufacture is very labour intensive.

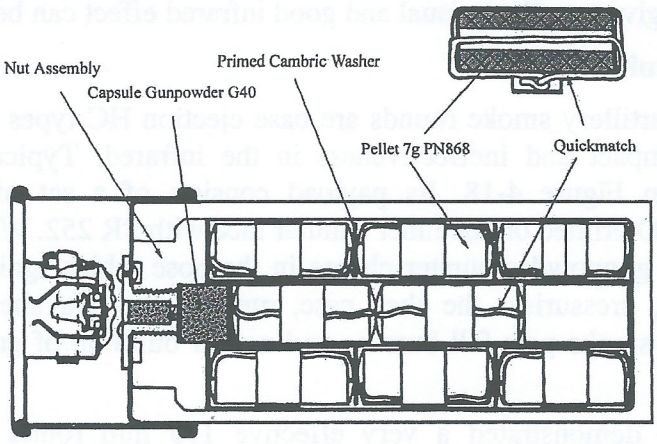


Figure 4-19 : Grenade L27

HAND GRENADES

Hand grenades containing white phosphorus such as the No 80 are seldom encountered now because of the marked toxicity of white phosphorus, and because burns inflicted by it are particularly unpleasant.

Training grenades are relatively common and their basic requirement is for a reasonably good white smoke with low toxicity. As has been discussed earlier, cinnamic acid volatilised from a lactose / potassium chlorate mixture is deemed by the UK to be particularly suitable. The composition will burn as loose pellets, but for reasons of safety, are always burned within a container.

A typical example of a recent design is the G60 Mk 1 (later the L72) grenade shown in section in Figure 4-20. Ignition is provided by a standard fly-up lever arrangement ; in this case the lever is retained to the grenade body by a strap because of a requirement to use the grenade from a helicopter. The striker hits an Eley 0.22" percussion cap which spits onto a length of quickmatch which provides the delay. The quickmatch ignites gunpowder in a capsule glued over the end, and this transfers the ignition to a cylinder of primed cambric held against the inner face of the annular smoke pellet by a coil of spring steel. The smoke emits through holes in the upper end of the body which until that moment are sealed against moisture with adhesive metal foil.

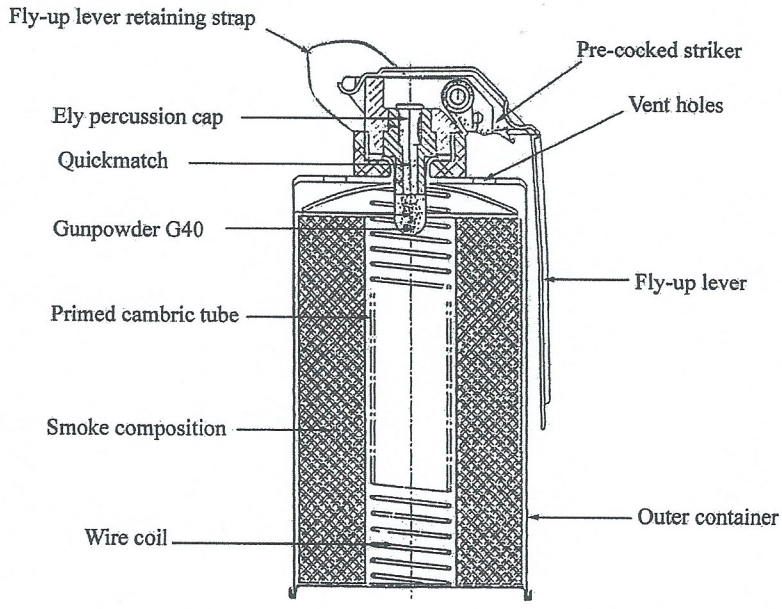


Figure 4-20 : Training Screening Smoke Grenade

It is found more convenient to use a pellet which burns radially rather than cigarette fashion because the larger surface area provides more copious smoke even from a composition of lower burning rate.

SUMMARY

Pyrotechnically generated smokes are used for screening in the visible and infrared spectral regions and research is trying to extend that into the millimetric. The most useful current screening formulations are based on red phosphorus which provide a good yield factor and smokes of (presently) acceptably low toxicity. Smokes based on HC are in widespread use, but should really be considered obsolescent because of their toxicity and absence of effect in the infrared.

Training smokes, where a low incendiary effect is necessary, coloured signalling smokes, an d anti-riot smokes are produced by volatilising the active material from a fuel/oxidant mixture.

Metal powders are uniquely effective in the infrared, but cannot be pyrotechnically generated.