

MINISTRY OF DEFENCE (ARMY)
ROYAL ARMAMENT RESEARCH
AND DEVELOPMENT ESTABLISHMENT



**MONOGRAPH
ON
PYROTECHNIC COMPOSITIONS**

by

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1965

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A handwritten signature in dark ink, appearing to read 'E. W. Chivers', with a long, sweeping horizontal stroke underneath.

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INTRODUCTION

Pyrotechny as an art is of great antiquity, having been known to the Chinese and other Eastern peoples for many centuries. Originally, fireworks were employed for display and celebrations during times of peace and possibly to boost morale and to terrify their enemies in time of war. In war, the advantages of projected pyrotechnics as incendiaries was quickly realised and from this use the self-propelled pyrotechnic or rocket eventually developed. From early accounts it appears that they have always been filled with a gunpowder-like mixture that propelled them, belching flame and smoke, towards their enemies, and these early rockets must have resembled pyrotechnic rockets prior to World War II remarkably closely.

Modern military pyrotechnics stem mainly from the advances made in rocketry during the nineteenth century by Congreve, Boxer, Hale and others when larger and better constructed rockets were devised for a variety of military purposes including those of signalling and of illuminating forward areas of battle. However, the real impetus to the expansion of this branch of Warlike stores came in World War I with the development of trench warfare and the growth of the Royal Air Force and their consequent need of signals and illuminants of many kinds. The Second World War saw a far greater variety of pyrotechnic stores in use than ever before and since its close the demand for them has persisted. Nowadays, pyrotechnics are expected to function satisfactorily and reliably under far more varied conditions than they were in the past and for this reason they have to be fully engineered stores and are therefore much more expensive to produce. Because of their cost, they must be capable of lasting for many years in storage without deteriorating.

The term pyrotechnics in the modern military sense covers a wide variety of explosives that are needed to produce effects other than those produced by high explosives, initiating compositions and propellants; these may also be included on occasion to produce special effects. Broadly speaking, pyrotechnics are employed to produce light, either to illuminate objects or to be seen as a signal; to produce smoke to screen objects or for signalling; to produce fire and incendiary effects; to measure intervals of time. They may also be required to function as propellants, igniters and primers etc. Pyrotechnic explosives are rarely composed of single substances as may be the case with high explosives, and they usually consist of finely divided combustible substances and oxidants which, upon suitable initiation, explode violently or burn steadily as required. The choice of combustible powders is very wide indeed, ranging from metallic and non-metallic elements and binary compounds on the one hand to all manner of carbonaceous material, both natural and synthetic, on the other. The choice of oxidants is more restricted and is confined to metallic and some non-metallic oxides, oxygenated salts and some halides. Air and oxygen may also be used.

Mixtures that are required to explode violently to produce a flash of light or a loud bang are filled into the store as a loose powder which, upon initiation, ignites and burns very rapidly throughout its mass, producing high temperatures and gas pressures. Mixtures that are required to burn over a longer period of time with a steady evolution of flame or smoke, or to burn for a specified interval of time, are consolidated under pressure into a column surrounded by non-combustible or heat-insulating material that ensures the column burning regularly layer by layer from one end to the other.

The principal varieties of pyrotechnic compositions in current military use and their main functions are shown in table 1.

The rapid development that has taken place in modern pyrotechnics in the United Kingdom really started during the first World War in the Research Department of Woolwich Arsenal. Compositions of this period include a shell time-fuze composition RD 202, a green signal composition SR 490, and a star-shell illuminant SR 30. During the period between the wars the variety of pyrotechnic stores required by the services increased at a great rate, and most of the types of composition outlined in table 1 came into being.

This was an important period of applied research in this field and many of the now well-established basic principles concerning pyrotechnic design were laid down prior to 1939. One of the most important developments of the early 1920's was the use of magnesium powder and sodium nitrate in illuminating compositions. Earlier fillings made use of mixtures of aluminium powder or magnesium powder and barium nitrate since this oxidant was non-hygroscopic and, once consolidated, the compositions were chemically stable for long periods. Sodium nitrate had never been considered suitable because of its hygroscopicity and the rapid corrosion of magnesium when in contact with saline solutions. In 1923 it was demonstrated that magnesium-sodium nitrate mixtures were at least twice as efficient as light-producers than the corresponding mixtures containing barium nitrate and that, provided the ingredients were thoroughly dried and handled in relatively dry atmospheres, the moisture absorbed was very small and did not seriously affect the stability of the composition. This knowledge was applied to such good purpose in the development of new stores that at the outbreak of World War II British illuminants were second to none, and this superiority was maintained throughout the war. Moreover, illuminating compositions such as SR 562, SR 563 and SR 568A that were developed during the early 1930's, still remain among the most reliable and efficient compositions of the 1960's.

The intense activity in research and in the development of new pyrotechnic stores that went on between the two World Wars, led to a widespread search, on a basis of trial-and-error, for new materials as ingredients of pyrotechnic compositions. This resulted in the introduction of new fuels such as scaroid resin, lactose and ivory nut powder and new combustion-controlling materials such as the oxalates of the alkaline earth metals. These substances and many others like them were found to meet the need to widen the scope and

range of pyrotechnic compositions, and, provided their chemical properties were compatible with those of the other ingredients, they were accepted as useful additions to the stock of basic materials. Later, as they became available, plastic moulding powders such as phenol-formaldehyde resins, polvinyl chloride, chlorinated rubber etc., were also utilised.

As a result of all this activity the number and variety of pyrotechnic compositions increased with great rapidity and it was inevitable that in the quality of their performance some compositions were better than others. Ingredients that were satisfactory during early development were sometimes found to have certain inherent faults that only became apparent after long periods of use, and they had to be abandoned. The basic ingredients of fuel, oxidant, pelleting material and moderator necessary to produce certain pyrotechnic effects were established during the early years of investigation, and the variants to those that were introduced in the subsequent period were largely in the nature of refinements to vary the rate of burning, to improve the efficiency, the colour of the flame, or the chemical stability of the composition.

During the second World War and subsequently, investigations of a more basic nature were put in hand to ascertain, for example, the conditions leading to the corrosion of magnesium powder in pyrotechnic compositions and the means of preventing it, or to discover the reason for the superior illuminating qualities of flare compositions containing sodium nitrate. The mechanism of producing coloured signal flames was also examined and the limitations in quality, set by the type of radiation emitted from pyrotechnic sources, were determined.

The practice of taking aerial photographs of ground targets by night increased enormously during the war and led to the development of a variety of photoflashes and their fillings. Much of the work was concerned with producing less vulnerable fillings such as that consisting of a central core of high explosive surrounded by fine metal powder, and with tailoring the luminous characteristics of the resulting flashes to the requirements of the aerial cameras with which they were used. Much valuable information was obtained on the combustion of metal powders, the temperatures reached and the radiation emitted.

Fillings for incendiary bombs were further subjects of research and development. Two main types of filling were investigated, thermite in the form of a mixture of aluminium powder, iron oxide and barium nitrate, which was used as a central heating core within a casting of magnesium metal, and combustible viscous fluid mixtures such as solutions of rubber or perspex in benzole.

Many other investigations and developments were stimulated by the demands of the fighting services for new weapons and signals, and as knowledge of the complex processes taking place during combustion increased, pyrotechnics became a little less of an art and a little more scientific in concept and outlook.

Since the end of the war the course of pyrotechnic development has changed considerably to meet the changed requirements of the

armed services. Pyrotechnic stores must now function more accurately and reliably over far wider ranges of conditions than ever before. Flares carried by long-range missiles are expected to burn under conditions of near vacuum and at very low temperatures. Delays must burn equally accurately at high and low ambient temperatures and pressures, while accelerating or decelerating or while spinning rapidly during flight, and they may have little space in which to vent. Pyrotechnic stores must remain serviceable for much longer periods. To meet these demands, it has been necessary to examine the behaviour of pyrotechnic compositions in the new conditions in order to eliminate all unsatisfactory ingredients and to seek alternatives that will function properly in all circumstances. This has led to the study of pyrotechnic combustion under varied conditions of temperature and pressure, particularly that of so-called gasless mixtures.

The much longer service-life now demanded of pyrotechnic stores has underlined the importance of eliminating moisture both from the filling and from the empty components, and of designing stores in such a way as to prevent water from the surrounding atmosphere entering the filled stores. Non-hygroscopic ingredients now replace starch, resins and other natural materials that absorb moisture, metals and plastics replace paper in the manufacture of components, and stores are now hermetically sealed against the atmosphere with suitable rubber seals and well designed closures.

In recent years much thought and effort has been directed towards producing a waterproof plastic type of pyrotechnic filling that can be extruded or moulded into containers. Such a filling would simplify mixing and loading operations and make them less hazardous. It would also be waterproof and would eliminate many of the current corrosion and storage problems. It is too early, as yet, to say how far these new mixtures can replace the conventional consolidated powder fillings in all their various roles, but specific compositions are gradually being introduced as they are developed to meet the requirements of new stores.

In the chapters that follow, an attempt has been made to describe some of the basic principles on which pyrotechny, as currently practiced within R.A.R.D.E., is based. The information contained therein has been gleaned from the notebooks, reports, technical memoranda and other communications of members of the pyrotechnic section over a period of more than forty years. It is thus a representative summary of the wisdom and skills that they acquired during their long struggle to satisfy numberless Service requirements. Much of that wisdom was never put to paper and, except for a few items of information that have been included in this account from memory, it is probably lost forever or must be rediscovered after much labour and thought by a new generation of pyrotechnists. This book has been written in order to make their task a little easier.

REFERENCES FOR GENERAL READING

1. Chemistry of Powder & Explosives, T. L. Davis, Wiley, 1943
2. Pyrotechnics, G. W. Weingart, Chem. Pub. Co., 1943
3. Modern Pyrotechnics, H. Ellern, Chem. Pub. Co., 1961

TABLE I THE PRINCIPAL CLASSES OF S.R. PYROTECHNIC EXPLOSIVE COMPOSITIONS

Class	Examples	Main Constituents	Store or use	Main features
Illuminating	(a) SR. 562 SR. 563	Magnesium and sodium nitrate	Reconnaissance flares, star shell, rocket flares	High luminosity for illuminating surface targets
	(b) SR. 568A	Magnesium and sodium nitrate	Tracking flares	High luminosity for observation of missiles from great distances against the sky
Signal	(a) SR. 232 SR. 701	Magnesium, Potassium perchlorate Barium or Strontium salts	Coloured very signals used at low or medium altitudes	Produce red or green flames for observation during day or night at medium altitudes
	(b) SR. 178 SR. 188 SR. 193	Magnesium barium and strontium nitrates, chlorinated rubber	Signals for burning at high altitudes. Tracking flares	Coloured signal compositions that burn at altitudes up to 80,000 feet
	(c) SR. 399	Magnesium, barium peroxide	Tracking flares for very high altitudes	Gasless compositions burning with a white flame at altitudes of 200,000 feet or more
Tracer	(a) SR. 372AB	Magnesium, Strontium nitrate, Wax and resin	Gun shell tracers	Withstand firing stresses and burn under high rates of spin
	(b) SR. 458	Potassium dinitrophenate and barium peroxide	Small arms ammunition tracers	
Igniter	(a) SR. 371C	Magnesium, Potassium nitrate, resin	Cordite rockets and power cartridges	Produces very hot flames, sparks and gas
	(b) SR. 623	Magnesium, barium and strontium nitrates	Ramjet engines	Hot flame with rapid release of heat for igniting kerosene/air mixtures at medium to high altitudes
	(c) SR. 666	Boron, aluminium, Potassium perchlorate thiokol rubber	Guided missile motors	Hot, sparky flame for ignition of kerosene/Lox mixtures

Priming	(a)	SR. 252	Potassium nitrate, silicon, gunpowder	Ignition of flare and signal compositions	Produces hot molten slag and gas suitable for ignition at low altitudes only
	(b)	SR. 92	Boron, Bismuth oxide	Ignition of flare and signal compositions	Gasless, produces hot molten slag, for ignition at high altitudes
Incendiary	(a)	SR. 306	Aluminium, hammer-scale, and barium nitrate	Magnesium incendiary bombs	High heat of combustion and produces molten iron
	(b)	SR. 425	Perspex-benzole, aluminium and sodium nitrate	Incendiary gel bombs	Viscous fluid which burns vigorously with large evolution of heat
Delay and Time fuze	(a)	SR. 214 SR. 112 SR. 227A	Potassium nitrate and natural or synthetic organic material	Stores having vented delays or time-fuzes	Produces much gas and combustion is affected by external pressure
	(b)	SR. 75 SR. 53	Boron, bismuth oxide or potassium dichromate	Stores having unvented delays or time fuzes	Produces little gas and combustion is little affected by external pressure
Photoflash		SR. 812	Aluminium and Potassium perchlorate	Photoflashes for night reconnaissance photography	Rapid rise in luminosity to a very high peak-intensity that is synchronised with the camera shutter
		SR. 541	Magnesium and sodium nitrate		
Smoke and Flame		SR. 414 SR. 622	Red phosphorus, manganese dioxide or calcium sulphate	Signal stores ejected from submarines	Slow-burning compositions producing a yellow flame and white smoke
Screening smoke		SR. 269M	Calcium silicide, zinc oxide, hexachlorethane	Smoke shell, grenades and bombs	Produces dense clouds of greyish white smoke
Coloured smoke		SR. 904	Potassium chlorate, lactose and dyestuff	Coloured smoke signals	Produces dense coloured clouds of the vaporized dyestuff
Plastic Compositions		SR. 666 SR. 797	Thiokol rubber loaded with magnesium powder or boron, oxidants and flame colouring materials	Possible replacements for some powdered pyrotechnic compositions	Extrudable mixtures that are safe to handle and require no consolidation. Resilient and waterproof

CHAPTER 1

GUNPOWDER

Gunpowder was first made in Europe in the thirteenth century and continues in use at the present time because it is easily ignited, because it is not easily fired by percussion or rough handling, contains no ingredients which are chemically highly reactive and is cheap. Compositions are available which have similar explosive properties but they are either less easily ignited, or more readily fired by blows or friction, or they contain ingredients which are undesirably reactive and are not cheap. Gunpowder, however, possesses several disadvantages. It cannot be readily dried, it has a high moisture-content which varies with the vapour-pressure of the ambient air and it cannot be easily prepared so that different batches have the same rate of burning.

The properties of gunpowder are due in the main to the properties of the potassium nitrate and the charcoal; the sulphur plays a less important role. Potassium nitrate and sodium nitrate are capable of burning organic compounds more thoroughly and quickly than the chlorates, perchlorates, peroxides or the other nitrates. A good example of their efficiency is the method which can be used for destroying printed paper. When a bundle of paper is mixed with three or four times its weight of potassium nitrate and ignited, the paper will be reduced to a molten mass in a few minutes. None of the other oxidisers mentioned will bring about such a complete destruction so quickly. The reason is not clear but it is connected with the temperatures at which the nitrate, nitrite and carbonate of potassium melt. The influence of the charcoal is much clearer. Charcoal combines with oxygen at a low temperature and since it does not melt or volatilise, the minimum of heat is required to raise its temperature to the point at which it burns in the oxygen supplied by the decomposing nitrate. As a consequence, the temperature of ignition is low and the rate of burning (2 - 2½ seconds per inch) is high. The role of sulphur is twofold. Under normal conditions it makes black powder burn more readily because of its low temperature of ignition, and under the influence of pressure, not only in the press but also in the incorporating mill, it flows and becomes colloidal, cementing together the particles of charcoal and the minute crystals of saltpetre. Brown charcoal has a similar power of becoming colloidal under pressure, which is why brown gunpowders burn more slowly and regularly than black, and why the percentage of sulphur can be reduced or abolished altogether. Sulphur is abolished altogether in sulphurless gunpowder and the comparison of some of its properties with those of black powder reveals how small a part sulphur plays in the combustion of the latter.

Sulphurless gunpowder was first manufactured for the British Service for use in propellant-igniters because it was considered that the sulphur might be responsible for the corrosion spots in Mark I and M.D. cordite. Extended trials showed that its igniting power was inferior to that of black powder and it would not have survived this condemnation if it had not been adopted for priming compositions in pyrotechnic stores. By this substitution the deterioration of metallic powders brought about by contact with sulphur and the formation of spontaneously ignitable mixtures with chlorates were avoided. The rates of burning of black powder and sulphurless gunpowder when compressed under a pressure of 4 tons per square inch are about the same, 2.2 seconds per inch and both fail to burn under reduced atmospheric pressure. However, sulphurless gunpowder ignites from a flash at a lower ambient pressure than black powder.

Sulphurless powder has therefore better pyrotechnic properties than black powder when burnt in a partial vacuum whereas sulphur makes the powder burn more readily at higher pressures. Sulphur facilitates the milling of the nitrate and charcoal because it reduces the proportion of charcoal without impairing too much the burning properties and it binds the particles of these two ingredients together in the press-cake. The familiar black grains that are formed from the press-cake are hard and free from dust. Sulphurless gunpowder is more difficult to manufacture. It contains 30 per cent of charcoal, twice as much as black powder, and it takes a much longer time to grind the charcoal with the nitrate so that when compressed it will form a coherent press-cake which can be successfully granulated. The charcoals of some woods will not form a good press-cake and at the beginning of the last war, owing to shortage of suitable woods, the only sulphurless mealed powder available would not pellet, i.e., compress to a hard cake under pressure. The grains of granulated sulphurless powder are thus softer and more friable than the grains of black powder and are therefore much less suitable for use as a propellant. That sulphur plays only a secondary role even in the combustion of black powder is shown by the classical researches of Nobel and Abel who analysed the products of combustion and found that half the sulphur was unburnt.

The high and variable moisture-content of gunpowder and the difficulty of manufacturing it consistently are due to the charcoal and much research has been devoted to discovering a substitute for this ingredient. It must be a substance which when heated neither melts nor volatilises before it decomposes, and two classes of organic compound have been found which have this property, the alkali salts of aromatic acids and highly polymerised compounds. Potassium salicylate is an example of the first class and bakelite moulding powder of the second. But though these compounds give mixtures having the same rate of burning as gunpowder, they fail because they do not begin to burn in the oxygen supplied by the potassium nitrate at as low a temperature as charcoal. The molecules of the compounds of these two types must therefore be modified so as to reduce the temperature at which they decompose or react and by far the easiest

way of doing this is to introduce nitro-groups. The other groups which might be introduced to bring about what is tantamount to a destabilization of the molecule would probably produce compounds which are more dangerous and less reliable.

Two nitro-compounds, one a salt and the other a nitro-polymer, which were intended to act as substitutes for charcoal in gunpowder were introduced into the Services. A powder can be made by processing a mixture of potassium dinitrophenate and potassium nitrate which burns at the same rate as gunpowder, but it does not ignite or burn under very low pressure. Moreover, the salt is easily decomposed and is toxic. Despite these drawbacks, it has been very successfully mixed with barium peroxide and a small quantity of varnish in a priming composition for small-arms tracers. Nitroindene polymer is a constituent of the fuze composition S.R. 346B which it seemed at one time might take the place of R.D. 202. This composition is now used only as a delay composition because of its ability to ignite and burn with great regularity.

The Germans suggested and tested a third compound, tetranitro-carbazole. The pyrotechnic properties of a composition containing this compound and potassium nitrate are similar to those of gunpowder but it is not quite so ignitable. This deficiency in igniting power is ascribed to the fact that the compound melts before it decomposes.

The problem of finding a substitute for gunpowder is a difficult one since it is unlikely that a compound will be found which can take the place of charcoal and which will have all its advantages and none of its disadvantages. The advantage of charcoal is that it is cheap, stable, and compatible with all sorts of materials, and the gunpowders formed from it are readily ignited, burn rapidly and are almost the least sensitive of all the pyrotechnic compositions. The most likely general substitute for it is a polymer of some kind but it is difficult to imagine a stable polymer which will be so easily ignited as charcoal. There are some nitro-compounds which, mixed with potassium nitrate, produce powders whose pyrotechnic properties are similar to those of gunpowder, but nitro-compounds are more easily decomposed than charcoal and are more toxic, and the powders formed from them are more sensitive than gunpowder and have not the same degree of compatibility with other materials.

Gunpowder is used in many Service stores, but its function is not always the same. Sometimes it is a propellant, sometimes a burster, sometimes an igniter, sometimes a priming composition, sometimes it merely carries a flash from one place to another, and sometimes it acts as a delay or time-fuze composition. Occasionally it is completely sealed off from the rest of the store, but more often it is in contact with other chemicals and is free to absorb any moisture and any gases which may be present in the store. The more this large variety of uses is considered and examined, the closer one is driven to the conclusion that it is unlikely that a complete substitute for gunpowder will be found and that if a substitute for gunpowder when acting in any one of its roles is found, it will not be suitable for any of the others.

It is more probable that gunpowder will be replaced not by one composition but by several and a process of replacement of this kind has been taking place in pyrotechnic stores. But there are other stores, not generally considered pyrotechnic, in which gunpowder is used, and for which substitutes might be considered.

REFERENCES

Explosives. - Marshall (2nd. Edition) Volume 1.
Solid Propellants and Exothermic compositions - James Taylor.
The Initiation, burning and thermal decomposition of gunpowder -
Blackwood and Bowden.

CHAPTER 2

MAGNESIUM POWDER

Magnesium powder is one of the most important combustible ingredients of pyrotechnic compositions and is employed wherever a high output of energy is required in the form of light or heat. It is supplied in two varieties, cut and blown, depending on the method of manufacture.

Cut magnesium powder consists of flattened turnings produced by machining billets of the metal with a scratch brush or file card. The turnings are broken down by milling and the resulting powder is graded by sieving between specified limits. Blown magnesium powder is produced by forcing the molten metal through a jet surrounded by a stream of inert gas moving at high speed into a cooling chamber, also filled with inert gas. The jet breaks up into droplets that condense to form spherical or near-spherical particles, the exact size and shape depending on the conditions. The inert gas may be natural gas, helium, argon or nitrogen. An alternative means of producing condensed droplets of magnesium consists of impinging a fine stream of the molten metal on to a disc rotating at high speed in an inert atmosphere. Control of the speed of rotation permits a close control of the particle-size distribution of the resulting powder. By adjusting the conditions in either process it is possible to produce an ultra fine (atomised) powder, the bulk of which passes the finest sieves. Attempts have been made to condense the molten droplets in mineral oil but the results have not been very satisfactory because of the high oxide and carbon content of the product.

Blown magnesium powder contains a small percentage of magnesium nitride even when condensed in argon and helium. Samples have contained up to 0.1 per cent nitride when nitrogen was used and 0.045 per cent with helium. The nitride is slowly hydrolysed by atmospheric moisture and most of it eventually disappears. The small proportion remaining is not considered sufficient to affect the stability of compositions.

The pyrotechnic behaviour of magnesium powder in compositions is affected by those of its properties governing the ease with which oxidation can take place, the shape and size of the particles, the proportion of fine and coarse particles present, the degree of surface oxidation etc. For practical purposes magnesium powder is graded according to its apparent density and the particle size distribution within specified sieving limits. The British Specification C. S. No. 787F for the various grades of magnesium powder used in S.R. compositions defines them as light, medium and heavy grades according to their apparent densities as shown in Table 2.

The apparent density is governed by the size and shape of the particles and has a value of 1.24 for closely packed spheres of

TABLE 2 SPECIFICATION OF MAGNESIUM POWDER USED IN BRITISH
SERVICE STORES

HIGH DENSITY GRADES

Grade	0 (heavy)	3 (heavy)	5 (heavy)
All pass B.S. Sieve No.	30	72	200
Not more than 7 per cent retained on B.S. Sieve No.	-	100	-
Not more than 15 per cent retained on B.S. Sieve No.	44	-	240
Not more than 15 per cent pass B.S. Sieve No.	100	240	-
All retained on B.S. Sieve No.	120	-	-
<i>Apparent Density</i>			
Not less than	1.0	1.0	1.0

MEDIUM DENSITY GRADES

Grade	14/44	0	3	5
All pass B.S. Sieve No.	14	30	72	200
Not more than 7 per cent retained on B.S. Sieve No.	-	-	100	-
Not more than 15 per cent retained on B.S. Sieve No.	-	44	-	240
Not more than 15 per cent pass B.S. Sieve No.	-	100	240	-
All retained on B.S. Sieve No.	44	120	-	-
<i>Apparent Density</i>				
Not less than	0.65	0.65	0.65	0.65
Not greater than	0.85	0.85	0.85	0.85

LOW DENSITY GRADES

Grade	2	2A	4	6
All pass B.S. Sieve No.	30	44	72	200
Not more than 7 per cent retained on B.S. Sieve No.	-	-	100	-
Not more than 15 per cent retained on B.S. Sieve No.	44	-	-	240
Not more than 15 per cent pass B.S. Sieve No.	100	-	240	-
Not more than 50 per cent pass B.S. Sieve No.	-	100	-	-
All retained on B.S. Sieve No.	120	240	-	-
<i>Apparent Density</i>				
Not less than	.40	.30	.40	.40
Not greater than	.60	.50	.60	.60

magnesium of uniform size. The particles of low density grades consist of well curved thin flakes, those of medium density grades of flatter, thicker flakes, and those of the heavy grades of spheres, pear-shaped droplets or irregular lumps. The apparent density is determined by measuring the volume of 10 gms. of magnesium powder in a measuring cylinder 6 inches high and 0.8 inch in diameter after dropping it thirty times from a height of 2½ inches on to a piece of hard leather.

Another property of the magnesium powder which conceivably affects the manner in which compositions burn is the surface area presented by the particles to the effects of oxidation. This cannot be measured absolutely, especially in fine powders, but a measure of the effective area can be determined from the permeability of a packed bed of the powder to air or a liquid, the rate of sedimentation in a suitable fluid, or the amount of light scattered by a suspension of the powder. The method most frequently used is the air-permeability method of Carman (J. Soc. Chem. Ind. 57 225 (1938)).

When a fluid flows through a porous bed of uniform cross-sectional area consisting of rigid grains, the rate of flow of the fluid is related to the specific surface of the medium. Thus, by preparing a bed of magnesium powder of unknown specific surface under conditions ensuring uniform packing and by measuring the rate of flow of air through the bed, it is possible to calculate the specific surface of the powder. Several types of apparatus for measuring specific surface are in use and differ mainly in operational technique and in the precise form of the calculated result. In the Fisher sub-sieve sizer, the calculations are contained in nomographs and determinations are made by a series of routine operations.

It is possible to determine the particle-size distribution of very fine powders with a Micromerograph. In this instrument a small weighed quantity of the powder is scattered into the top of a tall cylinder filled with nitrogen and the particles settling at the bottom of the cylinder are collected on the pan of an electronic balance and weighed continuously. The sizes of the particles thus collected are deduced from considerations of Stokes's Law.

For coarse powders the distribution is determined by sieve-analysis. Each grade of magnesium powder contains particles with dimensions varying approximately between those of the apertures of the limiting sieves. It is the aim of the manufacturers to adjust production so that the bulk of the particles lies close to the middle of the range; thus in magnesium powder, grade 0, with sieving limits of B.S.S. No. 30 and B.S.S. No. 120 the bulk of the powder lies around B.S.S. No. 72. Information regarding the particle-size distribution of magnesium powder is most readily obtained by passing a sample through a nest of British standard sieves in a series of diminishing apertures. The powder is carefully brushed through with a camel-hair brush or jolted mechanically, and the portions remaining on the sieves weighed.

The state of sub-division of magnesium powder profoundly affects the manner in which pyrotechnic compositions containing it burn;

compositions made with a coarse powder burn more slowly and tend to emit sparks, those made with a fine powder burn rapidly with few large sparks. The variation in the rate of burning of a composition with grade of magnesium powder is modified by the actual proportion of magnesium powder present since the effect is less noticeable with a small proportion. For one containing about 50 per cent of cut magnesium powder the reciprocal rates of burning* for various grades are approximately in the following ratios.

Grade of Cut Magnesium Powder	0	3	4	5
Rate of Burning (reciprocal)	1.00	0.75	0.65	0.55

This change in the rate of burning is brought about by the increase in the interface between particles of metal and oxidant as shown by the increase in the specific surface of the metal powder.

The specific surface of a particular grade of magnesium powder can vary considerably, especially in the cut variety, depending as it does on particle shape as well as size. Different manufacturers, using slightly different processes, may produce powders of the same grade having specific surfaces varying by as much as 2 to 1. This variability was especially noticeable during the 1939-1945 war when the specifying limits of grades of magnesium powder were relaxed. The correlation between the specific surfaces of some samples of cut magnesium powder, grade 0, and the rates of burning of composition S.R. 563 made with them is shown in table 3.

TABLE 3

<i>Specific Surface</i> <i>sq. cms. per gm.</i>	<i>Rate of Burning</i> <i>seconds per inch</i>
225	15.0
245	14.2
275	12.5
344	11.3
403	10.0
570	8.1

The apparent density of magnesium powder is a rough measure of the shape of the particles and the manner in which they pack. The correlation between apparent density and rate of burning is less

*Note In pyrotechnics it is convenient to measure rates of burning in reciprocal units, i.e. in seconds per inch, since this simplifies the calculation of the length of the column necessary to burn for a specified time. Reciprocal units are used throughout the text.

apparent but there is a definite trend to slower rates of burning with higher apparent densities.

With blown magnesium powder variation in particle shape is less pronounced although the particles may vary from almost perfect spheres to pear-shaped droplets or irregularly shaped lumps depending on such conditions of manufacture as the temperature of the cooling chamber and the manner of breaking-up of the jet of molten metal. The specific surface of blown magnesium powder is smaller than that of the equivalent grade of cut powder and because the particles vary less in shape it is more reproducible. Similarly the apparent density varies less.

The greater constancy of specific surface and apparent density of blown magnesium powder makes for smaller variations in rates of burning and this variety is therefore preferable to cut magnesium powder. Other advantages it possesses are better packing properties, producing denser compositions and hence providing more energy per unit volume of filling, and a smaller interface for chemical reaction, corrosion as well as combustion, both of which are slowed down to some degree. A slower rate of corrosion is advantageous for long storage, but slower rates of burning may require compensation by modifying the proportions of the ingredients of compositions.

The substitution of blown magnesium powder for cut has been the subject of extensive investigations in which the behaviour of magnesium powder blown in helium, argon, natural gas and nitrogen has been examined in a series of compositions originally designed for cut magnesium powder, all the powders having similar particle-size distributions. The correlation between the rates of burning of compositions containing nitrogen-blown magnesium powder and cut magnesium powder is shown in figure 1. It is apparent that compositions containing blown magnesium burn more slowly and in extreme cases some modification to the proportions is necessary. In general, however, the replacement of one type of powder by the other does not seriously modify combustion.

Difficulties do occur, however, in replacing cut magnesium powder, grade 4, by blown magnesium powder. Grade 4 powder has a low apparent density and a high specific surface and is used for many coloured signal compositions. There is no equivalent grade of blown powder but it has been shown that many compositions made with grade 5 blown magnesium powder burn in a similar manner, and that this material can be used as an alternative.

TABLE 4 THE RATES OF BURNING OF SIGNAL FLAME COMPOSITIONS
MADE WITH CUT AND BLOWN MAGNESIUM POWDER

Composition	Magnesium Powder per cent	Rate of Burning, seconds/inch	
		Grade 4 Cut	Grade 5 Blown
S.R. 170A	48	6.5	6.4
S.R. 232	40	14.9	13.7
S.R. 427	38	12.9	14.5
S.R. 428	43	10.2	10.8
S.R. 486A	35	10.9	10.8
S.R. 700	42	13.3	11.0
S.R. 502	35	11.5	12.5
S.R. 568	55	3.6	4.7
S.R. 580	60	2.2	2.9

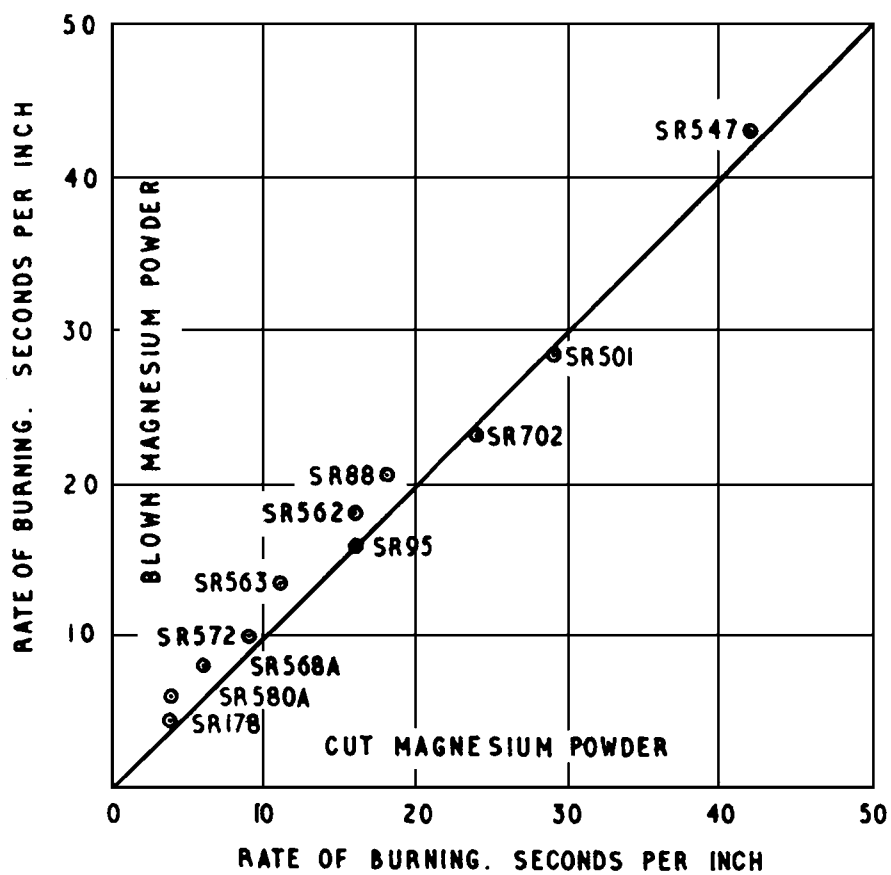


Fig. 1. Comparison of Rates of Burning of Compositions containing Cut and Blown Magnesium Powder.

CHAPTER 3

THE COMBUSTION OF MAGNESIUM POWDER

Magnesium powder is most frequently used in pyrotechnics to produce light and heat. Aluminium, antimony, boron and other materials are used to a smaller extent and then usually for special purposes as in photoflashes, delays and incendiary mixtures. At one time aluminium powder, mixed with barium nitrate and sulphur, was the basis of all illuminating compositions and it still remains the main ingredient of photoflash compositions. However, it produces less light than magnesium powder when burnt in consolidated mixtures and has been entirely replaced in all flare and signal compositions.

Mixtures of metal powders and oxidants behave differently when ignited as a loose powder and as a consolidated pellet. The first results in explosive combustion producing a very rapid evolution of light and heat; the second in steady burning layer by layer with a correspondingly steady liberation of energy. This is the kind of combustion that obtains in flares and signals and will be considered in this Chapter.

The oxidants commonly used in mixtures with magnesium are the nitrates of sodium, potassium, barium and strontium, potassium perchlorate and to a lesser extent barium and strontium peroxides. Potassium chlorate is rarely used because of the extreme sensitiveness of mixtures with metal powders and their low temperatures of ignition.

Up to 1923 sodium nitrate had never been used as an oxidant because of its alleged hygroscopicity, but it was then demonstrated in the Research Department that the salt was not only insufficiently hygroscopic to prevent its use as an oxidant but that mixtures of magnesium and sodium nitrate were, in fact, the most efficient light-producers so far devised. The absorption of moisture by sodium nitrate does not become significant until the relative humidity of the ambient air exceeds 75 per cent, and there are few working days in this country when favourable conditions cannot be maintained in laboratory or filling shop. Nowadays, magnesium-sodium nitrate mixtures are used almost universally in military pyrotechnics in spite of the instability of such compositions in the presence of moisture. Mixtures of magnesium or aluminium and barium nitrate are chemically more stable but are less efficient as illuminants.

When mixtures of magnesium powder and sodium nitrate are burnt in pellet form in a confined space, the products of combustion are mainly magnesium oxide, magnesium nitride and metallic sodium. Where there is free access to air the sodium burns to sodium peroxide. The reactions may be represented by the equations:-

1. $9\text{Mg} + 2\text{NaNO}_3 \rightarrow 6\text{MgO} + \text{Mg}_3\text{N}_2 + 2\text{Na} + 769.2 \text{ K.cals.}$
2. $2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2 + 119 \text{ K.cals. in excess air}$
3. $\text{Mg} + \frac{1}{2}\text{O}_2 \rightarrow \text{MgO} + 146 \text{ K.cals. in excess air}$

Reactions 1 and 2 occur together during combustion under normal conditions in the open and may be combined as:-

4. $9\text{Mg} + 2\text{NaNO}_3 + \text{O}_2 \rightarrow 6\text{MgO} + \text{Mg}_3\text{N}_2 + \text{Na}_2\text{O}_2 + 888.2 \text{ K.cals.}$

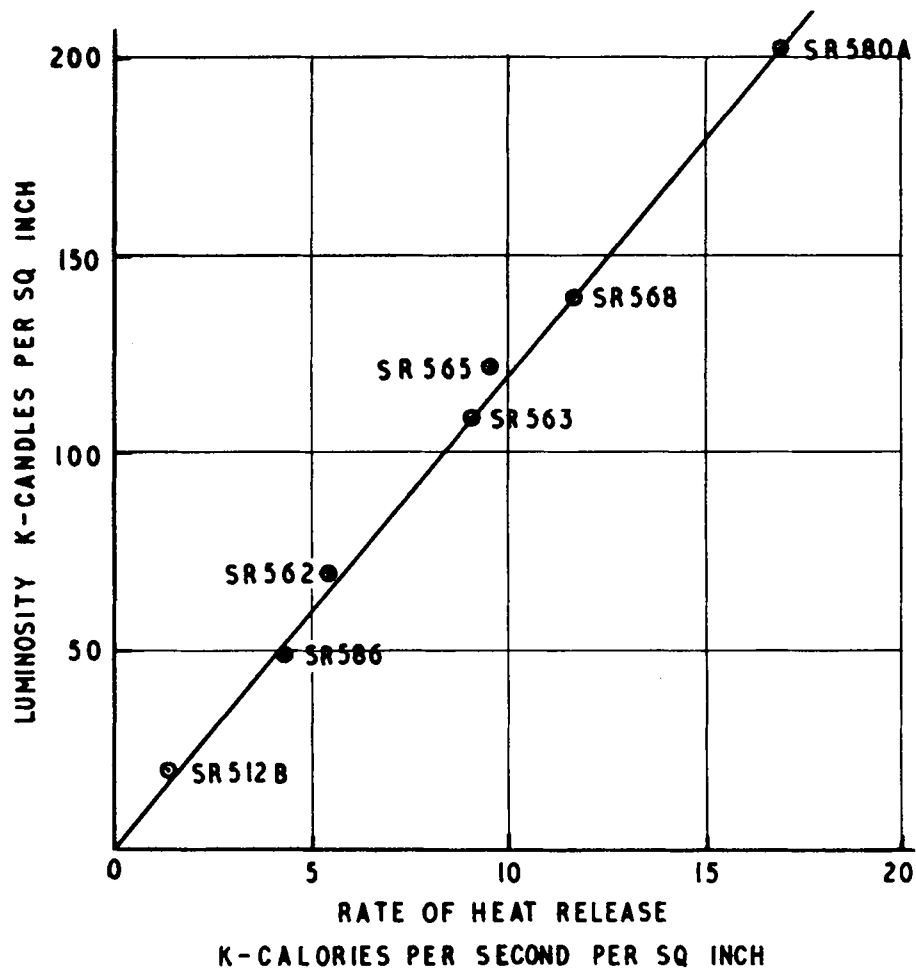


Fig. 2. Rate of Heat Evolution and Luminosity of Magnesium-Sodiumnitrate Compositions.

The stoichiometric mixture contains 56 per cent of magnesium powder and produces 1,978 calories per gram when burnt in a confined space (equation 1), and 2,300 calories per gram when burnt in excess air (equation 4). Magnesium in excess of 56 per cent burns in air to produce 6,080 calories per gram of metal (equation 3).

The heat of combustion of a composition depends on the proportions of the main reactants and the nature of the other ingredients. For example, the calculated heat of combustion in excess air of composition SR 562 (containing 50 per cent magnesium powder, lithographic varnish, sodium nitrate and calcium oxalate) is 2,546 calories per gram, and that for composition SR 580 (containing 60 per cent magnesium powder, acaroid resin and sodium nitrate) is 3,106 calories per gram.

The temperature and luminosity of the flame are governed by the rate of heat evolution, i.e. on the rate of burning as well as on the heat of combustion, and mixtures containing a high proportion of magnesium powder burn faster and brighter than those with less. The relation between luminosity and the rate of heat evolution is shown in figure 2.

The heats of combustion of a number of compositions containing magnesium and sodium nitrate have been determined in a bomb calorimeter and are shown in table 5.

TABLE 5 HEATS OF COMBUSTION OF COMPOSITIONS
CONTAINING MAGNESIUM POWDER BURNT IN A
LIMITED SUPPLY OF AIR

SR. Composition No.	Percentage Magnesium powder	Oxidant	Heat of Combustion Calories/gm.
Experimental	30	Sodium nitrate	1,040
"	50	"	1,760
"	70	"	1,380
562	50	"	2,035
563	50	"	2,063
568A	55	"	1,937
572	50	"	1,934
371C	42	Potassium nitrate	1,750
343A	50	Barium nitrate	1,550
700	42	{ Barium nitrate Potassium Perchlorate	1,943
105	53	Strontium nitrate	1,695
97A	22	Strontium nitrate	1,340
399	12	Barium Peroxide	638

When mixtures of magnesium powder and oxidants are burnt, only part of the liberated energy appears as light. The luminous intensity of the flame is measured by photometric techniques in candles and the luminous emission during the combustion period in candle-seconds.

The luminous emission from one gram of burning composition is known as the specific light-output or specific luminous flux. This quantity, subject to uniform conditions of combustion and photometry, is fairly constant for any one mixture. It is therefore used to compare the overall pyrotechnic performance of light-producing compositions under various circumstances. The specific light-output varies from about 5,000 candle-seconds per gram for slow-burning coloured signal compositions to about 45,000 candle-seconds per gram for the most efficient illuminating compositions burning as flare-candles in rolled paper cases. The figure is increased to 60,000 candle-seconds per gram or more for certain compositions containing lithographic varnish burnt as bare pellets with their cylindrical surfaces inhibited with lacquer.

The specific light-output of illuminating compositions increases with increasing proportion of magnesium powder to a maximum around 50-55 per cent magnesium and then diminishes. The stoichiometric mixtures are not the fastest burning and the fastest burning mixtures are not the most efficient.

The efficacy of pyrotechnic compositions to convert their chemical energy into light may be derived from the heat of combustion and the specific light-output by the equation:-

$$\text{Efficacy (lumens per watt)} = 2.99 \times \frac{\text{specific light-output}}{\text{Heat of combustion}}$$

With mixtures of magnesium powder and sodium nitrate the efficacy rises from about 20 lumens per watt for an illuminating composition containing 20 per cent magnesium to about 50 lumens per watt for one containing 60 per cent magnesium. Thereafter it falls off rapidly.

The flame from magnesium-sodium nitrate mixtures is yellowish white in colour and is larger and very much brighter than that with any other oxidant. The light flickers rapidly in intensity and analysis of the intensity-time oscillograms of flames show that the variations consist of a series of rapid oscillations with a frequency between 6 and 10 cycles per second together with a slower variation occurring every second. The flame is made up of the incandescent gases and solid particles of the products of combustion which are emitted at considerable velocity from the burning surface. The flame pulsates rapidly in size and the incandescent slag particles that emerge from it also vary in size. The complicated form of the intensity-time traces is related to the variations in the size and brightness of the flames and to the emission of incandescent particles. Large pieces of burning material ejected from the burning surface cause momentary peaks and the veiling of the flame by thin wisps of smoke cause depressions.

The light produced by magnesium-oxidant mixtures burnt as pellets is made up of three spectral components, grey body thermal continuum, line-systems from the elements present and band-systems from molecular species. The temperature continuum is the result of the general incandescence of the flames; the band systems are derived from the oxide products of combustion and from excited molecules such as BaCl^+ and SrCl^+ that are present in coloured flames. The spectral-energy curve shows a continuous rise from the blue end of the spectrum to the red with occasional peaks and humps where the lines and bands occur.

This description is broadly true for flames from mixtures of magnesium and the nitrates of potassium, barium and strontium but the spectral-energy curve of magnesium-sodium nitrate mixtures is different. There is the same general rise in energy from the blue end of the spectrum and a few irregularities due to band systems. The curve rises very steeply to two equally high peaks one on either side of the position of the sodium doublet which is indicated in absorption by a deep trough. After the second peak the energy curve follows the general form to the red end of the spectrum. The outer envelope of these flames consists of a layer of burning sodium vapour and the additional luminosity comes from this source. There is strong evidence that sodium hydride ions, which are present in the flame, play an important part in the increased luminosity, since the most efficient flames are derived from mixtures containing linseed oil products and these mixtures show the strongest NaH^+ bands in their spectra.

The temperatures of flames from some magnesium-sodium nitrate mixtures have been determined both from the spectra and from direct measurements with a pyrometer. A 50/50 mixture of the ingredients has a flame temperature of about $2,800^\circ\text{K}$. The substitution of 4 per cent sodium nitrate by lithographic varnish, (composition SR 563) reduces the flame temperature to $2,600^\circ\text{K}$ and the substitution of a further 11 per cent by calcium oxalate (composition SR 562) reduces the flame temperature to $2,400^\circ\text{K}$. Variants of composition SR 562 in which calcium oxalate is replaced by other calcium salts may have flame temperatures of $1,900^\circ\text{K}$ or lower.

Mixtures of magnesium powder and potassium nitrate behave similarly to those of magnesium powder and sodium nitrate and their thermo-chemical reactions are similar. Metallic potassium is produced in limited quantities of air and burns to potassium peroxide in excess air. Rates of burning are also similar. However, since the potassium spectrum shows strong emission in the violet and the red only, to which the eye is least sensitive, this element contributes little to the luminosity of the flame and the efficiency is very low. More usually, potassium nitrate is used in conjunction with barium nitrate in mixtures with magnesium powder in white signal compositions. Easier ignition and smoother burning is obtained than when barium nitrate is used alone.

Barium nitrate was at one time the only oxidant considered suitable for illuminating flare and white signal compositions but it has long been replaced in the first role by sodium nitrate. The earliest service flare compositions were mixtures of aluminium, barium nitrate and sulphur, the next were those containing magnesium, barium nitrate and wax or resin, and the youngest are those containing magnesium, sodium nitrate and other ingredients. The changes have brought a steady increase in the efficiency of flares and a decline in the steadiness of the flame and hence of the illumination produced. The flames from aluminium-barium nitrate mixtures are small but remarkably steady with a specific light-output of some 7,500 candle-seconds per gram. Those from magnesium-barium nitrate mixtures are larger and more luminous but they have longer periodic fluctuations. They have a specific light-output of about 12,000 candle-seconds per gram. Finally, magnesium-sodium nitrate mixtures have large fluctuating flames and a specific light-output of up to 45,000 candle seconds per gram.

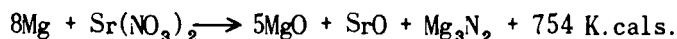
In the combustion of magnesium-barium nitrate mixtures there has been no evidence to date of the formation of metallic barium and the most representative equation for the reaction appears to be:-



The stoichiometric mixture contains 42 per cent of magnesium and the heat of combustion is 1,640 calories per gram. The efficacy of mixtures of these materials is about 15 to 20 lumens per watt. The flame is greenish white in colour, its spectrum being composed mainly of radiation continuum, band systems from MgO^+ and BaO^+ and atomic lines, and there is no emission comparable to the sodium continuum. Mixtures of magnesium and barium nitrate burn at rates similar to those of comparable mixtures containing sodium nitrate.

The melting and decomposition temperatures of barium nitrate are higher than those of sodium nitrate and the burning layers of compositions containing it are less readily disturbed by shock or rough treatment. This becomes apparent in such stores as shell-stars which are subjected to the forces of setback on firing the shell and of ejection from the shell during flight. Shell stars on parachutes burn flame downwards and there is a strong tendency for large pieces of burning composition to break away when sodium nitrate is the oxidant. With barium nitrate this effect is much less apparent and the consolidated filling burns steadily without breaking up. A compromise filling in which the more luminous sodium nitrate composition is surrounded by an annulus of a barium nitrate composition aims to combine high luminosity with regular combustion.

Strontium nitrate behaves very similarly to barium nitrate in mixtures with magnesium powder. The basic reaction during combustion is probably represented by:-

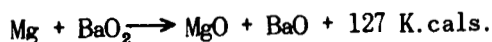


The stoichiometric mixture contains 48 per cent of magnesium powder and produces 1,870 calories per gram. Rates of burning are similar to those of comparable mixtures containing barium nitrate but the specific light-output is somewhat higher, around 16,000 candle-seconds per gram. The flame is pinkish-white in colour.

If chlorine ions are introduced into the flame of mixtures of magnesium with either barium or strontium nitrate the characteristic flame colour is produced from the green spectral band system of BaCl^+ or the orange and red systems of SrCl^+ and the luminosity of the flames is thereby increased. If both nitrates are included in one composition together with a source of chlorine such as an organic chloride, the flame colour tends towards white depending on the relative strengths of the band emissions. By adjusting the proportions of barium and strontium nitrates to 4 to 1 the flame becomes almost white and the luminosity is a maximum. The specific light-output of such mixtures is around 24,000 candle-seconds per gram. Minor adjustments to the proportions of the nitrates would doubtless produce a white flame. This type of illuminating composition is particularly suited to stores that may be subject to shock or rough treatment during combustion, since the burning layer is not readily displaced and the mixtures pellet well. The flame is steadier than that from sodium nitrate mixtures although it is not as efficient.

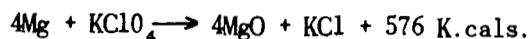
Barium peroxide is used as an oxidant in certain mixtures with magnesium which are virtually gasless and burn fiercely with small hot white flames. They are used principally as priming compositions and for ignition and combustion at high altitudes, since their rates of burning are least affected by variations in atmospheric pressure.

The reaction is represented by:-



and the stoichiometric mixture contains 12 per cent magnesium powder and produces 657 calories per gram.

Potassium perchlorate is used mainly in coloured signal compositions since it is also a source of Cl ions in the flame. The reaction is a straightforward oxidation-reduction process represented by:-



The stoichiometric mixture contains 41 per cent magnesium powder and produces 2,460 calories per gram.

Certain other oxidants are used with magnesium powder to produce special effects. Lead chromate, for example, is used to produce brown smoke, formed by its reduction to lead oxides, and iron oxide is used in thermite-like mixtures to produce slags of molten iron for incendiary effect. Oxidants are also mixed together for various reasons. The mixed oxidants may form more ignitable mixtures or more

fusible slags which do not choke the flame during combustion, or they may affect the colour or luminosity of the flame.

Several oxidants are barred from use with magnesium powder on grounds of hygroscopicity, the sensitiveness of the mixtures or the violence of combustion etc. Except in special cases, chlorates are never used because of the ease of ignition of the mixtures and the violent combustion that ensues. Permanganates and dichromates form very sensitive mixtures and are only used in small quantities. Nitrates of the heavy metals are readily reduced in solution by magnesium and mixtures containing them are unstable.

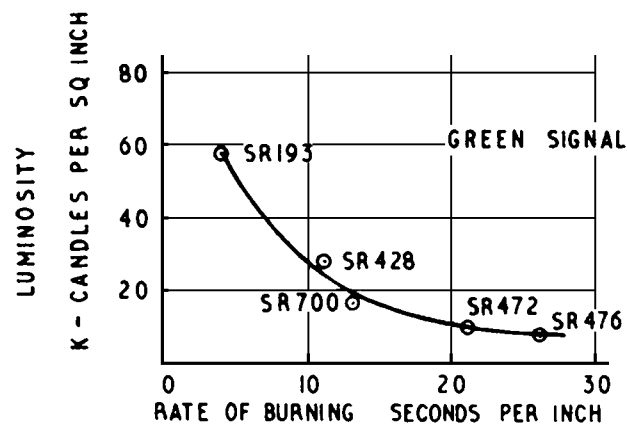
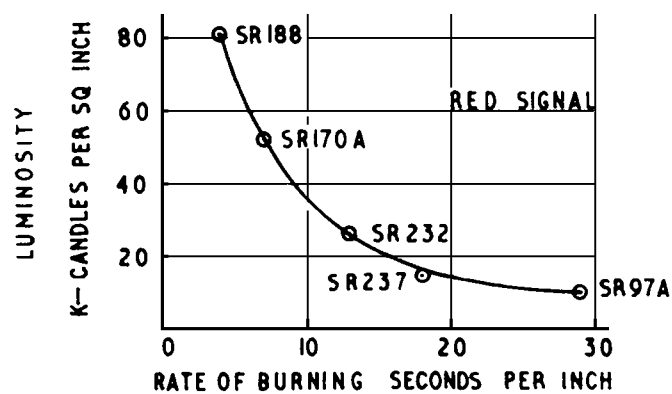
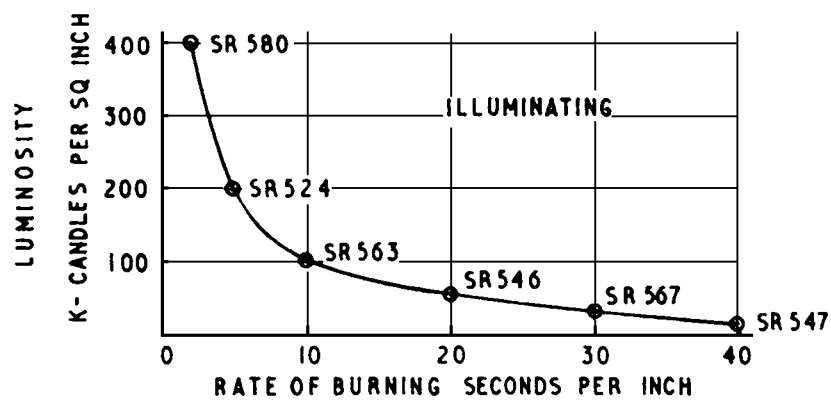


Fig. 3. Luminosity and Rate of Burning.

CHAPTER 4

ILLUMINATING AND COLOURED FLAME SIGNAL COMPOSITIONS - GENERAL PRINCIPLES

Illuminating and signal flame compositions must both provide steady sources of light; in the one case to illuminate targets for visual or photographic reconnaissance, and in the other to penetrate considerable depths of atmosphere as distinctive signals identifiable against adverse backgrounds. The stores in which they are used vary in size from reconnaissance flares to Very signals and in function from tracking guided missiles to revealing an intruder stumbling over a stretched wire.

BASIC REQUIREMENTS

In any light-giving store three basic requirements must be satisfied for it to function properly. They are (i) that it burns for the correct time, (ii) that it has the appropriate luminosity and (iii) that the colour of its flame is correct in hue and is as saturated as possible. Light suitable for illumination is yellowish-white or white in colour since the greatest luminosity is produced by compositions containing sodium or barium nitrates; signal flames red, green or yellow in colour are less intense on the whole than the equivalent illuminating flames.

The rate of burning and the luminosity of a composition are both closely linked to its heat of combustion. As would be expected, the faster burning mixtures evolve more heat and produce the brighter flames. The relation between the rate of burning and the luminosity of various compositions is shown graphically in figure 3. Illuminating compositions containing magnesium and sodium nitrate fall on a smooth curve in which composition SR 580, burning at approximately 2 seconds per inch, is at one end of the scale and composition SR 585, burning at 45 seconds per inch is at the other. The curve is hyperbolic in shape but the product of intensity and rate of burning is not quite constant, rising slowly from the fastest burning compositions to a maximum in the middle range (between 10 and 20 seconds per inch) and then falling off more rapidly as the slowest burning compositions are reached. The middle range of compositions, containing from 45 to 55 per cent of magnesium, burn the most efficiently with a light-flux per gram of composition of around 40,000-45,000 candle-seconds per gram. At one end of the curve composition SR 580 with 60 per cent magnesium has a specific light-flux of 28,000 candle-seconds per gram and at the other composition SR 585 with 26 per cent magnesium has a specific light-flux of 10,000 candle-seconds per gram.

This graphical relation is extremely useful in practice, since it shows the maximum luminosity for a given rate of burning that one can expect from current compositions, and a knowledge of it helps materially in formulating requirements. Broadly speaking, points above and to the right-hand-side of the curve represent compositions of an efficiency that has so far not been attained and may well be unattainable. Points below and to the left of the curve represent less efficient compositions that can always be produced if needed. It should be remembered that rates of burning and intensities vary somewhat from batch to batch and are to some extent dependent on the external conditions obtaining during combustion, so that the simple smooth line should strictly be replaced by a narrow band with somewhat indefinite edges.

Similar curves relating rates of burning to luminosity can be drawn for illuminating compositions containing barium nitrate and for red and green signal compositions. These are also reproduced in figure 3.

The luminosity of pyrotechnic compositions, depending as it does on the temperature of incandescent particles in the flame, is closely related to the rate at which heat is supplied to the flame i.e. to the rate of burning and the heat of combustion. Figure 2 shows the linear relation between the luminosity of magnesium-sodium nitrate compositions and their rates of heat evolution.

THE COLOUR OF PYROTECHNIC FLAMES

Spectroscopic analysis shows that all pyrotechnic flames have a very complex spectral composition. Spectra of illuminating and coloured signal flames are composed of three distinct elements. There is a general temperature continuum derived from the thermal excitation of solid and gaseous products of combustion and which is the main source of the white light that is always present. Next, there are complex systems of band-spectra derived from molecular emitters such as ionised oxides and chlorides. Finally, there are line-spectra derived from the atomic emitters magnesium, sodium, strontium etc.

White light is produced by several methods: (i) Increasing thermal excitation by raising the temperature. This is normally achieved by increasing the proportion of aluminium or magnesium and so increasing the rate of burning. (ii) Developing an extensive continuum such as that of sodium in emission. (iii) Exciting extensive band-systems such as that of BaO^+ . (iv) Exciting simultaneously two more or less complementary band-systems such as those of BaCl^+ and SrCl^+ .

Methods (i) and (ii) are employed in producing very intense illuminating compositions such as composition SR 580, method (iii) in mixtures of magnesium and barium nitrate such as composition SR 343, and method (iv) in compositions containing barium and strontium nitrates and a source of chlorine as in composition SR 595.

When sodium is introduced into a flame the yellow light is derived mainly from continuum that extends either side of the sodium doublet which, except with very small concentrations of sodium, is seen in absorption. With the high concentrations of sodium burning in an atmosphere of oxygen such as obtains in flames of illuminating compositions there is very strong emission from continuum extending from $5500\text{\AA}$ to $7000\text{\AA}$. The intensity of the emission appears to be connected in some little-known manner with the formation of NaH^+ ions in the flame, and their spectra can always be detected in flames from certain compositions. Hence, it has been found in practice that the presence of linseed oil products such as lithographic varnish in the composition leads to greater luminosity, presumably because they favour the formation of sodium hydride ions in the flame. It is noticeable that the spectral energy from the sodium continuum is very much less with binary mixtures of magnesium and sodium nitrate than with those containing magnesium, sodium nitrate and lithographic varnish or boiled linseed oil. The energy from the sodium continuum is additional to that emitted as general thermal radiation and the spectral-energy curve increases very sharply indeed to maxima on either side of the sodium doublet.

Red flames are produced by strontium compounds usually in the presence of chlorine, derived either from oxidants such as potassium chlorate or perchlorate or from the decomposition of chlorinated organic materials. The colour of the flame is derived from two distinct band-systems, one from strontium chloride ranging from $6200\text{\AA}$ to $6800\text{\AA}$ and one from strontium oxide ranging from $6000\text{\AA}$ to $6900\text{\AA}$. In addition, there are contributions from the potassium of the oxidant in the resonance lines $7699\text{\AA}$ and $7665\text{\AA}$. Calcium, if present as an impurity, may also contribute through the CaCl^+ system $5800\text{\AA}$ to $6380\text{\AA}$.

Green flames usually rely for their colour on the well-known band-system of barium chloride which ranges from $5050\text{\AA}$ to $5350\text{\AA}$. Spectrograms show band-systems in the orange and red regions from CaCl^+ and SrCl^+ which are usually present as impurities. They also invariably show the extensive band-system of BaO^+ ranging from $4000\text{\AA}$ to $8000\text{\AA}$. This system is always present in greater or lesser degree and its strength, relative to that of the chloride, increases with the intensity of the source. Thus the degree of saturation of green flames is diminished by (a) temperature continuum (b) orange and red emission from BaO^+ and (c) orange and red emission from CaCl^+ and SrCl^+ and (d) yellow emission from sodium. By careful treatment the impurities can be eliminated but the two main factors tending to degrade the colour remain. Both increase their effect with temperature and it is therefore not possible to produce good green flames of high intensity. Alternative emitters to BaCl^+ are not very promising although BO^+ , derived from elemental boron, boron carbide or boron nitride has been tried with varying success.

Blue flames rely for their colour on the band-system of CuCl^+ ranging from 4200Å to 4600Å and to weaker systems in the blue-green and green regions which are simultaneously developed. The oxidant and source of chlorine is usually potassium chlorate or perchlorate and leads to strong emission of the potassium resonance lines 7665Å and 7699Å. An additional source of chlorine is sometimes used in the form of mercurous chloride which, however, contributes nothing from the mercury spectrum. The energy emitted by pyrotechnic sources and the sensitivity of the human eye are both low in the blue region of the spectrum and blue flames can never be intense. Moreover, the saturation of a blue flame is much reduced by relatively small proportions of light from secondary emitters i.e. impurities and the potassium in the oxidant as well as the weaker systems of longer wavelength from CuCl^+ itself. Unfortunately there is no satisfactory alternative either to potassium salts as oxidants or to CuCl^+ as emitter.

INGREDIENTS

The essential ingredients of illuminating and signal compositions are a fuel, an oxidant, a pelleting or binding material, a means of modifying the rate of burning and a means of colouring the flame.

FUELS

Most modern illuminating and signal compositions contain magnesium powder as the main fuel because it generates more light than any other material. The emphasis on high luminosity in all modern pyrotechnic stores is very necessary because of the greater distances over which they must be observed. Magnesium powder is preferred to aluminium powder for this reason in spite of the fact that compositions containing the latter are more stable and have a longer storage life. Magnesium powder is also preferred for signal compositions in spite of the difficulties in producing coloured flames, particularly green, described in the previous section. The majority of coloured signals are now designed for observation during day or night, and the less intense but more saturated light from non-magnesium signal compositions that were used at night are no longer required. Fuels for low-intensity night-signal compositions are usually antimony, antimony sulphide, arsenious sulphide or sulphur for white signals and acaroid resin, shellac or lactose for those of other colours. Aluminium oleate is used in certain blue signal compositions.

OXIDANTS

Oxidants in pyrotechnic compositions are frequently called upon to perform functions in addition to that of providing oxygen for the fuel. Their principal functions may be enumerated as follows.

- (i) To provide oxygen in which to burn the fuel. In the case of illuminating and signal compositions the proportion of fuel is frequently different from that required by stoichiometry and atmospheric oxygen is used to burn excess metal powder. The reason for this practice lies in the consideration of the rate of burning of the composition. The rate of burning of a stoichiometric mixture of magnesium powder and an oxidant will have a certain value depending principally, under normal conditions, on the size, shape, specific surface, and state of surface oxidation etc. of the metallic particles, on the chemical characteristics and the particle-size of the oxidant, and on the degree of consolidation and other physical aspects of the mixture. Divergence from these proportions changes the rate of burning, making it slower when the proportion of magnesium is less than stoichiometric and faster when it is more. The addition of other ingredients also changes the proportion or restricts the amount of available oxygen and hence influences the rate of burning. Thus variation in the proportions of fuel and oxidant is a direct means of modifying the rate of burning.
- (ii) To modify the colour of the flame by providing atomic or molecular emitters. Sodium oxysalts supply the sodium ions responsible for the continuum that provides high luminosity, barium and strontium oxysalts provide the corresponding cations necessary for the formation of spectral emitters in the flames, while chlorates and perchlorates provide the corresponding chloride anions. Oxidants such as barium peroxide may supply spectral band-systems and general thermal continuum that contribute mainly to providing white light.
- (iii) To modify the products of combustion and so affect the smoothness and regularity of combustion. Compounds of potassium have lower temperatures of melting and decomposition than those of barium, and potassium nitrate is sometimes added to barium nitrate in white signal compositions in order to make the compositions more readily ignitable and smoother burning. The mixed nitrates form a eutectic with lower melting and decomposition temperatures than those of barium nitrate alone and the slag resulting from combustion is more fluid. Also, the violet colour of the potassium flame neutralises the greenish tinge in the barium flame. The lower luminosity due to the presence of potassium may seriously affect the characteristics of the flame and such mixtures are therefore not used in illuminating compositions. Mixtures of sodium nitrate and barium nitrate are used in some yellow signal compositions.

PELLETING OR BINDING MATERIALS

The ability of mixtures of powdered pyrotechnic ingredients to form strong pellets when consolidated under pressure is closely related to the shape and size of their particles. Generally speaking, cut magnesium powder with its flattened, irregularly shaped particles and oxidants with elongated crystalline form pellet better than blown magnesium powder and oxidants with cubic crystals. The particles of the latter form bridges under pressure and the pellets are not so resistant to shock and rough usage. The pelleting ability can be improved considerably by the addition of waxes, drying oils, varnishes or resins which fill the interstices and bind the particles together by adhesion. As is usual with all pyrotechnic ingredients these pelleting materials perform more than one function in a composition and the choice of any one particular material is often the result of weighing-up pros and cons quite unconnected with its pelleting power.

The principal functions of pelleting materials are:-

- (i) To increase the cohesion between the particles of the ingredients when consolidated under pressure
- (ii) To protect the particles of magnesium powder from corrosion by the moisture and the electrolytes present in the mixture
- (iii) To modify the rate of burning
- (iv) To enhance the luminosity or colour of the flame
- (v) To modify the sensitiveness of the mixture to ignition by friction or blows.
- (vi) To enable rigid pellets to be obtained with lower pressing loads.

The binding material is invariably incorporated with the magnesium powder by stirring in liquid oils and varnishes or molten waxes in order to coat the particles as thoroughly as possible. The success of this operation depends on the specific surface of the powder, on the viscosity of the fluid and on its proportion in the composition. Obviously, a fine magnesium powder will absorb the binding material more completely than a coarse one and a small proportion is more difficult to incorporate than a larger one. To facilitate uniform mixing, the binding material is sometimes dissolved in a volatile solvent.

Pelleting materials fall into four principal groups, waxes, oils, resins and rubbers. Table 6 shows the broad effect that some of these materials have on important properties of flare and signal compositions. In studying the table the correct interpretation must be given to the terms "good", "average" and "poor" relevant to the property being studied. Thus a "good" effect on the rate of burning refers to a pronounced ability to slow it down, a good effect on the sparkiness of the flame refers to a relative absence of sparks and a good effect on the sensitiveness refers to the ability to reduce the sensitiveness to friction and impact. The magnitude of an effect depends, of course, on the proportion of the pelleting material present, often, but not always becoming more pronounced as the

TABLE 6 PROPERTIES OF SOME PELLETING MATERIALS
(G = good effect, A = average effect, P = poor effect)

Property Material	Flow properties of composition	Non-Segregation of ingredients of composition	Pelleting power	Retardation of Rate of Burning	Sparkiness of Flame	Effect on efficiency of composition	Ignitability of Composition	Sensitiveness of Composition	Waterproofing power of materials	Remarks
Paraffin Wax	A	A	G	A	G	A	A	A	P	Applied molten to magnesium powder
Beeswax	P	G	G	G	G	G	P	G	G	" " " " "
Carnauba Wax	G	A	A	G	A	A	A	G	A	" " " " "
Candelilla Wax	A	G	G	A	G	A	P	G	G	" " " " "
Chinese Wax	G	A	A	A	A	A	A	G	A	" " " " "
Boiled linseed oil	G	P	P	A	G	A	P	A	A	
Lithographic oil	P	G	A	G	G	G	P	G	G	
Tung oil	P	G	A	A	A	A	P	A	A	
Caster oil	P	A	A	G	A	A	P	A	A	
Shellac Resin	G	P	A	P	P	P	G	P	A	Applied as spirit varnish to magnesium powder
Acaroid Resin	G	P	P	P	A	P	G	P	G	" " " " " "
Bakelite Resin	G	P	A	P	P	A	G	P	G	" " " " " "
Polyester Resin	G	A	G	P	A	A	A	A	G	Applied as the liquid monomer to magnesium powder and cured after incorporation of the other ingredients
Chlorinated Rubber	A	A	G	P	G	G	G	P	G	Gelled by the addition of a suitable solvent to the composition
Thiokol Rubber	P	G	G	G	G	A	P	G	G	Applied as the liquid monomer to magnesium powder and cured after incorporation of the other ingredients
Silicone Rubber	A	G	G	A	G	A	P	A	A	" " " " " " " "

proportion is increased. The comparisons in the table are for equal proportions. Although beeswax appears to be particularly outstanding in this table, (it is one of the best desensitisers of explosives known and its retarding effect on the rate of burning amounts to about one second per inch for every one per cent of beeswax added) it is not often used in pyrotechnics. Other pelleting materials are used for quite the opposite effect. For example, acaroid resin has little effect on the rate of burning but tends to increase the ignitability of a composition and is often used in igniter compositions. Lithographic varnish is used in most illuminating compositions because, among other properties, it has a large retarding effect on the rate of burning and generally improves the specific light-flux.

Among the new materials that are coming into more extensive use polyester resin and thiokol rubber are the most promising. Both are water-resistant and have many of the desirable properties of pelleting materials but, whereas the former makes a very strong rock-like pellet after curing, the latter makes one that is flexible and resilient. It is claimed that polyester resin mixtures require smaller consolidating pressures than those made with other pelleting materials to produce the same density of loading. Thiokol rubber mixtures can be injected into containers without consolidation and cured in situ by heating.

The characteristics of some of the more important pelleting materials are described in the following paragraphs.

Paraffin wax. Used with barium nitrate but not with sodium nitrate since it does not waterproof magnesium powder very well and moisture in the composition must be kept to a minimum. It has no very strong effect on the rate of burning and is now used only in a few compositions, such as composition SR 343A.

Beeswax. Beeswax is a first-class material in most respects but it is not used to any great extent in pyrotechnics because of the demand for it in desensitising high-explosives. It has been used in tracer compositions and in a desensitised flare composition SR 557, which was much less ignitable than composition SR 562 when struck by small arms ammunition or shell-fragments. Its effect on the rate of burning is similar to that of lithographic varnish.

Lithographic varnish. (Lithographic oil or stand oil) is a heat treated linseed oil which oxidises and dries slowly. It is used in almost all flare compositions and forms a slightly tacky mixture that pellets well but which does not pour well. It retards rates of burning strongly (about 2 seconds per inch for each additional 1 per cent of varnish), desensitises compositions and is a good waterproofing material for magnesium powder. Lithographic varnish oxidises slowly in air and generates some heat especially in the early stages of exposure. Hence loose compositions containing it are not stored in bulk immediately after mixing but are exposed in layers to a dry atmosphere for 48 hours to enable most of the oxidation to take place under conditions where a dangerous accumulation of heat cannot arise. Oxidation is not complete after this period but the compositions can be stored in bulk or consolidated without risk. It has been found that the drying process always requires some oxidant to be present in order to proceed at a satisfactory rate.

Boiled linseed oil is also a heat-treated linseed oil in which lead or manganese oxides (preferably the latter for pyrotechnic use) have been dissolved during the heating process. This oil oxidises and dries hard in eight hours and compositions containing it pour very readily. The oil is therefore used especially in signal compositions which are poured into small, narrow star-containers prior to consolidation. The rapid oxidation liberates considerable heat and the temperatures of freshly made compositions have been observed to rise to 80°C or more in the first few minutes. It is therefore even more essential for these compositions to be spread out in layers after mixing.

Since boiled linseed oil dries harder than lithographic varnish, compositions containing it flow better, tend to segregate more, are more sensitive to friction and are possibly more ignitable than those containing lithographic varnish. Protection against corrosion is no better.

Shellac, acaroid resin and bakelite resin are usually applied to magnesium powder as spirit varnishes and dried before mixing with other ingredients. Since they all dry completely on the magnesium, compositions containing them are similar in that they flow easily, their ingredients tend to segregate, they burn faster, they are more sensitive to friction and more ignitable than equivalent compositions containing linseed oil. They do not pellet so well. Shellac is porous to moisture but both acaroid resin and bakelite resin protect magnesium satisfactorily in spite of the fact that acaroid resin is very hygroscopic and also flakes off the metal particles readily. Compositions containing shellac and bakelite resin tend to burn sparkily, the sparks consisting of small agglomerates of composition ejected from the burning surface. The resins can be plasticised by adding small quantities of dibutyl phthalate to the varnishes. They are then more elastic, pellet better and burn more slowly with fewer large sparks.

Chlorinated rubber powder has been used successfully as a pelleting medium when it has formed one of the main ingredients of compositions as a chlorine carrier. By moistening the mixed composition with a suitable solvent the chlorinated rubber is gelled and becomes adhesive. Pellets formed in this way are very strong indeed. Since, after gelling it is difficult to evaporate all the solvent, those with low vapour pressures such as the alkyl phthalates are often used and remain permanently in the composition. The rate of burning is slowed down by this addition.

Polyester resin is a more recent pelleting medium. It is mixed with the composition in the form of a liquid monomer together with a suitable organic peroxide by which it is polymerised to a solid plastic in situ. By varying the proportions of monomer to catalyst the polymerising process can be controlled to a very slow rate which allows the composition to be consolidated in its container before becoming hard. In this way a very strong rock-hard pellet is formed and since the resin is waterproof it adequately protects magnesium powder from corrosion. Compositions containing polyester

resin are similar in most respects to those containing lithographic varnish. Similar compositions have been made with styrene monomer and a suitable catalyst, and with isobutyl crotylidene cyanacetate which only requires the degree of alkalinity supplied by magnesium powder to polymerise it.

Thiokol rubber formed within the composition from the monomer and a cross-linking agent is being satisfactorily exploited in plastic pyrotechnics (see chapter 14). The proportion of rubber is high (15-20 per cent) compared with the 3 to 7 per cent of pelleting material usually employed, and these compositions can be looked upon as heavily loaded rubbers rather than mixed powders held together with small additions of adhesive. The compositions are extruded in a semi-fluid state into moulds or containers and cured to a rubber-like material by heating at 70°C for 24 hours. They are resilient, relatively insensitive to friction and impact and are quite water-proof. Their pyrotechnic characteristics are similar in many respects to those of the consolidated powder type.

MODERATING MATERIALS

Whenever a third ingredient, which is neither a combustible metal powder nor a powerful oxidant, is added to a binary mixture of magnesium powder and oxidant, it usually has the effect of cooling the flame and retarding the rate of burning. Some materials are more effective than others and it is generally found that carbonaceous substances, which generate gases other than oxygen on combustion are the most effective. The pelleting materials described in the previous section come into this category and their influence must be taken into account. However, if a desired result cannot be obtained with pelleting materials alone, further ingredients are added. Ingredients, included to produce specific effects, are called moderating materials or moderators. They may be added to retard the rate of burning, to improve the smoothness and efficiency of combustion, or to modify the colour of the flame.

Most moderators have been adopted as a result of trial and error, and some are much more effective in particular aspects than others. Many of them are naturally occurring products such as sugars, starches, cellulose and resins, but some of them are very hygroscopic and are responsible for the deterioration of compositions in storage. There is therefore greater discrimination in the choice of moderators for current compositions and non-hygroscopic alternatives have to be found for what are otherwise perfectly satisfactory ingredients.

In addition to purely carbonaceous materials, a number of organic salts of the alkali and alkaline earth metals are used to retard the rate of burning of illuminating compositions and also to supply flame colorants. Oxalates are the most commonly used and their effect depends upon the cooling effect of the carbon oxides produced during thermal decomposition and on the oxide slags which modify the

nature of the burning surface. Other organic salts such as formates and citrates produce similar effects in varying degrees. Calcium carbonate has also been used.

When the colour of the flame is one of the primary considerations attention must be paid not only to the main colouring power of the moderator, whether it is due to barium or strontium ions or chloride ions, but also to the increase in thermal radiation which is brought about by solid products of decomposition. The addition of barium salts invariably increases the intensity of orange and red spectral-band systems that tend to mask the green colour of the flame. This becomes worse the higher the temperature and carbonaceous fuels are therefore added to cool the flame. The best fuels for this purpose are carbohydrates such as sugars, starches and cellulose. Their decomposition produces water as well as carbon dioxide. Lactose, sucrose and starch are the principal additives but, because starch is very hygroscopic, it is now being replaced by the alcohol mannitol which adequately performs the same functions and is non-hygroscopic.

In the case of illuminating compositions, any increase in light due to radiating oxides may be an advantage and calcium oxalate is frequently added for this purpose. The decomposition of the salt has a twofold effect, since it slows down the rate of burning and the gases evolved tend to expand the flame so that, up to a point, the luminosity is increased in spite of a reduction in temperature.

Moderators employed to colour the flame include sodium nitrate or oxalate for yellow, barium nitrate, chlorate or oxalate for green, strontium nitrate, oxalate or carbonate for red and copper oxychloride or basic carbonate for blue. The energy emitted in the blue spectral-bands is weak and blue signal compositions must not contain magnesium or the blue emission will be completely masked. Blue signal flames are therefore very feeble. Since green, red and blue emissions are derived from the ionised chlorides of the respective metals, there must also be an available supply of chlorine. This is usually achieved by including potassium perchlorate in the oxidant component and by adding such chlorinated organic materials as polyvinyl chloride, chlorinated rubber, chlorinated paraffin wax, hexachlorobenzene, chlorinated diphenyls etc. The degree of saturation of the flame colour is governed entirely by the relative intensities of the dominant wave-length and white light from thermal radiation. The quality of the signal flame is the result of a compromise between various opposing factors, namely, (a) raising the temperature to increase the intensity, (b) lowering the temperature to reduce the thermal radiation to a minimum, (c) increasing the concentration of chloride ions in the flame, etc. Good colours in flames, especially green flames, require a careful balance of effects and a careful choice of ingredients.

Table 7 gives an analysis of the functions of ingredients of typical illuminating and signal compositions.

TABLE 7

Ingredient	Function
(1) <i>Illuminating Composition</i>	
Magnesium powder	Fuel produces heat and temperature continuum for intense white light.
Sodium nitrate	Oxidant for magnesium. Complete reduction produces Na ions in flame and hence the sodium-continuum to make the light yellowish white.
Lithographic varnish	Binding or pelleting material. Waterproofs magnesium powder. Retards the rate of burning, provides H-ions to flame thus increasing the sodium-continuum and the luminosity.
Calcium oxalate	Reduces the rate of burning (a) by reducing the oxygen balance and (b) by cooling. Increases the luminosity by expanding the flame and possibly by providing incandescent oxide particles.
(2) <i>Green Signal Composition</i>	
Magnesium powder	Fuel produces heat and luminosity but white light from the temperature-continuum is a disadvantage.
Barium nitrate	Oxidant for magnesium. Provides Ba ⁺ ions in flame for the formation of BaCl ⁺ ions, the green-band emitters. BaO which is formed also emits in wavelengths which tend to mask the green.
Potassium Perchlorate	Oxidant for magnesium. Assists in producing a fusible slag. Provides chlorine to the flame for the production of BaCl ⁺ ions. K-lines in spectrum help to modify the quality of the flame-colour.
Boiled linseed oil	Binding or pelleting material waterproofs magnesium, not tacky and the composition has good flow-properties. Retards the rate of burning to a small degree.
Polyvinyl chloride	Provides chlorine to flame. Retards the rate of burning. When suitably gelled it also acts as a pelleting and waterproofing material.
Mannitol	Retards the rate of burning, cools and expands the flame and so improves both colour and luminosity.

REFERENCES

Spectrographic observations on Pyrotechnic Flames.
Barrow and Caldin. Proc. Phys. Soc. Reprint.

CHAPTER 5

ILLUMINATING COMPOSITIONS

Illuminating compositions, that is compositions that burn with a white or yellowish-white flame of high intensity, are to be found in one of two roles, namely, to illuminate areas of land or sea for observing visually or photographically targets within the areas, or to observe the trajectories of missiles in flight. In the first role they form the pyrotechnic filling of flares projected over the area of observation with or without parachutes, including reconnaissance flares dropped from aircraft, flares ejected from gunshell and rockets, and small flares or stars fired from hand-held pistols. They also form the filling of flares burnt at rest on the ground to provide illumination for nocturnal actions or to illuminate intruders. In the second role they form the filling of a variety of flares attached to missiles in order to follow their flight visually or photographically over long distances.

The manner in which the illuminant is used determines the particular aspects needing special attention during development. For example, the fillings of flares subjected to severe stresses in shell stars, in freely falling flares or in those attached to missiles must have the greatest possible mechanical strength, while the fillings of tracking flares must also be capable of burning in rarefied atmospheres. Compositions for illuminating stars, burning for a few seconds only, must produce as much light as possible to facilitate observation or recognition during the short period of time available.

The first stage in the development of any illuminating composition is to study the requirements relating to the functioning of the flare-candle. These may be enumerated as follows:-

1. The precise use to which the flare is to be put, whether for observation of targets or for tracking missiles
2. The altitude at which the flare is required to function or to reach during functioning
3. The range at which the flare is to be observed in relation to the conditions of visibility likely to obtain and to any optical aids that may be used, or to the minimum photographic exposure necessary.
4. Where the flare is to be used to illuminate targets from above, it is necessary to know the area under observation, the illumination needed at the margin of the area, the height at which the flare ignites, the rate of fall of the flare on its parachute and the time required for observation.
5. Possible effects of motion either of translation or of rotation during combustion.
6. The time of burning required and the intensity of the flare calculated to satisfy those aspects set out in items 1 to 5.

RESTRICTED

7. The material of the candle-case
8. The dimensions of the flare-candle
9. The degree of shock and rough treatment the filling is expected to withstand
10. The ambient conditions of temperature and humidity in which the flare may be stored and their effect on its useful life in service.

The conclusions reached after considering all these aspects may be far from compatible with one another. For example the overall dimensions of a flare necessary to give the time of burning and the intensity, or, the desired range of observation of a tracking flare may be too great, especially after due allowance has been made for the diminishing effect of both altitude and atmospheric scattering of light on its intensity.

The two principal considerations in the development of an illuminating composition are its rate of burning and its specific intensity. From the first is obtained the length of filling to give the time of burning requirement and from the second the area of burning surface necessary to provide the candlepower. Let us consider how they may be affected by environmental changes.

The rate of burning and the intensity of a flare composition are both affected by the pressure of the ambient air, burning more slowly and less brightly as the pressure is reduced. This variation in combustion with pressure is exhibited by all pyrotechnic compositions to different degree depending on the volume of their gaseous products of combustion. The rate of burning, R , at a particular ambient pressure is related empirically to the rate of burning at normal atmospheric pressure, R_1 , by:-

$$R P^n = R_1$$

where the rates of burning are expressed in seconds per inch, and P is expressed in atmospheres. " n " is a fractional index varying from approximately 0.1 to 0.6 depending on the type of composition and the amount of gas that it generates while burning. The precise value of n must be determined from the rates of burning at two or more different pressures. The rates of burning of selected compositions at various pressures are shown in Fig. 4.

For many illuminating compositions in service the value of n lies between 0.22 and 0.38. This means that if the ambient pressure changes by a factor of 10 the rates of burning will change by factors ranging between 1.66 and 2.4. Thus, composition SR 562, which may have a rate of burning at 1 atmosphere pressure of $R_1 = 16.8$ seconds per inch and a value of $n = 0.26$, will burn at a rate of 31 seconds per inch at 0.1 atmosphere pressure, (53,000 feet altitude) and at 9.2 seconds per inch at 10 atmospheres pressure.

Combustion becomes more difficult with decreasing pressure and eventually most compositions fail to burn completely. The altitude at which this occurs depends on the nature of the ingredients and particularly on the characteristics of the oxidant. Compositions

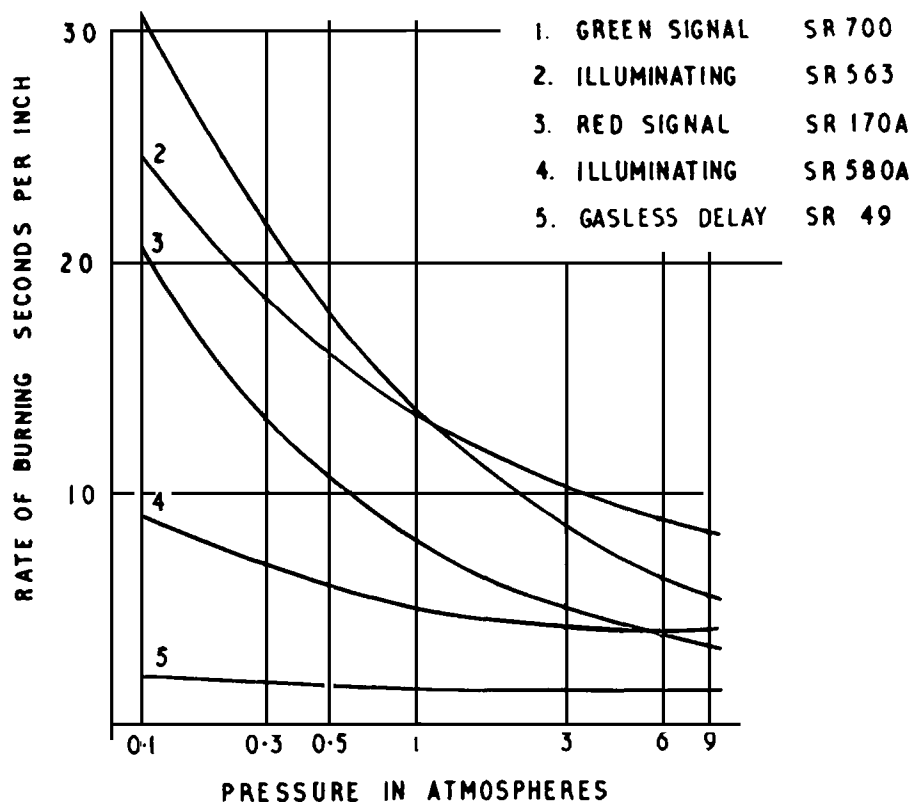


Fig. 4. Variation of rate of burning with ambient pressure.

containing strontium nitrate cease to burn around 80,000 feet, and those containing sodium nitrate or barium nitrate at 90,000 feet. Compositions containing much gas producing fuel such as calcium oxalate, starch and other organic materials fail to burn at lower altitudes than those containing little or none. For combustion at very high altitudes it is necessary to reduce the gaseous products to a minimum by using barium peroxide as the oxidant in a binary mixture with magnesium powder. As a composition burns more slowly the flame receives less energy, its temperature falls, and it becomes less bright. The specific intensity of illuminating compositions falls off rapidly with increasing altitude and at 50,000 feet it may be only one-sixth of its value at ground level.

Although any reduction in ambient pressure tends to affect combustion, the effects only become serious at altitudes greater than 30,000 feet. Hence, stores functioning below this height may be considered to be burning at ground-level so far as their rates of burning and intensities are concerned. This applies to illuminating stars, shell stars, most parachute flares and the tracking flares of missiles with low trajectories. Above 30,000 feet due allowance for the reduction in both rate of burning and luminosity must be made in any pre-design calculations, particularly for tracking flares.

Another factor affecting the rate of burning and the luminosity of a flare composition is its motion relative to the surrounding atmosphere. Here, knowledge is less precise, but rapid motion through the air, whether translational as with tracking flares or rotational as with shell-tracers, tends to accelerate the rate of burning. The luminosity of tracking flares is considerably reduced in flight by cooling, and measurements have shown that a velocity of 600 knots at ground level reduces the light to about one third. A similar reduction occurs in rarefied atmospheres.

Having discussed some of the more important factors that affect the functioning of a flare, it is now necessary to examine the use to which flares are put and the effect of the environment on observation, whether visual or photographic.

Flares used for observation fall into two groups, namely, tracking flares that are attached to guided missiles and parachute flares which move comparatively slowly and which illuminate objects beneath them.

The problem of observing tracking flares resolves itself into that of observing a receding point-source of light against a background, the brightness of which depends on the time of day or night and the presence or absence of celestial bodies. The problem also involves the scattering of light from the source by the atmosphere through which it passes.

The threshold illuminance visible against sky backgrounds of different brightness has been studied by several investigators whose results, plotted on graphs, generally agree amongst themselves. As an example, a flare, in order to be seen against a mid-day sky with a brightness of 400 candles per sq. foot, must produce an illuminance at the observer of at least 500 candles per sq. mile. This illuminance corresponds to that from a flare of 500 C.P. seen from 1 mile, one of 2000 C.P. seen from 2 miles or one of 8000 C.P. seen from 4 miles etc. Anything brighter than this would be seen under these conditions. If the use of optical aids is stipulated, their effect must be included in the calculations. Likewise, any reduction in illuminance brought about by atmospheric scattering must be allowed for as far as possible.

From what has been said the estimation of the intensity necessary to satisfy service requirements of tracking flares is a complicated process and may involve reference to original papers. It is possible that the size of the flare needed to give the calculated intensity is too large, and a compromise has to be made between optical requirements and physical dimensions.

The intensity of a parachute flare necessary to illuminate a circular patch of ground to a specified degree can be calculated by simple optics. The candlepower (C) of the flare, its height (H) and the radius of the circle (R) illuminated at its periphery to the required illuminance (I) are related by the following equations

$$C = I \frac{(R^2 + H^2)^{3/2}}{H} \quad \text{or} \quad R^2 = \left(\frac{CH}{I} \right)^{2/3} - H^2$$

where R and H are measured in feet, C in candles and I in foot-candles. Often, the illuminance at the periphery and the radius of the area to be illuminated are specified and C and H can be chosen to suit either the dimensions of the flare, if stated, or any special features of the store.

For given values of C and I there is an optimum value of H for which R is greatest. The relations for optimum conditions are:-

$$H_o = 0.4387 \sqrt{\frac{C}{I}}; R_o = \sqrt{2} H_o = 0.6203 \sqrt{\frac{C}{I}}; \frac{C}{I} = 5.195 H_o^2$$

In general, it is convenient to arrange for the falling flare to reach its optimum height by the time half of it has burnt.

The foregoing paragraphs indicated how the specific intensity and the rate of burning needed to satisfy the conditions laid down in a requirement (or the best possible compromise of them) are calculated. It is now necessary to see how a composition having these properties can be developed.

The specific intensity and the rate of burning of an illuminating composition were seen in chapter 4 to be interdependent in a manner expressed by the curves shown in fig. 3. This interdependence provides the practical limitations to current fillings in the sense that brighter compositions can only be produced by making them burn faster, and faster burning compositions require a greater length to accommodate a given time of burning. Within these limitations development can proceed in the manner now to be described.

The three basic ingredients of modern illuminating compositions are the fuel, magnesium powder, the oxidant, which can be the nitrate of sodium, strontium or barium or a mixture of them, or barium peroxide, and one of the pelleting materials such as lithographic varnish, acaroid, bakelite or polyester resins or thiokol rubber. Normally, the minimum proportion of pelleting material required to ensure good consolidation is four per cent, but as little as two per cent has been used on occasion. Any pelleting material in excess of four per cent will progressively reduce the rate of burning, lower the intensity and cause the flame to become more orange in colour and sparky. How much of it can be tolerated will depend on the particular material. For example, the limit for lithographic varnish is about 6 per cent whereas up to 10 per cent polyester resin can be used without serious effects. Much depends on the type of magnesium powder, the coarser the powder the less of the pelleting material can be tolerated before

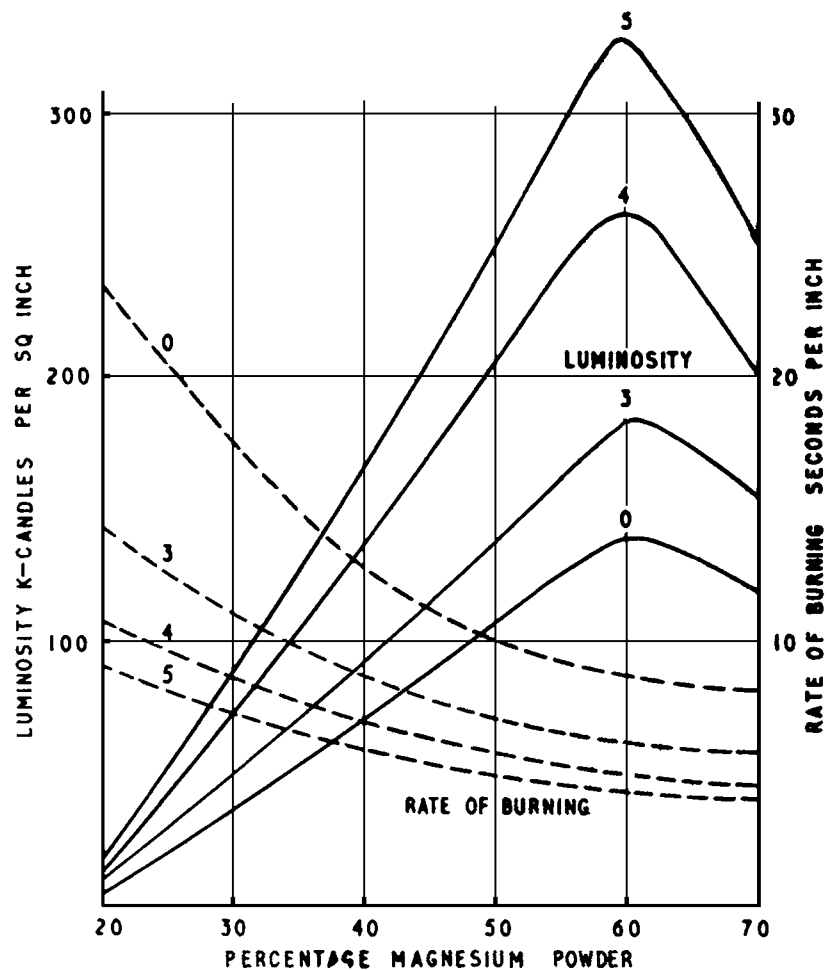


Fig. 5. Variation of Luminosity and Rate of Burning with Grade and Proportion of Magnesium Powder in Magnesium-Sodium Nitrate Compositions.

the flame becomes inefficient. The remainder of the composition is divided between the fuel and the oxidant in the first instance.

For a flare composition burning at low or medium altitudes, it is not essential that the proportion of fuel to oxidant be exactly balanced according to stoichiometry, since any excess fuel will burn in the surrounding air. However, there are practical limitations to this

since it has been found that compositions with proportions of magnesium powder much in excess of 60 per cent burn irregularly with large sparks and are inefficient.

The effect of the grade of magnesium powder and the particle-size has been indicated in Chapter 2, and the changes that can be expected by varying both the grade of magnesium powder and its proportion can be seen in the curves shown in Figure 5. Faster rates of burning and higher intensities are obtained with the finer grades of magnesium powder and with increasing proportions. It is seen that the maximum intensity is reached with about 60 per cent of fuel. The lowest practical proportion of fuel to use in a composition is about 20 per cent. If this does not reduce the rate of burning sufficiently a moderator must be added in place of some of the oxidant.

The principles thus briefly outlined can be illustrated by taking one particular composition and observing the changes that occur when ingredients and proportions are varied. It should be remembered that (a) The rates of burning quoted are not invariable, because of slight variations in ingredients, in the degree of mixing and consolidation of the composition, and in the conditions of burning the flares and (b) that, in general, intensities vary with the rates of burning in the manner indicated by the curves in figure 3.

Composition SR 563 contains 50 per cent Magnesium powder, Grade O, 4 per cent lithographic varnish, 46 per cent sodium nitrate, and burns at 10 seconds per inch with a specific intensity of 100,000 candles per square inch. If the grade of magnesium powder is changed to Grade 3 the rate of burning increases to about 7 seconds per inch, Grade 4 changes it to about 5.5 seconds per inch and Grade 5 changes it to about 5 seconds per inch. Atomised magnesium powder which has an even greater specific surface than that of the finest cut grades of powder causes the composition to burn faster still.

Returning to the original composition, the proportion of magnesium powder, Grade O, can be varied at the expense of sodium nitrate. A mixture containing 25 per cent fuel burns at about 22 seconds per inch, one containing 40 per cent burns at 14 seconds per inch and one containing 60 per cent burns at 9 seconds per inch.

By substituting shellac for lithographic varnish in composition SR 563, its rate of burning is accelerated to about 8 seconds per inch and with acaroid resin it becomes 6 seconds per inch.

Finally, the proportion of pelleting material can be varied. A change of one per cent of lithographic varnish changes the rate of burning by almost 2 seconds per inch, and by increasing the proportion of lithographic varnish in composition SR 563 from 4 to 7 per cent at the expense of the oxidant, its rate of burning decreases to about 18 seconds per inch.

Thus by suitably varying the proportions in the 3-component system Magnesium powder - pelleting material - sodium nitrate it is possible to produce compositions whose rates of burning and specific intensities range from 1.7 seconds per inch and 450,000

candles per sq. inch on the one hand, to about 25 seconds per inch and 8,000 candles per sq. inch on the other. These compositions are not equally efficient and those burning slower than 12 seconds per inch fall off in efficiency as the rate of burning decreases. In order to maintain the efficiency as high as possible when burning slowly, it is necessary to replace more of the oxidant by a moderating material.

The commonest, and by far the most effective moderating material used in illuminating compositions is calcium oxalate. The salt occurs in the form of the monohydrate and when heated it breaks down into water, carbon monoxide, carbon dioxide and calcium oxide. The gases have the effect of expanding and cooling the flame and calcium oxide adds to the thermal radiation by its incandescence. The retarding effect on the rate of burning is well marked, and the net effect of adding it to a mixture is to slow down combustion without seriously reducing the intensity.

This beneficial effect is observed with additions of up to 12 per cent of calcium oxalate. Further addition leads to degradation of the flame and increased slagging of the burning surface so that combustion becomes progressively inefficient and the flame becomes sparky and orange in colour.

Some idea of the effect of calcium oxalate is seen in table 8 in which composition SR 563 is metamorphosed into composition SR 562, the filling used in most reconnaissance flares.

TABLE 8 THE EFFECT OF REPLACING SODIUM NITRATE BY CALCIUM OXALATE IN FLARE COMPOSITIONS

	Composition SR 563				Composition SR 562
Magnesium powder, Grade O	50%	50%	50%	50%	50%
Lithographic varnish	4%	4%	4%	4%	4%
Sodium nitrate	46%	43%	40%	37%	35%
Calcium oxalate	0%	3%	6%	9%	11%
Rate of Burning seconds per inch	11.0	13.1	14.8	16.0	17.3
Specific intensity Candles per square inch	112,000	106,000	77,500	68,400	64,200
Specific light-flux Candle-seconds per gram.	40,800	45,000	36,600	35,100	35,200

The addition of calcium oxalate progressively reduces the rate of burning and diminishes the specific intensity of the composition but a small addition of some 3 per cent actually makes the composition burn more efficiently.

Barium and strontium oxalates produce similar effects, modified in proportion to their relative molecular weights. Sodium oxalate has a smaller retarding influence, presumably because of the volatility of sodium oxide.

Other organic salts of calcium also retard the rate of burning but only the tartrate and the formate approach the oxalate in effectiveness. Kaolin and precipitated chalk have been used as alternatives to calcium oxalate in wartime but they are not nearly so effective.

The only other modifying material that has been used to any extent in illuminating compositions is ivory-nut powder, obtained from the corozo nut of Ecuador. Although this material is very hygroscopic, retaining 14 per cent moisture, there is little evidence of any adverse effect on the stability of compositions. However, since it has now become difficult to obtain, it has been replaced by mannitol, a hexahydric alcohol, which is non-hygroscopic and equally effective as a retardant.

The relations between the various ingredients of illuminating compositions and the burning characteristics that they produce are shown graphically in Figure 6.

The diagram shows the effect of various materials used to produce different rates of burning in SR compositions. The ranges of the various components frequently overlap and there are alternative ways of changing the rate of burning, since there are no sharp boundaries where one component is effective and another is not.

The foregoing paragraphs describe the general principles governing the development of flare compositions for all purposes. Flare compositions used under special conditions must receive additional considerations.

Tracking flares may be required to burn in rarefied atmospheres where ignition and combustion are difficult. Since all compositions burn more slowly at altitude, the specified characteristics will only be obtained with a composition that burns faster at ground level. Experience has shown that in order to burn satisfactory at altitude a flare composition must have few ingredients and must be as gasless as possible. This reduces it to three components at the most and possibly to two, i.e. to magnesium powder, oxidant and perhaps a pelleting material.

Flares that are to be subjected to shock or to impact with the ground while burning are liable to be extinguished by the breaking up of the burning layer. Compositions containing sodium nitrate are more vulnerable in this respect than those containing barium or strontium nitrates, because the lower melting-point of the former gives rise to a softening and weakening of the layers adjacent to the combustion layer. A high proportion of moderating material such as calcium oxalate and many carbonaceous ingredients also affects the strength of the consolidated pellet adversely. On the other hand polyester resin-bonded compositions are admirably suitable for this purpose, as are those compositions containing chlorinated rubber or polyvinyl chloride that have been gelled prior to consolidation by the addition of a small quantity of a suitable solvent.

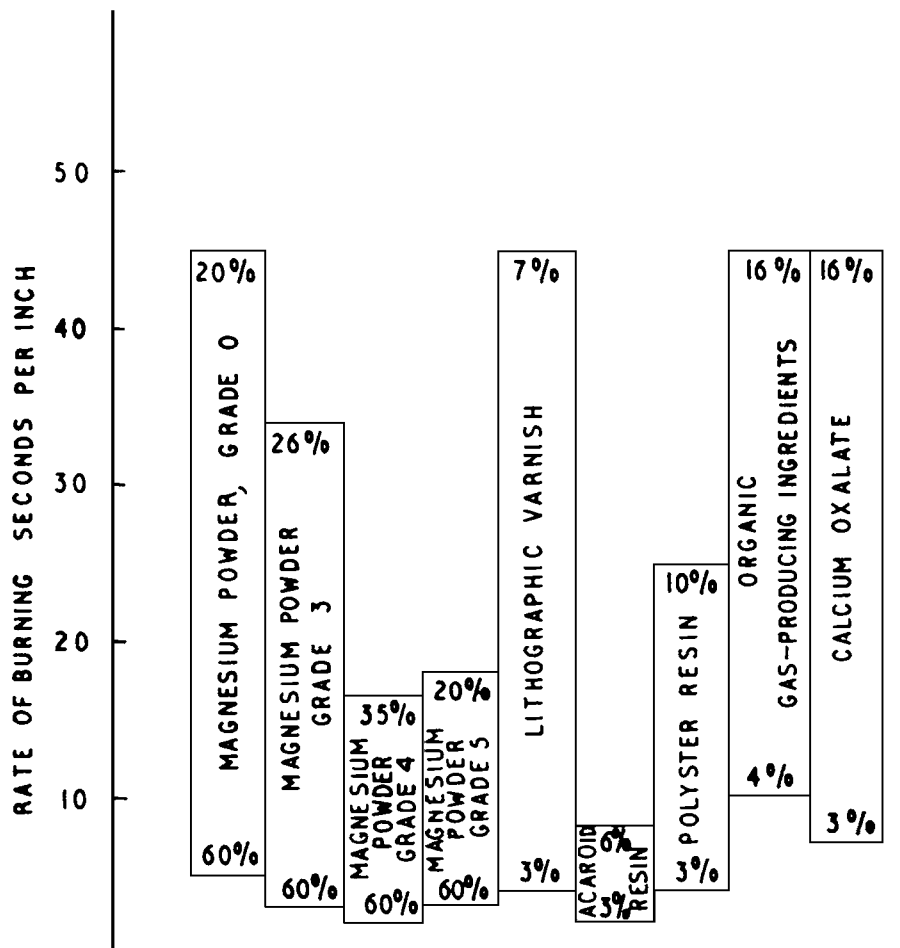


Fig. 6. Approximate effect of ingredients on Rate of Burning and the practical limits in their proportions.

Compositions containing strontium nitrate or barium nitrate are less luminous than corresponding compositions containing sodium nitrate, but they are better able to resist shock. For equivalent rates of burning the specific light-flux of the most efficient compositions containing various oxidants are given in Table 9.

TABLE 9

Fuel and Oxidant	Specific light-flux Candle-seconds/gram.
Magnesium and sodium nitrate	40,000
" " 4 parts barium nitrate + 1 part strontium nitrate	24,000
" " strontium nitrate	20,000
" " barium nitrate	16,000
Aluminium and Barium nitrate	8,000

REFERENCE

Vision through the atmosphere - Middleton.

CHAPTER 6

COLOURED FLAME SIGNAL COMPOSITIONS

Coloured signals are used to transmit concise messages through the atmosphere over distances that may be considerable. The signals may be simple warnings, codes of recognition or identifiable markers, but in all cases it is essential that they should be clear, unmistakable in colour and easily recognised under a wide variety of atmospheric conditions and against widely different backgrounds. Two types of pyrotechnic compositions are used for signalling, self-luminous compositions that burn with a coloured flame and which are used in signal flares and stars, and coloured smoke compositions which produce a cloud of coloured smoke. This section is concerned with the self-luminous type of composition.

Three aspects of the combustion of coloured signal compositions need to be considered in relation to service specifications. They must burn at a rate proper to the time requirements and dimensions of the store, they must have sufficient intensity to be visible over the specified range, and the hue of their light must be as saturated as possible in order to be easily recognisable.

It was explained in Chapter 4 that modern pyrotechnic signal flames are produced mainly from compositions containing magnesium powder, an oxidant and a suitable emitter to colour the flame. Hence the light of all pyrotechnic coloured flames is very unsaturated and success in producing one of a distinctive hue depends on finding the best compromise between the temperature continuum and the selective emission of the flame-colouring additives. Tests have shown that the signal colours that can be identified at a distance without ambiguity is limited to red, green and yellow or white. Of these red is most easily recognised and one of the easiest to produce, green is satisfactory when viewed against a suitable background and under suitable atmospheric conditions (against bright sky it can appear yellowish or white), yellow is satisfactory provided the conditions for viewing are good and that the viewer is not called upon to distinguish between yellow and white. Blue is not a suitable colour for signals of high intensity for the reasons outlined in Chapter 4.

Since the colours produced by signal compositions are inevitably unsaturated, it is essential to take all possible steps to increase the degree of saturation by reducing the intensity of the white light continuum to a minimum. This involves lowering the temperature of the flames to a degree consistent with the time of burning and the intensity requirements, and is best achieved by reducing the proportion of magnesium powder and by including carbonaceous fuel in the composition.

Many of the best signal compositions contain between 35 and 45 per cent of magnesium powder and up to 20 per cent of carbonaceous

material. Slow-burning compositions contain smaller proportions of coarse magnesium powder and fast burning ones larger proportions of the finer grades. Wherever possible, a fine grade of magnesium powder is used in order to avoid the emission of large white sparks from the burning surface. These represent a loss of useful energy to the coloured flame and their effect is to degrade its hue especially when viewed from a distance.

The pelleting material is almost invariably boiled linseed oil coated on the magnesium powder, and may or may not be dried before the other ingredients are added. The resulting composition forms a free-flowing powder which is necessary for filling small signal-star containers. Beeswax is also used in certain instances in place of, or in addition to, boiled linseed oil, especially in shell-tracer compositions which are required to function at very high linear and rotational velocities. The proportion of pelleting material varies between 3 per cent and 6 per cent and affects the rate of burning to only a small extent.

One of the most important oxidants used in signal compositions is potassium perchlorate which serves the dual purpose of supplying both oxygen and chloride ions. It has the additional advantage of making the slag fusible when barium and strontium salts are present. The other oxidants used are sodium nitrate in yellow signal compositions, barium nitrate in green signal compositions and (together with potassium nitrate) in white signal compositions, and strontium nitrate in red signal compositions. Barium chlorate is used in certain green signal compositions in addition to potassium perchlorate.

Carbonaceous fuels include lactose, sucrose, starch, mannitol, shellac, acaroid resin, and ivory nut powder. Most of these materials are hygroscopic and preference is now given to lactose and mannitol which do not suffer from this defect.

Chlorinated materials are included in signal compositions to assist in the formation of BaCl^+ and Sr Cl^+ ions in the flame. They are usually chlorinated organic substances containing between 60 per cent and 70 per cent chlorine and include polyvinyl chloride, chlorinated rubber, chlorinated paraffin wax, chlorinated naphthalene, chlorinated diphenyl, hexa-chloro-ethane, dichloralurea and hexa-chloro-benzene. Metallic chlorides cannot be used in modern signal compositions because of their corrosive action on magnesium powder. Insoluble Mercurous chloride or calomel is used as a chlorine-carrier in blue signal compositions which contain no magnesium powder.

RED SIGNAL COMPOSITIONS

All red signal compositions rely on the formation of Sr Cl^+ and Sr O^+ ions in the flame to produce their characteristic spectral bands. In practice, attention is focussed on developing the Sr Cl^+ ions to a maximum as the Sr O^+ ions are always present in the flames

of compositions containing strontium salts. Since the formation of strontium oxide also enhances the temperature - continuum, it is necessary to minimise its influence as much as possible by reducing the temperature.

Two types of red signal composition are in use, those containing potassium perchlorate for both oxidant and chlorine carrier together with strontium oxalate or strontium carbonate, and those containing strontium nitrate as the oxidant and a chlorinated organic material such as polyvinyl chloride or chlorinated rubber. The first type is the longer established in the SR series of compositions and frequently contains starch and other hygroscopic natural materials as additional fuel. The second type is of more recent origin and usually relies on the chlorinated organic material to act both as the secondary fuel and as the chlorine carrier.

Each type of composition has its advantages and disadvantages. The first gives very good red flames in the medium and medium-fast ranges of rates of burning. The second type is well suited to slow-burning compositions, since the addition of the secondary fuel to make it burn slowly automatically increases the available chlorine and so improves the hue. The latter class of compositions withstand the shock of ejection or impact during combustion better than the former class.

Examples of these compositions are shown in Table 10.

TABLE 10 RED SIGNAL COMPOSITIONS

Ingredients	Type 1 composition		Type 2 composition	
	SR 170A	SR 232	SR 91	SR 97A
Magnesium Powder Grade 0 per cent			35	22
Magnesium Powder Grade 4 " "	48	40		
Boiled linseed Oil " "	4	3	4	5
Potassium Perchlorate " "	38	29		
Strontium nitrate " "			41	53
Strontium oxalate " "	10	12		
Chlorinated Rubber " "			20	8
Polyvinyl Chloride " "				12
Starch		16		
Rate of burning, secs/inch	7.0	13.0	13.0	21.0
Specific intensity, candles/sq. inch	85,000	25,000	32,000	10,000

YELLOW SIGNAL COMPOSITIONS

Yellow signal compositions rely on the sodium continuum for their distinctive colour and hence contain sodium nitrate as the oxidant. When viewed through haze or over long distances, they may appear orange through scattering of the shorter wavelengths and barium nitrate is sometimes added to correct this tendency. At the same time the excessive emission of continuum which would make the colour too pale is reduced by the addition of organic fuel. The main difficulty with yellow compositions for use in signal-stars appears to be the prevention of excessive brightness for the required rate of burning. Examples are shown in Table 11.

TABLE 11 YELLOW SIGNAL COMPOSITIONS

Ingredients	SR 560	SR 583B	SR 590A
Magnesium Powder Grade 0 per cent			35
Magnesium powder Grade 3 " "	45	30	
Lithographic varnish " "	4		
Acaroid Resin " "		4	4
Sodium nitrate " "	46	40	39
Barium nitrate " "		10	10
Sodium oxalate " "	5		
Mannitol " "		16	12
Rate of Burning seconds/inch	7.0	14.0	16.0
Specific Intensity, candles/sq. inch	150,000	30,000	31,000

WHITE SIGNAL COMPOSITIONS

The oxidant used in White Signal Compositions is invariably a mixture of barium nitrate and potassium nitrate. The compositions are less efficient than red and yellow signal compositions with comparable rates of burning and have a lower specific intensity. A typical composition is composition SR 300A which contains:-

Magnesium powder Grade 0	50 per cent
Boiled linseed oil	4 " "
Barium nitrate	20 " "
Potassium nitrate	26 " "

and which burns at a rate of 11 seconds per inch with a specific intensity of 36,000 candles per square inch.

GREEN SIGNAL COMPOSITIONS

Green signal compositions, that have really good green flames, are difficult to produce because of the unsaturated hue which is the result of diluting the BaCl^+ spectral band with white temperature-continuum and with orange and red spectral bands from BaO^+ and from strontium salts as impurities.

As with red signal compositions, there is more than one type of composition in use. The first and longest established type contains potassium perchlorate as the principal oxidant and barium chlorate as a secondary oxidant and source of barium chloride. These compositions produce some of the best green flames but are rather unstable when moist due, possibly, to the acidity developed by barium chlorate. The second type contains barium nitrate and a chlorinated organic material. The flames are yellowish-green and are not very satisfactory when viewed over long distances. The third type contains potassium perchlorate, barium nitrate and a chlorinated organic material and combines the flame-quality of the first type with the chemical stability of the second. The main difference between compositions in the first group and those in the other two is that they frequently contain hygroscopic natural materials such as starch as a secondary fuel, whereas the others utilise the relatively non-hygroscopic chlorine-carrier for that purpose.

From experience, it is apparent that the best quality green flames are produced when both potassium and barium salts are present and that an optimum quality can be obtained with the proportions approximately 3 parts of the former to 2 parts of the latter.

Typical examples of green signal compositions are shown in Table 12.

TABLE 12 GREEN SIGNAL COMPOSITIONS

Ingredients	Type 1		Type 2		Type 3	
	SR 428	SR 429	SR 486	SR 487A	SR 700	SR 703
Magnesium powder Grade 0				20		
Magnesium powder Grade 4	43		35		42	
Magnesium powder Grade 5		48				42
Boiled linseed oil	4	4	3	5	6	6
Potassium Perchlorate	30	30			27	25
Barium nitrate			47	53	17	15
Barium chlorate	13	12				
Chlorinated Rubber				9		12
Chlorinated diphenyl			15			
Polyvinyl Chloride				13	8	
Starch	10					
Lactose		6				
Rate of Burning secs/inch	10.7	8.0	9.7	23.0	13.0	7.0
Specific Intensity candles/sq. inch	28,000	49,000	25,000	7,500	21,000	37,000

BLUE SIGNAL COMPOSITIONS

It was stated in Chapter 4 that consideration of both the relative spectral energy and the spectral sensitivity of the eye showed that it was not possible to produce blue signal flames of high intensity and any attempt to do so by raising the temperature resulted in masking the hue completely.

It follows that blue signal compositions cannot contain magnesium powder and that their flames are not bright enough for use in daylight. The fuel used is usually lactose and the oxidant is potassium perchlorate. Copper salts provide colour to the flame and the basic carbonate, the oxychloride and cuprous chloride have been used in various SR compositions. Additional chlorine is supplied by hexachloroethane, hexachlorobenzene or mercurous chloride.

SIGNAL COMPOSITIONS NOT CONTAINING MAGNESIUM POWDER

Most signals in current service are required to function satisfactorily under all conditions including full daylight and must be capable of recognition over ranges of several miles. They must all produce intense flames and their fillings therefore contain magnesium powder.

If, however, use is restricted to the hours of darkness and the range is short, magnesium powder need not be used. Non-magnesium signal compositions have several advantages for, since their main fuel is carbonaceous, flame-temperatures are lower and incandescence from magnesium oxide is absent. The flame-colours are often purer and more distinctive. This is particularly true of green flames. The fuel for red or green signal compositions is usually acaroid or shellac resin powders, starch or lactose, the oxidant is potassium nitrate, potassium or ammonium perchlorate, and sometimes potassium chlorate, and suitable flame-colorants are strontium oxalate and barium chlorate. White signal compositions use powdered antimony, antimony trisulphide, realgar or arsenic trisulphide for fuel as well as carbonaceous matter.

REFERENCES

1. Some spectrographic observations on Pyrotechnic Flames. Barrow & Caldin Proc. Phys. Soc. reprint.

CHAPTER 7

PHOTOFLASH FILLINGS AND COMPOSITIONS

A photoflash provides the light whereby aerial photographs may be taken at night from aircraft flying at altitudes ranging from 500 to 60,000 feet. At low altitudes up to 3,000 feet it is ejected from aircraft as a cartridge, and at higher altitudes as a bomb, and is fuze to explode in mid-air after a fixed interval of time. The flash is synchronised with the opening of the camera-shutter and is positioned just outside the field of view.

The light from the flash grows in intensity to a maximum that is reached within milliseconds of initiation, and then diminishes more or less slowly as the luminous cloud expands and cools. The shape of the curve relating light-intensity with time from initiation is very important and must be closely linked with the open period of the camera-shutter. If the shutter remains open for the duration of the flash the photographic image will be blurred unless the flash is very brief or the film is moved with the image. Normally, the shutter is open only for part of the duration, about 0.03 second, and synchronised with the brightest period of the flash.

Synchronisation is achieved by a photocell relay in circuit with the electrically operated shutter. In one system the opening of the shutter is triggered by the early light of the flash and, because of inertia, the fully open position may not be reached until some 10 to 15 milliseconds have elapsed. It is then closed mechanically after a fixed interval of time. To obtain the maximum efficiency in the optical system, peak-illumination should occur during the open period, i.e. 10 to 15 milliseconds after initiation. In a second system the shutter is fully open when the flash occurs and it is closed after an interval by the photoelectric relay. This system has the disadvantage of exposing the film to extraneous light prior to the flash but it avoids the difficult pyrotechnic problem of synchronising flashes with an opening shutter.

Flashes suitable for night photography are produced by the rapid scattering and combustion of finely divided aluminium or magnesium powder to form clouds of incandescent particles having a very high temperature and luminosity. Oxygen for combustion is supplied by the atmosphere into which the metal particles are scattered or by oxidants with which they are mixed either prior to ignition or during the scattering process. The products of combustion are mainly solid oxide products of high reflectivity, and emission from the cloud is confined to an outer layer a few millimeters in thickness.

The radiation corresponds to that emitted by a grey-body and the spectrum shows strong continuum over the whole visual range with fainter line and band systems derived from elements and the oxide

products of combustion. It is noteworthy that when sodium nitrate is used as the oxidant the sodium continuum is not prominent but the sodium doublet is often reversed as it is in spectra from flares.

As the radiating cloud cools, the colour of its light changes from bluish white in the early stages to orange and then to red. Measurements of the colour-temperatures of flash-clouds show temperatures as high as $4,000^{\circ}\text{K}$ or more in the early stages and $2,000^{\circ}\text{K}$ to $1,500^{\circ}\text{K}$ in the later stages.

The luminous cloud varies from spherical to lenticular in shape depending on the type of filling and the manner in which it is exploded. Radiation around the flash varies in intensity according to the surface presented, hence the distribution of light may be uniform in all directions or it may be assymetric, with much higher intensities in some directions than in others. Photoflash bombs with an assymetric distribution of light need to be ballistically stable while falling from aircraft in order to illuminate the target in a reproducible manner.

The film in current use for night-photography requires the target to be illuminated to about 0.05 foot-candle-seconds during the open period of the camera-shutter. The illumination is greatest vertically below the flash and decreases towards the periphery of the area being photographed. The variation in illumination can be reduced to an acceptable minimum by increasing both the intensity of the flash and the height at which it is functioned. The functioning height is usually between one third and one half that of the photographing aircraft.

The design of a photoflash, subject to the limitation of size and ballistic stability laid down in requirements, is almost entirely governed by the intensity-time relation of the light that it produces. This relation is shown most clearly in the shape of the curve produced by a photometer recording the variation of intensity with time throughout the duration of the flash. A typical curve is reproduced in Figure 7. In general, the intensity rises more or less rapidly to a high peak within milliseconds of initiation and then falls off more slowly, eventually approaching zero intensity asymptotically. The overall duration is difficult to assess and it is usual to quote the time taken for the light to diminish to one-tenth of its peak-intensity. The shape of the curve varies widely with different types of photoflashes. In some types it appears as a high narrow finger, in which the intensity rises extremely rapidly to the peak, then falls off nearly as rapidly at first, later diminishing more slowly. In others, it appears as a rounded shallow curve in which the rise to the peak and the subsequent falling-off is much more gradual. The shape is governed by many factors, the more important of which are the type of filling, i.e. whether the metal powder is burnt in the atmosphere alone or has an oxidant mixed with it, the metal powder used, the fineness of sub-division of the particles, the mass of the filling that is burnt, and the degree of confinement offered by the container.

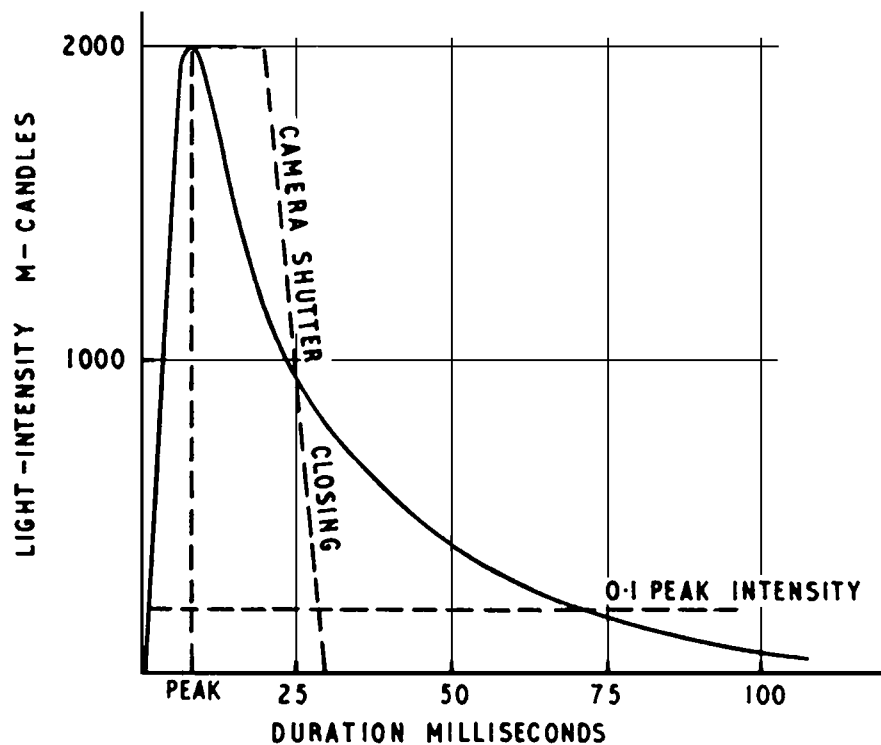


Fig. 7. Variation of light-intensity of a large photoflash with time.

The principal aim when designing a photoflash is so to arrange the variables affecting the shape of the intensity-time curve that the maximum emission of light is attained during the open period of the camera-shutter. Such an aim is rarely achieved in practice but the following discussion on the various ways of producing flashes may be of some value.

METAL POWDER - EXPLOSIVE TYPE OF PHOTOFLASH

When certain finely divided metal powders are scattered and ignited in air by an explosive they burn with a brilliant flash suitable for photography. Aluminium and magnesium powders provide the brightest flashes. Aluminium is used in the form of a finely divided flake

which passes a 240 mesh sieve and which has an apparent density of not less than 0.4. It can also be used as an atomised powder but is then not so ignitable as the flake. Magnesium is used either as a finely divided cut powder, Grade 6, or as an atomised powder.

The explosives range from grained gunpowder and pyrotechnic mixtures to high explosives. The former are used with both aluminium and magnesium powders and the latter with aluminium powder only. The explosive is housed in a central cylindrical burster which is surrounded by an annular space packed with the metal powder. Cut magnesium powder is more difficult to ignite than flake aluminium, and with high explosive, it tends to sinter into a compact mass without igniting. It is therefore used only with gunpowder and pyrotechnic mixtures, and the resulting flash-cloud burns slowly. The flash has a long duration and the intensity rises very slowly to a relatively low, rounded peak. The flash produces much light, but it is limited in usefulness for photography.

The commonest photoflashes of this type contain a central cylindrical burster of high explosive surrounded by flake aluminium. Experience has shown that the best ratio of high explosive to aluminium to use in this particular design is 1 to 3. The high-explosive is compressed into cylindrical pellets which are housed in a thin central cylinder and the aluminium flake is loaded round it to a packing density of 0.7 gms. per cc. More high explosive results in a very rapid peak-intensity of short duration due to the high explosive and some aluminium powder burning, followed by a further slow rise in intensity to a second shallow peak produced by the remainder of the aluminium powder burning in air. This kind of flash is useless for photography. Less high explosive produces a smaller cloud and hence less light.

The shape of the flash is roughly lenticular with its greatest projected surface normal to the axis of the photoflash. The circumference of the flash cloud is very irregular in outline owing to compacted lumps of burning aluminium powder shot out at high velocity. Since the luminous intensity is the product of the projected surface of the flash cloud and its brightness, it is greatest in the direction of the axis of the photoflash.

High temperatures and pressures are necessary for the success of this photoflash and they are achieved by using aluminised C.E., aluminated TNT or torpex in the exploder. C.E. is a sensitive high-explosive and torpex presents some filling difficulties since it must be melted and poured into the burster-tube, so aluminised TNT, containing 30 per cent aluminium, in pellet form is preferred for the smaller photoflashes.

A considerable improvement in the light-characteristics of the flash is achieved by changing from a cylindrical burster of aluminised TNT to a conical one of lean torpex containing 30 aluminium/50 TNT/20 RDX. The base of the cone is made equal to the diameter of the photoflash and is situated at the rearward end. There is less space for aluminium powder and the proportion of high-explosive in the filling is doubled. This produces a larger, hotter

flash but there is no adverse effect on the shape of the intensity-time curve, as would happen with a larger cylindrical exploder. This is attributed to the configuration of the blast-wave produced by the cone of high explosive. The increase in peak-intensity brought about by this change in filling is 100 per cent, and that in the luminous-flux is 50 per cent.

The time-interval between initiation and peak-intensity of photoflashes depends, among other things, upon the mass of the filling, the shape and the weight of high explosive, and the degree of confinement. In a 4.5-inch photoflash made of thin sheet steel and containing 10-12 lbs. of filling, the peak-intensity is reached in 8 milliseconds using a cylindrical burster of Al/TNT, and in 4 milliseconds using a conical burster of torpex. In an 8-inch photoflash, made of thicker steel and having a conical burster, the interval is 8 milliseconds, and in a 16½-inch photoflash of the same type it is 13 milliseconds. These peaks are brief in duration, the period obtaining at the ¾-maximum intensity level being roughly equal to the time to reach peak-intensity.

The shape of the intensity-time curves of high explosive-aluminium powder flashes can be modified within certain limits by modifying the design of the burster. The modifications nearly all result in the peak-intensity being reached more slowly and being maintained for a longer period, the curves having a gentler, rounded form. As a result of the later rise to the peak the flashes become more effective for certain types of cameras. The modifications are as follows:-

1. The high explosive in the cylindrical burster can be distributed among four small-bore parallel burster-tubes set at the corners of a square within the aluminium powder and detonated simultaneously. The time to peak-intensity is lengthened from 8 to 14 milliseconds and the duration at ¾ peak-intensity increases to 11 milliseconds.
2. With a pyrotechnic mixture of magnesium powder and potassium perchlorate in place of the high explosive in the small burster-tubes, the delay to the peak is further extended to 35 milliseconds and the duration at ¾ peak-intensity to 31 milliseconds.
3. A short cylindrical burster of pyrotechnic composition has a similar effect.

Table 13 shows the changes in light-characteristics brought about by various types of burster.

TABLE 13 THE LIGHT EMITTED FROM 4½-INCH PHOTOFLASHES
FITTED WITH VARIOUS BURSTERS

Filling	Attitude	Duration milliseconds			Peak Intensity Million Candles	Light-flux candle-seconds		
		At 1/10th Peak	At ¼ Peak	To Peak		In 50 milliseconds	Total	per gm. of metal powder
Central burster of 2½ lbs. TNT/Al. and 7½ lbs. aluminium flake	End	74	8.2	9.2	340	Millions		3210
	Side	94	10.8	8.8	117	7.4	10.9	
Conical burster of 6 lbs. Torpex and 6 lbs. aluminium flake	End	72	7.7	3.7	625	2.9	4.2	
	Side	96	6.7	1.3	190	11.9	16.2	6010
4-tube burster of 1½ lbs. CE and 7½ lbs. aluminium flake	End	88	11.0	14.0	370	5.0	7.2	
	Side	82	14.0	15.0	101	9.4	13.1	1850
4-tube burster of 13 ozs. Pyrotechnic Composition and 7½ lbs. aluminium flake	End	150	31.0	34.7	318	11.1	22.3	6570
	Side	137	38.3	29.0	136	5.4	9.8	

The shape of the intensity-time curve can also be changed in a striking manner by concentrating the aluminium powder more and more towards one end of a cylindrical burster of high explosive. In this region there is less compacting of the metal powder into lumps and it tends to burn more as a dust cloud. The effect has been demonstrated with small photoflashes in which the aluminium powder was housed in conical containers around the cylindrical burster. The cones were of equal volumes but were successively shortened in height and widened in diameter. The burster-tube contained 75 gms. of high explosive and the cones contained 230 gms. of aluminium powder. From the results of the experiment, set out in Table 14, it is apparent that, by concentrating the aluminium powder more and more at one end of the burster, the peak-intensity is progressively delayed, the peak is broadened and the flash becomes more and more efficient. Similar modifications were made to the larger $4\frac{1}{2}$ -inch photoflash in which the aluminium powder was housed in a cone 10 inches high by 10 inches in diameter. The results are also shown in Table 14.

The main advantage of the metal powder/high explosive photoflash over other types is its inherent safety in relation to the effects of penetration of its filling by small arms ammunition and shell fragments. Such penetration leads to the immediate explosion of a mixture of metal powder and oxidant whereas the aluminium powder or the high explosive may only inflame and there is a reasonable chance of jettisoning the damaged photoflash before the high explosive burster explodes.

This type of photoflash, however, is a very inefficient light-producer, generating only 2.5 lumens per watt compared with, say, 27 lumens per watt from a tungsten-filament projection lamp. The reason for this low efficiency is best understood by studying the manner in which the flash functions.

The reaction between aluminium and air takes place in the vapour state at the temperature of the boiling point of its oxide Al_2O_3 (3250°K), the oxide immediately condensing to droplets with dimensions comparable with the wavelength of light. The brightness of the flash-cloud is less than that of a black body at that temperature (except immediately following detonation), because the emissivity of the particles is very low in the visible region, possibly owing to their small size. Spectrographic evidence shows that AlO is present in the early stages of the photoflash but since there is no dissociation of Al_2O_3 at its boiling point the initial temperature must be much higher, and is, in fact, about $4,000^\circ\text{K}$. The elevation of the boiling point is brought about by the very high pressures (3,000 atmospheres or more) obtaining at the detonation of the high explosive. This elevation of the boiling point accounts for the brightness of the flash in the first millisecond being greater than 5,000 candles per sq. cm., the brightness of a blackbody at $3,250^\circ\text{K}$. The brightness falls off very rapidly to about 2,000 candles per sq. cm. in the next millisecond, and thereafter more slowly. One of the effects of replacing the high explosive in the

TABLE 14 THE VARIATION IN THE LIGHT FROM SMALL PHOTOFLASHES
WHEN THE DISPOSITION OF ALUMINIUM POWDER AROUND A
CYLINDRICAL BURSTER OF HIGH EXPLOSIVE IS VARIED

Photoflash	Attitude	Duration milliseconds			Peak Intensity Million Candles	Light-flux candle-seconds		
		at 1/10th Peak	at $\frac{3}{4}$ Peak	To Peak		In 50 milliseconds	Total	per gm. of metal powder
Cone dia. 2 inch	End-on	43	3.7	2.8	35	0.50	0.53	2340
" " 3 "	" "	44	10.0	5.3	41	0.85	0.87	3860
" " 4 "	" "	42	9.7	9.3	57	1.24	1.26	5560
" " 5 "	" "	55	13.0	17.3	38	0.99	1.07	4720
" " 6 "	" "	72	14.3	22.0	44	1.28	1.55	6800
" " 7 "	" "	81	14.7	26.0	36	1.05	1.43	6310
" " 8 "	" "	89	22.3	25.0	28	1.00	1.31	5780
4½-inch cylindrical container	End-on	62	8.5	8.5	285	6.2	8.1	2380
	Side-on	91	11.0	8.5	91	2.3	3.2	950
10-inch conical container	End-on	117	28.3	21.0	278	10.0	15.7	4620
	Side-on	102	29.7	21.0	62	2.3	3.3	970

burster by a pyrotechnic composition is to reduce the initial pressure and temperature, and the brightness of the cloud remains constant at about 1,000 candles per sq. cm. during the first 30 milliseconds.

The aluminium powder surrounding the high explosive burster has an apparent density of 0.70 gms. per cc., and threequarters of its volume is taken up by air. On detonation of the high explosive, the aluminium is consolidated to a thin shell with a density approaching that of the solid metal, the trapped air is heated rapidly by adiabatic compression and combustion commences. The aluminium shell, which is raised to incandescence by the detonation, contains the gaseous products of detonation but little oxygen, so that combustion cannot continue except on the outside surface. In the 4.5-inch photoflash with a cylindrical high explosive burster, the shell expands to a diameter of 3 feet in less than a millisecond and breaks up into fragments that move outwards with a velocity of 3,000 feet per second. The fragments are thus supplied with air in which to burn by forced convection and the aluminium oxide is formed, at the temperature of its boiling point, as tiny droplets that decelerate rapidly and are left behind. The fragments thus diminish in size and the flash reaches its maximum size when all the aluminium in the fragments has been consumed. The time to peak-intensity is controlled by the velocity of the fragments. Thereafter, the light is that emitted by the rapidly cooling particles of aluminium oxide. Some of the aluminium powder in the photoflash is not pelleted but burns as a dust cloud in the later stages of the explosion and contributes to the light in the tail of the intensity-time curve.

Thus, the rapidity with which the peak-intensity of a photoflash is reached depends on the outward velocity of the fragments, and its value depends on the size of the cloud by the time the fragments have been consumed. Increasing the weight of the high explosive burster increases both the velocity of the fragments and the size of the flash and the peak is higher and occurs sooner, but the increased velocity cools the oxide particles quicker and so hastens the reduction in brightness and there is a steeper fall in intensity after the peak is passed. Less high explosive results in a lower peak-intensity which is reached more slowly and which falls off more slowly, and the flash lasts longer. The conical high explosive burster produces a more efficient flash than a cylindrical burster possibly because detonating it at the apex produces a relatively small radial pressure to begin with followed by rapidly increasing pressures as detonation proceeds, and so affecting the disposition of aluminium in space. The concentration of aluminium powder around the apex assists the formation of weightier fragments.

The overall efficiency of the aluminium powder-high explosive type of photoflash therefore appears to be restricted, for although its light can be delivered in a variety of ways depending on the geometry of the filling and on the explosive burster, it is the low emissivity in the visual region of the aluminium oxide particles that is the limiting factor and this can only be overcome by the formation of larger particles in the flash cloud.

A somewhat similar mechanism obtains when magnesium powder is used in place of aluminium powder, but the temperatures reached are lower and the brightness of the flash cloud is much less. Moreover, the particles of magnesium oxide cool more slowly than those of aluminium oxide and the flash has a much longer duration.

The combustion of aluminium can be made much more efficient if air is replaced by oxygen, the temperature produced being very much higher (4,250°K or more). Small scale experiments have shown that the light of flashes produced by igniting and scattering aluminium powder in pure oxygen or in a highly oxygenated atmosphere such as nitrogen dioxide vapour is twice that produced in air (30,000 candle-seconds per gram of aluminium in oxygen compared with 14,000 candle-seconds per gram in air). A similar improvement is brought about when aluminium is mixed with a solid oxidant such as potassium perchlorate in photoflash compositions.

METAL POWDER-OXIDANT-HIGH EXPLOSIVE FILLED PHOTOFLASHES

This type of filling for photoflashes is intermediate in many respects between the filling just described and the filling of mixed metal powder and oxidant.

It consists of a central cylindrical high explosive burster surrounded by two concentric annuli, the inner one filled with a powdered oxidant and the outer one with aluminium powder. The oxidant is usually potassium perchlorate, barium nitrate or a mixture of both and the quantity is adjusted to ensure the complete combustion of the aluminium powder. The detonation of the high explosive core forcibly mixes the two ingredients together and simultaneously ignites the aluminium powder.

The luminous effects from this type of filling lie between those of the aluminium powder-high explosive filling and those of the mixed composition; the peak-intensity is not as high as that of the first filling and the luminous flux is less than that of the second. By separating the metal powder from the oxidant the filling is made less vulnerable than a mixed composition to penetrating projectiles and fragments and hence it is less hazardous to the aircraft carrying the photoflashes.

PHOTOFLASH COMPOSITIONS

The third type of filling for photoflashes consists of intimate mixtures of metal powders and oxidants which are readily ignited and explode violently without the assistance of high explosives. The metals usually employed are Magnesium, aluminium, mixtures of the two or alloys. The oxidants used are the nitrates of sodium, potassium, barium and strontium, and potassium perchlorate.

COMPOSITIONS CONTAINING MAGNESIUM POWDER

Mixtures of magnesium powder and sodium nitrate probably react together in the photoflash explosion in the following manner:-

$5 \text{ Mg} + 2\text{NaNO}_3 \rightarrow 5 \text{ MgO} + \text{Na}_2\text{O} + \text{N}_2 + 584 \text{ K cal}$ and the stoichiometric mixture contains 41 per cent of magnesium and produces 2,010 calories per gram of composition. The light of the flashes is composed mainly of a continuum due to temperature-radiation, atomic line-systems from magnesium and sodium, and molecular band-systems from the oxide products of combustion. The sodium doublet is reversed and there is little evidence of the presence of the sodium continuum. The colour-temperature lies in the region of 2,800°K.

The light-characteristics of the flashes appear to be little affected by the fineness of subdivision of magnesium powder, as far as the ordinary grades 0 to 6 of cut powder are concerned, but atomised magnesium gives a flash somewhat shorter in duration.

Variations in the proportions of the ingredients produce marked changes in the light-characteristics of the flashes. As the proportion of magnesium powder increases the duration gets progressively shorter until the stoichiometric proportion is reached after which it lengthens steadily as more and more magnesium powder burns in the atmosphere as a metal-dust cloud. The peak-intensity and the light-flux also increase with increasing proportions. Mixtures around the stoichiometric proportions produce the sharpest flashes with peaks of short duration reached rapidly after initiation, thereafter the intensity rises more slowly to reach peak-intensities which last longer. The light-characteristics of flashes from 4.5-inch photoflashes containing mixtures in which the proportion of magnesium powder varies from 40 to 60 per cent are shown in Table 15. These figures are interesting since the photoflashes all contain the same weight of metal powder, 5 lbs., and the total weight of filling varies according to the proportions.

TABLE 15 4.5 INCH PHOTOFLASHES FILLED VARIOUS WEIGHTS OF COMPOSITIONS ALL CONTAINING 5-LBS MAGNESIUM POWDER

Magnesium Powder per cent	Total weight of filling lbs.	Duration milliseconds			Peak Intensity Million Candles	Light-flux candle-seconds		Colour Temperature °K
		At 1/10 Peak	At ¼ Peak	To Peak		Total million	per gm. of metal	
40	12.4	56	6.0	3.0	176	3.7	1600	2780
45	11.0	66	7.5	3.0	249	6.0	2700	2840
50	9.9	60	9.0	3.5	254	6.5	2900	2870
55	9.0	79	20.0	3.5	271	10.7	4800	2900
60	8.3	81	27.0	6.0	338	13.4	6000	2840

If the proportion of magnesium powder is increased to 85 per cent as in composition SR 807, the flash becomes very prolonged with the intensity rising slowly to a low peak and then slowly falling. There is often a second hump in the intensity-time curve produced by the slow combustion of magnesium in air. The flash lasts for more than a second and has no use in night-photography but the light-flux per gram of metal powder is high, namely, around 12,000 candle-seconds.

Mixtures of magnesium powder and the nitrates of potassium, strontium and barium produce flashes with light-characteristics somewhat similar to those from sodium nitrate mixtures. Some comparative results are shown in Table 16.

TABLE 16 4.5 INCH PHOTOFLASHES FILLED 9-LBS. 50/50
MIXTURES OF MAGNESIUM POWDER AND OXIDANT

Oxidant	Duration milliseconds			Peak Intensity million candles	Total light- flux million candle- seconds	Specific light-flux Candle secs. per gn. meta!
	at 1/10 peak	at 1/2 peak	To peak			
Sodium nitrate	80	9	5	223	6.0	3000
Potassium nitrate	110	14	5	243	8.8	4400
Barium nitrate	170	17	12	224	11.6	5800
Strontium nitrate	160	19	8	223	11.8	5900
Potassium perchlorate	108	17	6	415	14.0	6800

The data for the sodium nitrate-magnesium powder mixture agree well with those given in Table 15 where the quantity of material exploded was 10 per cent greater. The peak-intensities obtained with the other nitrates are similar but durations are somewhat longer and hence the light-flux is greater.

When potassium perchlorate is used, there is a considerable increase in both peak-intensity and light-flux, because of the higher temperatures generated and the more efficient combustion of the magnesium powder. Changes in the proportions of metal powder to oxidant cause variations in light-characteristics as would be expected, but they differ somewhat from those in the magnesium-sodium nitrate mixtures. A decrease in the proportion of metal powder not only shortens the duration but also raises the peak-intensity very considerably and causes it to occur sooner. This is illustrated by the data in Table 17, which is derived from 4.5 inch photoflashes containing a fixed weight of metal powder mixed with potassium perchlorate in different proportions.

Mixtures of magnesium powder and potassium perchlorate are more sensitive to friction and impact than those of magnesium and sodium nitrate and attempts have been made, from time to time, to reduce the sensitiveness by adding lubricants such as powdered graphite. This has the desired effect on the sensitiveness, but the light-

characteristics of the flashes suffer considerably with even small additions, and composition SR 801A, which contains some six per cent graphite, produces a very inferior flash to that of the corresponding binary mixture.

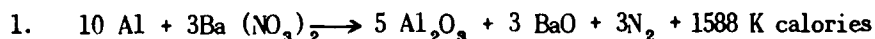
TABLE 17 4.5-INCH PHOTOFLASHES CONTAINING 5LBS
MAGNESIUM POWDER MIXED WITH DIFFERENT PROPORTIONS OF
POTASSIUM PERCHLORATE

Percentage Magnesium Powder	Total weight of filling lbs.	Duration milliseconds			Peak Intensity million candles	Light-flux Candle-seconds	
		at 1/10 Peak	at 1/2 Peak	To Peak		Total millions	per gm. of metal
40	12.4	40	13	7	341	7.7	3400
50	9.9	66	15	8	292	8.8	3900
60	8.3	100	35	12	194	11.0	4900

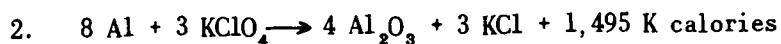
COMPOSITIONS CONTAINING ALUMINIUM POWDER

Aluminium powder is used in photoflash compositions with barium nitrate or potassium perchlorate as oxidants. It is never used with sodium nitrate because of the chemical instability of such mixtures in the presence of moisture, but potassium and caesium nitrates have been used on occasion.

The reactions taking place during combustion may be represented by the following equations:-



The stoichiometric mixture contains 25.6 per cent aluminium and produces 1,510 calories per gram.



The stoichiometric mixture contains 34 per cent of aluminium and produces 2,356 calories per gram.

Very little use has been made of binary mixtures of aluminium powder and barium nitrate for photoflashes, but generally speaking, they give flashes with light-characteristics similar to those of magnesium-sodium nitrate mixtures.

Barium nitrate is more frequently used in three-component flash mixtures containing aluminium powder, potassium perchlorate and barium nitrate. A mixture in which the components are present in stoichiometric proportions contains 30 per cent aluminium powder, 37 per cent barium nitrate and 33 per cent potassium perchlorate. It produces 1,972 calories per gram of composition.

This type of photoflash composition is used in the U.S.A. where the proportions have been modified to 40 per cent aluminium powder, 30 per cent barium nitrate and 30 per cent potassium perchlorate. It is a most efficient composition generating very high temperatures, peak-intensities and luminous flux. It produces around 11,000 candle-seconds per gram of composition. The high temperature and high light-output of such flashes are undoubtedly due to the presence of potassium perchlorate and to the fine state of subdivision of the atomised aluminium powder that is used. The fine metal particles vaporise readily and burn in an atmosphere very rich in oxygen and so reproduce the conditions necessary to generate high temperatures as laid down on page 67.

Binary mixtures of aluminium powder and potassium perchlorate explode violently with the generation of much light and heat. As with other photoflash mixtures, the light-characteristics of the flashes varying with the proportions of the ingredients. This is illustrated by data obtained in firing charges of 70 gms. of various compositions in small photoflashes.

TABLE 18 LIGHT-CHARACTERISTICS OF SMALL PHOTOFLASHES FILLED ALUMINIUM POWDER/POTASSIUM PERCHLORATE

Percentage Ingredients		Duration milliseconds		Peak Intensity Million Candles	Luminous flux candle seconds x 1,000	
Al.	KClO ₄	Total	To Peak		Total	per gram composition
30	70	20	1.2	12.5	68	0.97
35	65	27	1.2	75	433	6.17
40	60	36	2.0	78	644	9.23
50	50	54	3.7	62	807	11.53
60	40	88	5.0	39	612	8.74
70	30	77	5.5	11	148	2.11

Mixtures with proportions of aluminium powder around or less than stoichiometric produce brief flashes in which the peak-intensities rise and fall very rapidly and the luminous flux is low. With increasing proportion of aluminium powder there is a progressive increase in the duration of the flash and a progressive retardation in reaching peak-intensity. Maximum peak-intensity is reached with 40 per cent aluminium powder and thereafter it decreases steadily. The luminous flux however, increases up to 50 per cent aluminium and the 50/50 mixture is the most efficient although it does not give the highest peak-intensity. As the proportion of aluminium increases the peak of the intensity-time curve broadens and becomes more rounded, but with more than 50 per cent the peak-intensity diminishes more and more rapidly and the luminous flux falls off correspondingly.

Composition SR 812 which contains 50 per cent atomised aluminium powder and 50 per cent potassium perchlorate is used in British

service photoflashes because of its high overall efficiency. However, if the early part of the flash only can pass the aerial camera-shutter it is essential to raise the peak-intensity to its maximum in order to obtain maximum photographic efficiency. Composition SR 813, containing 40 per cent aluminium powder, achieves this purpose. The peak-intensity can be raised and the duration of the flash shortened by using very fine aluminium powder in which the average size of the particles is less than 5 microns.

The colour-temperature of the flash-clouds from these mixtures is very high and measurements made on airburst photoflashes containing compositions SR 812 give values of 3,400°K prior to reaching peak-intensity. The spectrum consists mainly of temperature-continuum with line-systems from aluminium and potassium and band-systems from Al_2O_3 . There is a rise in spectral energy around the main potassium lines at 7,668Å and 7,702Å which are seen in absorption.

Flash compositions containing mixtures of magnesium and aluminium powders or powdered alloys of the metals and potassium perchlorate have properties midway between those of mixtures containing the separate metals.

At one time, since the alloy is brittle and can be finely powdered quite readily, it was used in photoflash compositions in preference to magnesium powder, but with the advent of atomised aluminium powders having an average particle-size as small as 5 microns there is no further use for it.

CHAPTER 8

PRIMING COMPOSITIONS

The combustion of compressed pyrotechnic fillings is invariably initiated by a flame from a variety of sources such as electric caps, percussion caps, electric fuses, safety fuse, propellant etc. The ease with which they ignite depends largely on the temperature of ignition of the composition, on the physical state of the surface to be ignited, and on the characteristics of the impinging flame.

The temperature of ignition of pyrotechnic compositions varies widely according to the ingredients they contain and to their state of sub-division and intimacy of mixing. Mixtures of metal powders and nitrates have ignition temperatures in the region of 500°C to 600°C, many mixtures of organic materials, particularly finely divided natural products such as starches and resins, and nitrates ignite at temperatures around 250°C to 350°C, and mixtures of organic materials and chlorates ignite at temperatures around 150°C to 250°C.

The combustion of the surface layer of composition usually commences in one or two spots and then spreads over the surface at the same time as it penetrates in depth. The time required to raise the temperature of such spots to the ignition point is finite and will obviously be longer the higher the temperature of ignition. It will also depend on the heat available in the impinging flame. Certain pyrotechnic mixtures are readily ignited by a flame or a stream of very hot particles, others are difficult to ignite in this manner and require more prolonged heating to initiate combustion. The less ignitable compositions are usually covered by a layer of a readily ignitable composition pressed on to their surface and this layer of priming composition, when it burns, transmits sufficient heat to initiate combustion in the layer beneath.

Priming compositions to be efficient should have the following characteristics.

1. They should be readily ignitable from the flame or flash of an initiating device.
2. They should generate plenty of heat.
3. They should not burn too rapidly or too violently.
4. They should produce some non-volatile products of combustion in the form of fusible or solid slags.
5. As far as possible, their combustion characteristics should match those of the composition they are to ignite.
6. They should not be more sensitive than is necessary.
7. They should be compatible with the compositions to be ignited.

The obvious difficulty with igniting a composition from a layer of priming composition is that the gases and hot products of combustion are always carried away from the surface to be ignited, and ignition is achieved mainly by the heat transmitted through the priming and that generated by the layer in juxtaposition with the main composition. Hence the need for hot solid products of combustion to remain in situ, especially when the temperature of ignition is high.

The priming compositions currently in use in British pyrotechnic practice fall into three fairly distinct groups. Group 1 includes gunpowder in all its varieties, compositions derived from gunpowder and compositions similar in behaviour to gunpowder.

Group 2 includes mixtures of organic substances, both natural and synthetic, with oxidants, usually potassium nitrate or barium nitrate.

Group 3 includes mixtures that produce solid slags and little or no gas during combustion.

Gunpowder and its derivatives have for many years been the most important primings for pyrotechnics by virtue of the ease with which they are ignited from a flash and the heat that they produce. For pyrotechnic compositions, especially for those containing magnesium powder, sulphurless gunpowder, containing 30 parts of charcoal and 70 parts of potassium nitrate, is always used because of the corrosive action of sulphur on magnesium. Compressed gunpowder burns fiercely at approximately two and a half seconds per inch and a thin layer on the surface of many compositions burns away two rapidly for the underlying layer to be heated to its ignition temperature. The gunpowder is therefore modified to burn more slowly. One method is to mix it with an equal weight of the composition to be ignited. The mixture then has properties intermediate between those of the components, being less ignitable than gunpowder but generally able to transfer sufficient heat to the main composition. Layers of such mixtures are frequently sandwiched between a layer of gunpowder and the main composition. Gunpowder can also be made to burn less fiercely by the addition of organic materials such as starch, lactose, resins, etc.

The commonest priming composition is composition SR 252 containing potassium nitrate, powdered silicon and sulphurless mealed gunpowder. Its combustion products include fusible silicates that remain as hot molten glass on the surface to be ignited and ensure the transmission of adequate heat. This composition is nearly as ignitable as gunpowder itself.

All these priming mixtures have the disadvantage of gunpowder, namely, the ease with which moisture is absorbed from the atmosphere by the charcoal present. This leads, in time, to a reduction in ignitability and to the corrosion of magnesium powder in contact with the priming layer. There is therefore a need to replace gunpowder by a priming composition that has the advantages of its ignitability and insensitiveness without its moisture-absorbing tendencies. Non-hygroscopic alternatives to charcoal are not easy to find since it is desirable to have a material that

neither melts nor volatilizes before decomposing and which is readily combustible. One such substance is tetra-nitrocarbazole which forms mixtures with potassium nitrate with properties similar to those of gunpowder. Composition SR 112 contains 40 per cent of tetranitrocarbazole and 60 per cent potassium nitrate. When granulated, this composition is readily ignited, burns rather more slowly than grained gunpowder but in other respects is very similar to it, and it is non-hygroscopic.

The second group of priming compositions include mixtures of organic materials and potassium or barium nitrates. They burn more slowly than gunpowder and usually generate less heat. Strictly speaking, composition SR 112 is a member of this group but its behaviour is intermediate between groups 1 and 2. One of the more important compositions of this type is composition SR 214 containing 40 per cent lactose and 60 per cent potassium nitrate. It burns at 12 seconds per inch and is used to prime coloured-smoke pellets, which would inflame with a hotter priming composition such as composition SR 252.

The third group of priming compositions produce little or no gas when they burn but form slags that remain in contact with the main composition. The slags may be either infusible oxides or fusible metals or glasses but in either case they remain in contact long enough to heat the underlying composition to its ignition temperature. These primings are invaluable for the more inert slow-burning types of composition that require prolonged heating before ignition. For tracking flares and similar stores that may be ignited at low ambient pressure, the only reliable primings to use are gasless compositions whose rates of heat-evolution are less affected by variations in atmospheric pressure than those of gas-producing compositions.

The fuels used in these mixtures are finely powdered metals, metalloids or alloys. They include boron, silicon, zirconium, zirconium-nickel alloy, aluminium and magnesium. The oxidants include potassium nitrate, potassium perchlorate, barium nitrate, barium chromate and oxides of bismuth, lead, iron and molybdenum.

A 50/50 mixture of silicon and potassium nitrate has been used for many years as composition SR 251. It is slow-burning and is normally rather difficult to ignite, but this is improved by using very fine silicon powder. Once ignited it produces molten silicates that heat the underlying composition very efficiently.

Mixtures of silicon and red lead or bismuth oxide ignite readily from flashes and sparks and burn very fiercely. They are, however, very sensitive to friction and must be handled with great care. Mixtures of boron and bismuth oxide, barium chromate or potassium nitrate are now used almost exclusively for priming compositions ignited under reduced atmospheric pressure. They are readily ignitable, and burn vigorously under conditions of near vacuum but without explosive violence. Their rates of burning can be varied by varying the proportions of the ingredients or, as in the case of boron-bismuth oxide by the addition of a second, relatively inert,

oxide such as chromic oxide. The slags are fusible and involatile. The mixtures, with the exception of boron-potassium nitrate, are, however, difficult to pellet and the priming layers have little mechanical strength. They can be reinforced by a covering of fine mesh cotton or nylon fabric pressed on to the surface.

Mixtures of aluminium powder or magnesium powder and oxidants are usually less ignitable than those containing boron but they produce more heat. Aluminium powder mixed with iron oxide and barium nitrate is used to prime thermite and other solid incendiary mixtures. Composition SR 306 contains a mixture of flake and blown aluminium powders, hammerscale and barium nitrate together with a small proportion of boric acid to stabilise it. Composition SR 403 is a 50/50 mixture of this composition and composition SR 252 and is rather more ignitable by virtue of the mealed gunpowder present in the latter composition.

Composition SR 399 is a stoichiometric mixture of magnesium powder and barium peroxide with a small proportion of acaroid resin powder added to increase its ignitability. It is practically gasless, burning readily in a near vacuum and is invaluable for priming tracking flares to be ignited at high altitudes. It consolidates well.

CHAPTER 9

DELAY COMPOSITIONS

A delay is a device for producing a time-interval between two explosive events, and a pyrotechnic delay is one which utilises the time taken to burn a train of pyrotechnic composition ignited by the first event and which, after burning, initiates the second. The form taken by the pyrotechnic delay depends on the degree of precision required in the time-interval. In its simplest and least accurate form it consists of a length of slow match, quickmatch or safety fuse, which provides a long safety-interval before an explosion, and in its most sophisticated form it is an integral part of a delay-motor operating with great accuracy over a wide range of conditions within a ballistic missile.

All accurate pyrotechnic delays are trains of consolidated pyrotechnic composition that burn cigarette-fashion from one end to the other. The train may be contained in straight metal tubes, in spiral lead tubes set in a supporting "potting" medium or in circular or S-shaped channels cut into metal or plastic plates. They may have to burn vented or unvented under extreme conditions of ambient temperature and pressure, of acceleration and deceleration, and of spin. Their times of burning may be as short as a few milliseconds in detonator delays or they may last for many minutes. Their accuracy will vary according to the service needs, but for many applications times of burning may not vary from the mean by more than a few percent of its value over the whole range of operating conditions.

The modern practice of requiring pyrotechnic delays to function as very accurate clocks has led to an intensive research into the mechanism and control of combustion, both of gas-producing and of gasless pyrotechnic mixtures, and at the same time it has narrowed the field of investigation to the relatively few combustible materials that can be considered suitable for this kind of precise application.

TYPES OF DELAYS AND THEIR USES

Delays may be classified according to the conditions under which they are required to burn and to the time-interval required of them. Many materials used in delay compositions are carbonaceous and produce large volumes of gases during combustion. Their rates of burning are affected by changes in ambient pressure and they must be freely vented to the surrounding atmosphere in order to burn at a constant rate. Other materials produce mainly solid products of combustion with little or no gas. Ambient pressure has a much smaller influence on their rates of burning and they can be burnt

in confined spaces. If a gas-producing delay is burnt in a confined space the rate of burning accelerates as the pressure rises and it may eventually explode. This is one way of obtaining very short delays of the order of milliseconds, although it is not necessarily very accurate or reproducible.

Very short delays are used in bomb and shell fuzes to delay detonation of the high explosive until some penetration of the target has taken place. Their times of burning are seldom longer than 250 milliseconds and their fillings of potassium dinitrophenate, lead dinitroresorinate or lead styphnate are not normally looked upon as pyrotechnic materials since they contain their own source of oxygen. Short columns of fast-burning pyrotechnic mixtures such as powdered antimony and potassium permanganate or silicon and red lead are frequently used to produce suitable delays in detonators and by employing high-energy fuels such as amorphous boron, titanium or zirconium it is possible to produce delays as short as 100 milliseconds in a robust column of consolidated material.

Short delays ranging from, say, one quarter-second to one minute in duration are by far the commonest in Service use. They are widely used in all forms of missiles, whether fired from a gun or a projector or dropped from aircraft, whenever a chain of explosive events is to be initiated after an initial interval of time. The delay may be needed to provide a minimum safe distance between the operator and the projected missile, or to enable the missile to reach a certain position in space before functioning, and possibly to synchronise with other operations taking place elsewhere, or to initiate automatically the self-destruction of a missile should it miss its target.

These delays have a variety of forms depending on the space available to accommodate them. Where the time required is fairly short they frequently consist of straight columns of consolidated composition, but for longer times of burning, or for convenience in fitting into small spaces, delay-columns are housed in channels in flat metal or plastic plates. Many gun-shell time-fuzes are of this type having two plates with C-shaped channels in juxtaposition. The pyrotechnic train in the first channel burns from one end to the other, and by turning one plate relative to the other its terminal flame can be made to ignite the train in the second channel anywhere along its length, and so add a variable time of burning to the fixed time of burning of the first channel. Longer delays can be obtained by forming the delay column into a spiral, either as grooves in a plate or as a helix. Another type of short delay unit now in demand for certain missiles take the form of a completely sealed unit containing a very accurate delay, which, at the end of combustion causes mechanical work to be done either on a moveable piston or on an invertible diaphragm.

The longer pyrotechnic delays are usually employed in circumstances where great accuracy in the time-interval is not required but where the store having been initiated, must remain quiescent over periods of 20 minutes or more.

GAS-PRODUCING DELAY COMPOSITIONS

Gas-producing delay compositions are almost invariably mixtures of carbonaceous fuels and inorganic oxidants. Sulphurless gunpowder is a typical example and has been used for many years in delays both as the grained and the mealed variety. The rate of burning of consolidated columns of gunpowder is approximately $2\frac{1}{2}$ seconds per inch and it is frequently slowed down by mixing mealed gunpowder with various proportions of lactose, starch or acaroid resin.

The fuels used in gas-producing delay compositions may be conveniently classified into the following groups:-

1. Naturally occurring substances such as starches, sugars, resins and gums. Charcoal from various sources can also be included in this group.
2. The potassium salts of organic acids such as salicylic and sulphonilic acids, nitrated phenols and cresols and their derivatives.
3. Chlorinated materials such as polyvinyl chloride and chlorinated rubber.
4. Organic nitro-derivatives such as nitro-indene polymer, tetra-nitro carbazole and tetra-nitro oxanilide.

The oxidants are usually potassium nitrate, barium nitrate or mixtures of the two, but occasionally sodium nitrate and potassium perchlorate are also used. Generally, barium nitrate produces the slower burning mixtures but they produce solid slag and burn more erratically than mixtures containing potassium salts.

Historically, the fuels in group 1 are the longest established and have been employed wherever great accuracy in timing is not required. Gunpowder delays can be made accurate and reproducible, but moisture is absorbed by the charcoal during storage and their accuracy tends to deteriorate over long periods and under moist conditions. The proportion of fuel in these mixtures varies between 20 and 40 per cent and is frequently around 30 per cent. The proportion is usually adjusted to produce as complete combustion as possible without the evolution of free carbon particles in the issuing smoke. Rates of burning are controlled by adjusting the proportions of the ingredients within the limits of the range, varying the fuel, or varying the oxidant. Mixtures containing resins such as acaroid resin or shellac tend to burn the most rapidly with rates between 6 and 9 seconds per inch, mixtures containing sugars or mannitol burn at rates between 9 and 12 seconds per inch, and mixtures containing starches and gums burn slowest at rates of 20 seconds per inch or slower. Of these materials lactose and mannitol are the least hygroscopic and delay compositions containing them are relatively free from trouble in storage. However, changes in the rate of burning do take place slowly, largely owing to the growth of potassium nitrate crystals in the consolidated composition. This process has been detected in composition SR 214 (40 lactose-60 potassium nitrate) but it has not been specifically associated with the fuel. The growth probably takes

place in other mixtures also, but its effect is masked by changes brought about by the moisture absorbed by the fuel. Phenol-formaldehyde moulding powders have been successfully used as non-hygroscopic substitutes for powdered resins but the rates of burning of such mixtures tend to be slower.

Delay compositions containing fuels in groups 2 have been developed mainly for use in shell-fuze time-rings in which the delay-train must burn very regularly while spinning in flight. They are also suitable for combustion in straight columns. Much effort and thought has been given to finding better fuels for these compositions, especially during World War II, and has resulted in a definite conception of the desirable features that the ideal fuel should possess. It should be chemically stable and compatible with a wide variety of materials under varied conditions of storage. It should not readily absorb moisture and should not be very soluble in water. It should not volatilise readily and should not melt below the temperature at which it begins to decompose. It should be ignitable, should burn readily and the products of combustion should not form slags.

A number of potassium salts such as the salicylate, dinitrophenate and the more exotic nitrated sulphonates have many of the properties but none of them is entirely satisfactory. Mixtures containing 30 per cent of these salts and potassium nitrate burn slower than gunpowder and rates of burning lie mainly in the region of 6 to 10 seconds per inch.

Slow-burning delay compositions containing organic fuel other than tetra-nitro oxanilide usually rely on an inhibiting ingredient than retards the rate of burning. Inhibition of combustion can be brought about in a number of ways, the commonest being either to produce a large volume of gas to cool the flame and to absorb heat from the burning surface, or to use a fuel that melts before decomposition in order to absorb heat from the burning layer.

In the first method the inhibitor can be sodium bicarbonate which decomposes with the evolution of water vapour and carbon dioxide, or calcium oxalate which produces carbon oxides and leaves behind calcium oxide as a slag. One such composition, SR 120, containing sucrose and resin ester gum as the fuel, has 20 per cent sodium bicarbonate to inhibit its rate of burning to about 180 seconds per inch. Another, SR 124, contains sucrose and 23 per cent of calcium oxalate.

In the second method the fuel is a powdered plastic material having a relatively low melting point. Polyvinyl alcohol and polyvinyl chloride have been used successfully in this role, the latter having the added advantage of generating chlorine gas during decomposition, and so utilising the well-known inhibiting effect of this element on the combustion of hydrocarbons. Composition SR 141, containing P.V.C. and barium nitrate, burns at 130 seconds per inch, and composition SR 139, which contains calcium oxalate in addition, burns at 196 seconds per inch. None of these slow-burning delay compositions burn very regularly and times of burning

may vary by as much as 20 per cent. Moreover, since heat is evolved so slowly, the burning surface must be large enough to compensate for losses in heat, and delay-columns must be at least $\frac{3}{4}$ -inch in diameter to maintain combustion satisfactorily.

The use of certain organic nitro-derivatives as fuels arose out of the search for new fuels for time-fuze powders and for a non-hygroscopic alternative to charcoal in gunpowder, both as a delay composition and as a propellant. The characteristics looked for in these materials were those outlined above. Three substances that satisfy these conditions very closely are the polymer of nitro-indene which decomposes without melting, 1, 3, 6, 8 tetra-nitrocarbazole with a melting point of about 285°C., and tetra-nitro-oxanilide, melting point 182°C. Nitro-indene polymer is used as a straight substitute for charcoal in composition SR 346 in which it is mixed with potassium nitrate and sulphur. Variants of the composition contain small proportions of potassium perchlorate to achieve smoother combustion in time-fuze rings. The composition burns in a straight column at rates between 3 and 4 seconds per inch.

Tetra-nitro carbazole is one of the most successful fuels used so far and delay compositions containing it burn remarkably uniformly under widely varied conditions. It can be used with potassium nitrate, with barium nitrate or with mixtures of the two. Mixtures with barium nitrate burn the slowest.

Rates of burning with potassium nitrate vary from 4.4 secs. per inch for 25 per cent T.N.C. to 3.1 seconds per inch for 45 per cent. With greater proportions of T.N.C. the rate of burning decreases. Composition SR 112, containing 40 per cent T.N.C., burns at 3.3 seconds per inch and is very reproducible from batch to batch when made under identical conditions.

Tetra-nitro carbazole and tetra-nitro oxanilide are finding increasing uses as fuels in slow-burning delay compositions in which they are mixed with potassium nitrate and barium nitrate. The range in rates of burning of these mixtures varies from 3 seconds per inch to 50 seconds per inch, and the compositions burn remarkably steadily and with reproducible characteristics.

The uniformity with which delay and time-fuze compositions burn and the accuracy of the times produced by them depend very largely on the particle-size of the ingredients and the intimacy with which they are mixed. In practice this is achieved by milling the ingredients together under a suitable liquid for long periods in an edge-runner mill. Alcohol is mostly used as the liquid and the mixtures are milled as a thick paste and then dried. To facilitate filling they are granulated by moistening with water, milling for a further short period, forcing the paste through sieves and redrying.

GASLESS DELAY COMPOSITIONS

The basic reaction underlying the combustion of many gasless delay compositions is the Goldschmidt or thermite reaction in which a metal powder and a metallic oxide interact in an oxidation-reduction reaction with the evolution of much heat and the formation of solid products. Variations in the oxidants such as the use of oxy-salts in place of oxides may complicate the chemistry, but basically, only solid products are formed with little or no gas except, perhaps, that formed by the liberation of air occluded during consolidation. Thus, gasless delay compositions can be burnt satisfactorily in confined spaces with very little venting.

The fuels in these compositions are mostly finely powdered metals amongst which silicon, boron, titanium, zirconium, manganese, tungsten, molybdenum and antimony are the commonest. Alloys and binary compounds including zirconium-nickel alloy, ferro-silicon and ferro-titanium are also used. The oxidants include heavy metal oxides and peroxides and various oxy-salts of potassium and barium. Many delay compositions are binary mixtures of metal powder and oxidant but occasionally a second metal or a second oxidant is included to increase the flexibility of the system.

The rates of burning of gasless delay compositions depend on the chemical nature of the ingredients, their proportions, the fineness of the powders, the intimacy of mixing and the degree of consolidation. They also depend on the material and dimensions of the delay-bodies and on the ambient conditions under which they burn.

In binary mixtures the rates of burning vary with varying proportions of the ingredients in a characteristic manner, depending on their chemical reactivity. As the proportion of fuel increases the rates of burning usually get faster until a maximum is reached and then slow down again with further additions. The fastest rates of burning are usually attained with proportions of fuel greater than those required by stoichiometry. The shape of the rate of burning - percentage fuel curve is characteristic of the ingredients. With one pair of ingredients the change in rate of burning may be gradual and the curve may slope gently towards and away from the optimum proportions, so that small variations in proportions have little effect on the rate of burning. With another pair, the rate of burning may vary rapidly with proportions, and small variations in the percentage of fuel may change the rate of combustion considerably. Obviously, the former type of mixture is desirable in the interests of producing accurate delays and, wherever possible, proportions corresponding to the flattest portion of the curve are chosen. These changes in rates of burning are illustrated in Figure 8.

The rates of burning of ternary systems vary in a more complicated manner and depend to a large extent on the nature of the third ingredient.

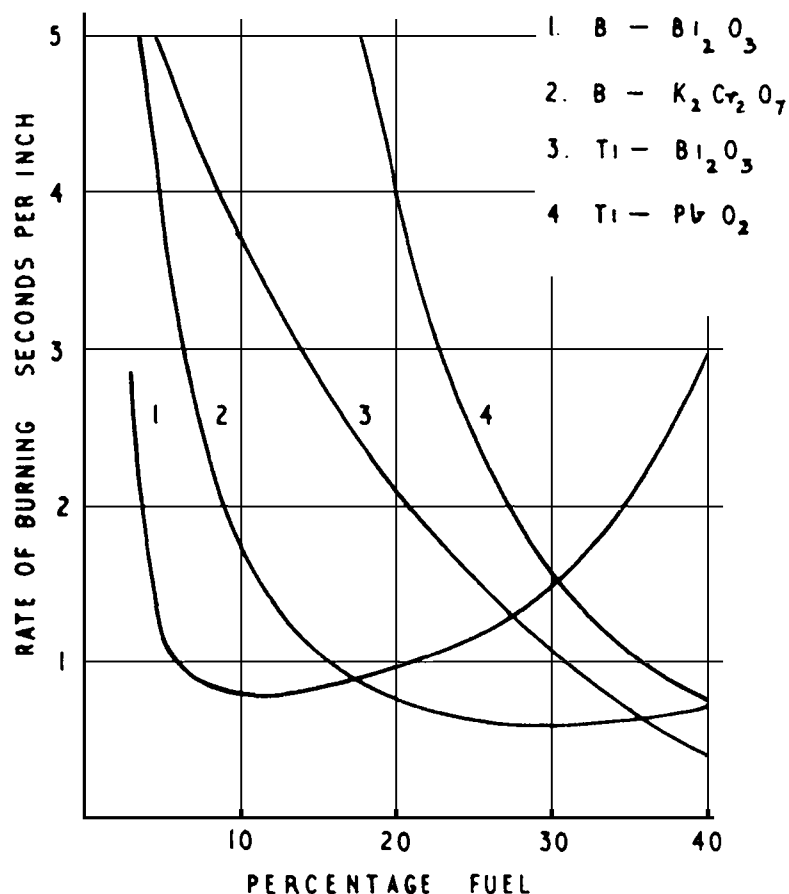


Fig. 8. Variation of the Rate of Burning of some Binary Delay Mixtures with proportion of Fuel.

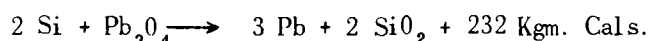
If it is a fuel, it may materially increase the rate of burning because it generates more heat or because its products of combustion are more fluid. If it is an oxidant, its decomposition products may be refractory and may slow down the rate of burning in the manner of a diluent. The behaviour of ternary systems is quite unpredictable, and can only be examined by the laborious process of plotting the measured rates of burning of various mixtures on ternary diagrams and observing the trends followed by lines of equal rate of burning.

The following is a brief description of the more important gasless delay systems in use.

SILICON AND LEAD OXIDES

Mixtures of powdered silicon and lead monoxide, lead dioxide or red lead burn very fiercely and rapidly with the formation of metallic lead and fusible lead silicate.

The primary reaction with red lead probably takes the course represented by:-

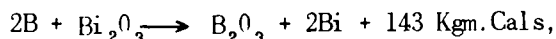


and the stoichiometric mixture contains about 7 per cent silicon and generates 300 calories per gm. Lead silicates are also formed in secondary reactions. Reactions with the other oxides are similar in nature.

Rates of burning vary from a fraction of one second per inch to approximately 10 seconds per inch depending on the oxide and the proportions. The mixtures are difficult to consolidate and delay columns tend to flake under rough usage. The addition of potassium nitrate to the mixtures causes them to burn slower and less violently and increases the mechanical strength of the delay column.

AMORPHOUS BORON AND BISMUTH OXIDE

Amorphous boron reacts vigorously with bismuth oxide to form fusible metallic bismuth and volatile boric oxide.



The stoichiometric mixture contains 4.4 per cent boron.

The rates of burning of mixtures increase from 1.7 seconds per inch with 3 per cent boron to 0.6 seconds per inch with 8 per cent and then decreases steadily to 3 seconds per inch with 40 per cent. The rate of burning is affected by the impurities present in the amorphous boron and mixtures with the pure metal burn faster. The impurities are mainly magnesium acquired during manufacture and boric oxide from surface oxidation. All the mixtures are very ignitable because of the small size of the particles of boron (0.5 to 1 micron) and the fastest burning mixtures are prick-sensitive when consolidated under high loading pressures.

AMORPHOUS BORON, BISMUTH OXIDE AND CHROMIC OXIDE

This is a ternary system in which the chromic oxide affects the rate of burning in the manner of a diluent since mixtures of boron and chromic oxide do not burn.

In general, the proportion of boron is maintained constant at 10 to 12 per cent and bismuth oxide is successively replaced by chromic oxide up to a maximum of 40 per cent. Rates of burning vary from 0.7 seconds per inch to around 6 seconds per inch according to the proportion of diluent present. The slag of the slower burning mixtures solidifies rapidly and tends to choke the delay-tube, causing combustion to become less regular and delay-times less accurate.

AMORPHOUS BORON, SILICON AND POTASSIUM DICHROMATE

The rates of burning of binary mixtures of amorphous boron and potassium dichromate vary continuously from about 0.6 seconds per inch with 40 per cent boron to 5 seconds per inch with 6 per cent. Below this proportion there is a sharp decrease in the rate of burning, and the mixture containing 5 per cent burns at 15 seconds per inch. The 4 per cent mixture burns very slowly with difficulty in wide-bore delay-tubes but combustion can be accelerated by adding powdered silicon to the mixture. In the ternary system thus produced, the proportion of amorphous boron is maintained around 4 per cent and the proportion of silicon is varied from 0 to 12 per cent. Rates of burning vary from about 40 seconds per inch for no silicon to about 6 seconds per inch for 12 per cent silicon. This type of composition is almost completely gasless and burns very smoothly in unvented delay units. There is virtually no flame and the slag remains in situ without affecting the regularity of combustion. The heats of combustion are low and the mixtures must be consolidated into delay-tubes of $\frac{1}{4}$ -inch bore or larger to ensure maintaining combustion.

The ignitability of delay compositions generally varies according to their rates of burning and the faster burning ones are more ignitable than the slower burning ones. The latter need to be primed with a small quantity of a fast burning composition for satisfactory ignition, and for this purpose composition SR 92 containing 12 per cent boron, 66 per cent bismuth oxide and 22 per cent chromic oxide, has come to be widely used. It burns at 2 seconds per inch and leaves behind a residue of hot molten slag that heats the surface-layer of the main delay composition to its ignition point.

AMORPHOUS BORON AND BARIUM CHROMATE

Mixtures of boron and barium chromate containing between 4 and 10 per cent boron burn very quietly and smoothly with little or no flame and with rates within the range 0.5 to 3.5 seconds per inch. They produce accurate delays which change little on storage. The range can be extended to 8.5 seconds per inch by introducing chromic oxide as a diluent.

Other delay compositions that are in use include mixtures of powdered antimony and potassium permanganate, powdered molybdenum or tungsten with barium chromate and potassium perchlorate and powdered zirconium and barium chromate. Antimony-potassium permanganate mixtures are used in commercial delays and have a wide range in rates of burning. They are practically gasless but are somewhat unstable in the presence of moisture, especially at elevated temperatures, and must be hermetically sealed for long storage. The molybdenum and tungsten mixtures have useful wide ranges of rates of burning and appear to suffer rather less from environmental changes than do some of the other systems. Many zirconium delay mixtures burn very fast and are useful for registering short intervals of time.

SOME CAUSES OF VARIATION IN DELAY TIMES

Since delays are for the most part mixtures of fuels and oxidants intimately blended together and consolidated incrementally into tubular delay-bodies, it is apparent that variations in manufacture and filling may adversely affect the manner in which they burn and so lead to inaccuracies in timing. The following are some factors that may well be critical in this respect.

1. The chemical nature of the ingredients
2. Their purity
3. Their particle-size and physical form
4. The uniformity of blending
5. The presence of moisture absorbed from the atmosphere
6. The loading pressure
7. The size and number of increments
8. The density of the consolidated composition
9. The ease of ignition of the surfaces of the increments
10. The method of initiation
11. The physical properties of the products of combustion
12. The dimensions of the delay column
13. The material and physical properties of the delay-body
14. The free space into which the products of combustion may vent.
15. The ambient temperature and pressure during combustion
16. The effect of spin on combustion

Variations in the constitution of organic fuels, water of crystallisation, impurities introduced during the manufacture of fuels such as the magnesium present in amorphous boron, can all affect the rate of burning and so need to be critically controlled. Oxidants are not so liable to such variability.

The speed of combustion is very dependent on the fineness of the powders blended together. In general, the finer the particles the faster compositions burn, and to ensure reproducible rates, the ingredients are frequently blended by milling in order both to reduce the particle-size and to bring fuel and oxidant into more

intimate contact, and hence to produce the fastest burning mixtures. With some powdered metal fuels, it is necessary to control the range and distribution of particle-size of the samples being used. The shape of the particles can be important, since it can affect the extent of the surface of contact of fuel and oxidant and hence the speed of combustion. This is apparent in the combustion of blown and flake aluminium. Crystalline boron burns less rapidly than amorphous boron largely for the same reason. It is obvious that reproducibility of delay-times depends on the thoroughness and uniformity with which ingredients are distributed throughout delay mixtures, but small variations can become critical when the proportion of one of the ingredients is small and its effect on combustion is considerable. This happens with slow-burning mixtures of boron, silicon and potassium dichromate, where the total proportion of fuel is only about 6 per cent and a variation of $\frac{1}{2}$ per cent changes the rate of burning by several seconds per inch.

Moisture absorbed from the atmosphere during manufacture can present something of a problem, especially where certain naturally occurring organic fuels, which may be hygroscopic, are used. Charcoal, for gunpowder and time-fuze composition RD 202 readily picks up moisture. These compositions must be conditioned in an atmosphere of controlled humidity before filling, since variations in the moisture present can produce variable times of burning. Wherever possible, non-hygroscopic alternatives to such ingredients are to be preferred.

The rates of burning of many delay compositions vary somewhat with the density of the compressed column, and are therefore dependent on the loading pressure, the time of dwell of the ram and the length of the increment. Since the density of an increment is greatest immediately beneath the ram and is least at the opposite end, the rate of burning varies throughout its length and tends to fluctuate over several increments. Increments should therefore be short and certainly no longer than the diameter of the delay-column. To avoid variations due to the loading pressure and to produce robust columns, it is usual to consolidate at pressures between 15 and 20 tons per square inch. These high pressures produce very hard, polished surfaces which do not ignite readily. The face of the ram is therefore deeply scored to produce a roughened surface to aid ignition.

The problems related to variable loading densities and rates of burning, and the hazards involved in the incremental filling of delay compositions, are entirely eliminated by what is known as the lead-tube method of filling. In this, a short length of lead tubing of half-inch bore, and closed at one end, is filled with the composition by hand-stemming and is then sealed off. The tube is passed between a pair of grooved steel rollers under pressure, the grooves being semi-circular in contour and decreasing slightly in size from one groove to the next. As the tube passes to and fro it is squeezed to a smaller diameter and lengthened, the composition within it being consolidated. This process is continued until the

lead tube will enter the delay-tube. A suitable length for filling is obtained by nicking the lead with a knife and breaking it off. It is then consolidated in the delay-tube by one pressing operation. After a few passes between the rollers, the composition is found to be consolidated to a degree equivalent to a loading pressure of 15 tons per square inch.

Delays are most frequently initiated by the hot gases from caps, detonators, electric fuses or propellants. The gas pressures to which they are subjected during this process may, if they are very high, cause rapid combustion of the delay composition or even erode part of the surface away and so lead to irregular times of burning. It is therefore necessary to protect the igniting face of the composition from such violent treatment and, wherever possible, to ensure that ignition takes place in a quiet and steady manner.

The products of combustion of delay compositions containing carbonaceous fuels are mostly gaseous and solid products from the oxidants tend to be swept out of the delay-body, thus maintaining steady conditions for burning. If, however, the composition burns slowly, the evolution of gas may be insufficient to remove continuously such products as calcium and barium oxides and the delay-tube becomes choked, giving rise to fluctuations in pressure and hence in rate of burning. The variations are accentuated in narrow tubes. This problem can be even more acute with slow-burning gasless delay compositions, especially those in which bismuth oxide is reduced to metallic bismuth during combustion. The molten metal quickly solidifies, and if the pressures generated at the burning surface are insufficient to eject the molten metal from the delay-tube before this happens, it may cause obstruction and produce a rise in pressure within the tube, resulting in an acceleration of combustion. The presence of the diluent chromic oxide increases the obstruction and compositions with more chromic oxide tend to burn less regularly than those with less. Choking by the products of combustion can be reduced by increasing the diameter of the delay-column. A larger diameter may also be necessary for certain slow-burning compositions which have small heats of combustion, so that sufficient heat may be generated to maintain the burning layer. For such compositions there is a critical diameter of column below which they will not burn regularly.

The material of the delay-body may affect the combustion in a pronounced manner. For example, if the delay-tube is made of a good heat-conducting metal, unburnt composition beneath the burning layer may be excessively preheated and will therefore burn faster, or alternatively, a mass of metal in contact with the delay body may absorb so much heat from the burning surface that combustion cannot be maintained.

The combustion of delay compositions, like that of all pyrotechnic compositions, is affected by the pressure of the surrounding atmosphere. High pressures cause them to burn faster and low pressures to burn slower. The effect is greater the more gas the composition produces during combustion. The relation

between the rate of burning and the ambient pressure is expressed by $R_1 = RP^n$, where R_1 is the rate of burning at normal pressure and R the rate of burning at the pressure P expressed in atmospheres. 'n' is a fractional index that varies from one composition to another and is greater the more gas produced. Sulphurless gunpowder, a typical gas-producing delay composition, has a normal rate of burning of 2.3 seconds per inch and a value of $n = 0.42$. Hence, under a tenfold increase in ambient pressure it will burn at 0.87 seconds per inch and under a tenfold decrease at 6.05 seconds per inch. (In practice, it fails to burn before this low pressure is reached). Ambient pressure has a much smaller effect on the so-called gasless delay compositions and their values of 'n' vary between 0.08 and 0.20. A composition whose rate of burning is least affected is SR 49 containing silicon, lead monoxide and bismuth oxide. It has a normal rate of burning of 2.5 seconds per inch and changes from 2.08 seconds per inch at the high pressure to 3.0 seconds per inch at the low. Mixtures of boron, silicon and potassium dichromate are affected to a somewhat greater degree ($n = 0.10$) and mixtures of boron, bismuth oxide and chromic oxide may be affected even more (n for SR 89 = 0.10 and for SR 87 = 0.20).

Changes in temperature also affect the combustion of delay compositions and they burn faster as the ambient temperature is raised and vice versa. Gasless compositions are affected more than gas-producing compositions. For example, if a delay burning for two seconds at 15°C , contains the gas-producing composition SR 112 it burns for 2.06 seconds at -40°C and 1.94 seconds at $+70^\circ\text{C}$. If, however, it contains the gasless composition SR 64 it burns for 2.56 seconds at the low temperature and 1.44 seconds at the high. The differences vary from one composition to another, some greater and some less, but the overall difference in behaviour of the two types of composition is always considerable.

Delays, used to produce time-intervals in projectiles that are spinning rapidly, usually take the form of a C-shaped channel in a metal plate lying normal to the axis of spin. If the delay-system can be vented a gas-producing composition such as gunpowder, composition RD 202, or one of the mixtures containing organic salts as fuels are used, the surfaces of the composition in the channel being covered with paper and boxcloth to prevent flash-over. If the system is unvented a gasless composition covered with a layer of refractory material such as powdered calcium fluoride or magnesium oxide must be used.

In general, high rates of spin cause gassy fillings to burn faster than they do at rest and gasless compositions to burn slower. Some gasless compositions fail to burn at all when spinning. The alternative type of straight tube delay situated along the axis of spin presents greater difficulties in the combustion of certain types of gasless compositions since the semi-fluid burning layer tends to be removed by centrifugal forces.

REFERENCES

Kinetics of layer to layer burning in Gasless compositions.
Bowen, Staveley et.alia.

CHAPTER 10

INCENDIARY MATERIALS AND COMPOSITIONS

Incendiary materials have been used in warfare from very early times whenever attacking armies besieged fortifications and cities or the defending forces attempted to drive them off. Inflammable mixtures of pitch, sulphur, tow etc. were projected by means of arrows and catapults in order to set fire to wooden structures sheltering the enemy. Greek fire, said to have been invented c.670 A.D., was the greatest fire-raising development until modern times. Its exact composition is unknown but it contained pitch, resin, petroleum or petrol and sulphur and was difficult to extinguish with water.

Modern incendiarism began during the 1914-1918 war with the evolution of the aeroplane whereby incendiary bombs could be dropped on strategic targets. In the second world war great emphasis was placed on the need to deprive the enemy of the means of waging war and aerial incendiary attack was one of the important means of achieving this end.

When combustible materials such as wood, paper, fabrics etc. are heated the moisture present is first driven off, followed by chemical decomposition of the materials and the evolution of combustible gases. Their ability to burn with flame depends on the nature of the combustible gases and the ease with which they are produced. The amount of gas evolved from a given fuel and with a given supply of heat, is largely determined by the moisture it contains and the rate at which heat is transferred to it. The latter depends on the temperature of the source of heat, the surface area of the solid exposed to radiant and convected heat, and the thermal conductivity of the material. The flame-temperature of the burning gases and the thermal conductivities of fuels lie within relatively narrow limits, although the effective surfaces of the fuels may vary over a wide range. Heated fuels therefore evolve gas at a rate mainly determined by their effective surfaces, and this parameter together with their moisture content, are the most important factors affecting the ease of ignition and the subsequent spread of fire.

Incendiary materials must, therefore, have a high heat of reaction which must be applied to the combustibles until the ignition temperature is reached. The heat must not be liberated too rapidly, and for ignition of the combustible to be certain, four times the minimum heat must be supplied to it.

In general, incendiary materials fall into two distinct groups, namely, metals and alloys which, once ignited, burn in air with a high heat of combustion and tend to concentrate their heat in small areas, and mixtures of combustible carbonaceous fluids that spread over the target while burning. Typical incendiary materials together with their heats of combustion, are listed in Table 19.

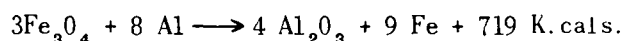
TABLE 19 HEATS OF COMBUSTION OF TYPICAL
INCENDIARY MATERIALS

Materials	Calorific Value Calories per gram
Aluminium	7,000
Magnesium	6,000
Thermite	790
Thermalloy	770
Potassium	1,240
Sodium	2,170
Phosphorus	5,900
Carbon Disulphide	3,250
Furfural Extract from lubricating oils	10,300
Naphthene base lubricating oils	10,800
Turpentine	10,830
Naphthalene	9,168
Toluene	10,200
Petrol (high grade)	11,180
Pentane	11,540
Petrol Gel. 13% Napalm.	10,461
Petrol/Toluene Gel. 4% isobutylmethacrylate	10,300
Cellocotton	3,850

Few incendiary materials are spontaneously inflammable in air, the exceptions being white phosphorus, potassium, alloys of sodium and potassium, and certain metal-alkyls such as aluminium triethyl. The remainder need to be heated to their ignition temperatures by pyrotechnic means before they will burn. Phosphorus has been tried as an incendiary but it burns slowly in the mass, and the phosphoric acid produced insulates the combustible material and confines the fire. It has been used for the spontaneous ignition of other incendiary material such as felt soaked in potassium nitrate and dried. Certain alloys of sodium and potassium are liquid at ordinary temperatures and are spontaneously inflammable in air. They are much more effective as fire-raisers but special precautions are needed to handle them. Metal alkyls, in general, have a low proportion of metal and their rate of combustion in air is too great to be effective as incendiaries.

The two metals best suited as incendiary agents are aluminium and magnesium, since they have large heats of combustion and reasonably low melting points. They are, however, difficult to ignite in the mass and require a considerable amount of heat to initiate combustion in air. If their exposed surface is increased by powdering, they are easier to ignite but tend to burn explosively as a dust cloud, especially if initiation is made with a small quantity of high explosive.

Ignition of the massive metals is achieved with heat supplied by the Goldschmidt or thermite reaction in which powdered aluminium reacts with iron oxide to form aluminium oxide and metallic iron.



The stoichiometric mixture contains 23.7 per cent aluminium powder, the heat produced in the reaction is 790 calories per gram of mixture, and the temperature reached is sufficient to melt the iron. The oxide is the stable one and is used in the form of hammerscale.

Thermite mixtures of this type are difficult to ignite and barium nitrate is frequently added as a more reactive oxidant. Barium peroxide is also used. The rate of combustion is varied by changing the particle-size of both the aluminium powder and the hammerscale. The aluminium powder is often a mixture of blown and flake powders, the latter producing faster burning compositions than the former. Boric acid is included to stabilize the composition.

The basic incendiary SR composition is SR 306 containing:-

Blown aluminium powder, size 25	10 parts
Flake aluminium powder, size 120	10 parts
Hammerscale, size 100	40 parts
Barium nitrate, size 120	35 parts
Boric acid	5 parts

When ignited, this composition burns rapidly and generates 650 to 700 calories per gram of composition. It does not ignite directly from a flame and is primed by a 50/50 mixture with composition SR 252, (SR 403), or by a similar composition containing barium peroxide instead of barium nitrate (SR 448A). A variant of composition SR 306 is composition SR 380 containing manganese dioxide (pyrolusite) instead of hammerscale.

Liquid incendiary fillings, like the Greek fire of old, are mainly composed of inflammable hydrocarbon oils that have large heats of combustion and can be ignited and scattered over the target by explosive charges. The scattering process leads to inefficiency through excessive loss of fuel by atomisation and flash on bursting, and improvement in performance is achieved by increasing the viscosity of the liquid. Various materials that are used to gel the hydrocarbons include aluminium soaps such as the cleate or the laurate, synthetic polymers such as perspex, and rubber. A typical

composition of this type which was used successfully in World War II is composition SR 425 which contains:-

5 per cent solution of perspex in benzole	50 parts
Flake aluminium powder, size 120	10 parts
Calcium Silicide, size 120	10 parts
Sodium nitrate, size 120	27 parts
Boric acid	3 parts

Another composition, SR 400, is essentially a 5 per cent solution of rubber in benzole.

REFERENCE

Solid Propellants and exothermic compositions. Taylor.

CHAPTER 11

COLOURED SMOKE SIGNAL COMPOSITIONS

Coloured smoke signals are used in daylight only and are seen by the light reflected from particles and droplets in the smoke cloud. They are best observed in bright daylight from a short distance with the sun behind the observer. Under less favourable conditions the colours of the clouds change markedly, the darker ones towards black and the lighter ones towards the redder tones.

In practice, only five colours are used in service smoke signals. Orange, which is the easiest to recognise against grey seas and skies, is universally used as a distress signal colour. The other four colours, selected for their distinctiveness under the majority of weather conditions, are red, yellow, green and blue.

For ease of recognition, a coloured smoke cloud should have a distinctive colour and should be as large and as dense as possible. This will depend on the rate of evolution of smoke, on the quantity of smoke composition consumed and on the relative motion of the smoke-cloud and the surrounding air. Thus, smoke signals can be used satisfactorily in ground-to-ground and ground-to-air signalling but not in air-to-ground signalling.

Little useful data is available on the visibility of coloured smoke clouds. In certain trials at sea, red smoke from compositions burning at $\frac{1}{2}$ -lb. per minute was difficult to see from three miles in a 25 m.p.h. wind, whereas that from composition burning at 1 lb. per minute was easily seen. In other trials at sea, red, yellow and green smoke generators, consuming 1 lb. of composition per minute in a 12 m.p.h. wind, were visible from aircraft flying at 5,000 feet altitude at a distance of 5 miles. Blue smoke was visible under the same conditions from only half the distance.

COLOURED SMOKE COMPOSITIONS

Coloured smokes for signalling can be produced by dispersing finely powdered materials, by chemical reactions which generate coloured smoke, and by vaporising dyestuffs. The last method is the only satisfactory one in practice because the first two give smokes with small volume and inferior colours. Black, or rather grey, smokes are an exception since they rely on the free carbon or soot generated by the combustion of naphthalene or anthracene in certain compositions.

INGREDIENTS

Coloured smokes are used in two ways, namely, as an instantaneously produced puff or smoke-burst, or as a steady evolution of smoke over a period of time lasting from a few seconds to several minutes. In either case heat must be generated to volatilise the dyestuff and is produced by the combustion of a suitable fuel.

In the coloured smoke-bursts produced by shell, the combustible part of the filling can be a mixture of nitrocellulose powder and inorganic nitrates, or pentaerythritol tetranitrate which has been coated with paraffin wax. The fuel is mixed with the powdered dyestuff and the mixture is exploded by a suitable detonating system.

The composition used in continuously burning coloured smoke signals consist of two component parts intimately mixed together, namely, the dyestuff to be vaporised and the vaporiser, which is the combustible mixture supplying heat.

An efficient vaporiser must satisfy as many of the following conditions as possible.

1. It must supply heat at a temperature sufficient to vaporise the dye completely but not high enough to decompose it and, in order to be efficient, there should be enough heat produced to vaporise its own weight of dyestuff.
2. The products of combustion should be mainly gaseous with a minimum of solid residue, since hot slag will tend to decompose the dye and will cause the composition to burn spasmodically.
3. It should not of itself produce smoke that would degrade the coloured dye-vapour.
4. It should not be unduly sensitive to friction or heat and should not be hygroscopic.
5. It should be in the form of a fine powder capable of intimate mixture with the powdered dyestuff.

Vaporisers that satisfy all the above conditions equally well are limited to a few combustible mixtures in which the oxidant is almost invariably potassium chlorate, and the fuel is lactose and, to a lesser extent, sucrose. Lactose compositions burn more regularly than those containing sucrose and there is less tendency for the colour of the smoke to fade.

Various other gas-producing fuels have been tried from time to time. Sulphur and charcoal, although satisfying the conditions of gas formation, form dangerously sensitive mixtures with potassium chlorate and, even when they are desensitised by the addition of sodium bicarbonate, great care must be exercised in handling them. Solid hydrocarbons cannot be readily obtained in finely powdered form and chlorinated hydrocarbons, which can be so prepared, burn too slowly and produce free carbon. Organic hydroxy-compounds such as polyhydric alcohols, carbohydrates such as glucose, starches, flours and resins have also been tried, but the mixtures usually burn too slowly or are slightly unstable, especially in the presence of moisture and so deteriorate in storage.

The colourants of smoke compositions are all dyestuffs that sublime below 350°C. The three properties related to chemical constitution, which determine the suitability of a dyestuff, are volatility, thermal stability and purity of colour. The flash-point should also be high or the vapour may inflame and thereby destroy the colour. The suitability of a dyestuff is closely linked with the following conditions:

1. The molecular weight must not be more than 450.
2. Preference is given to the following dyestuff series: anthraquinone, azine, azo, quinoline and xanthene.
3. The following groups must be absent:- sulphuric, hydrochloride, nitro, nitroso and quaternary ammonium and oxonium.
4. The following groups may be present:- amino and substituted amino, alkyl, aryl, chloro, bromo, hydroxy and alkoxy.
5. The dye must not tend to undergo auto-condensation.

It is not always possible to find a single dyestuff to give a suitable smoke, and mixtures of two or more are then used. For example, no single dye is known that gives a satisfactory green smoke, but this can be done with a mixture of blue and yellow dyes.

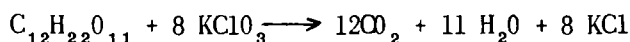
The anthraquinone series of dyes is the most important for smoke production, since its members are stable but volatile, and include all shades of red, orange, yellow, blue and violet. In addition they have relatively high flash-points.

The best cooling agents, used to lower the temperature of combustion and to regulate the rate of burning, are the bicarbonates of sodium and potassium.

PROPORTIONS OF THE INGREDIENTS

The proportions of oxidant, fuel and dyestuff must fall within fairly narrow limits.

The combustion of lactose and potassium chlorate takes place according to the following equation.



and the stoichiometric mixture contains 25.9 per cent lactose and 74.1 per cent potassium chlorate. If, however, the fuel and oxidant are used in these proportions the dyestuff is decomposed by the high temperature produced and in practice they are used in equal proportions.

The most satisfactory smokes are obtained when the vaporiser and the dyestuff are also in equal proportions so that the basic smoke composition is represented by:-

Lactose	25 parts
Potassium Chlorate	25 "
Dyestuff	50 "

Such compositions burn at rates between 45 and 90 seconds per inch when consolidated under loads of 1 to 4 tons per square inch, and rather faster when consolidated by hand-stemming. Any increase in the proportion of vaporiser, in order to speed the rate of burning, usually results in the decomposition of the dyestuff and the smoke turns grey in colour. Short times of burning with high rates of smoke-evolution are therefore only obtained by making use of large burning surfaces. The design of smoke-producing pellets is therefore of prime importance.

When coloured smoke compositions are consolidated into containers and burnt cigarette-fashion, the rate of burning is usually slow, the smoke is not very dense and in passing through the hot slag it may be discoloured. In order to avoid destroying the dye vapour, the smoke must be freely vented into the atmosphere without having to pass through the burning layers. This can usually be achieved with greater or less success by using annular pellets and venting into the central space, or by venting into an annular space surrounding solid pellets by means of escape holes in the internal or external walls of the container.

Another method of venting is to pack the container with smaller pellets with air-spaces between them. The pellets burn over their entire surface and the time of burning is controlled by their size. Coloured smoke compositions are consolidated into pellets under loads of 2 to 4 tons per square inch. The limit to the size of such pellets is about $1\frac{1}{2}$ -inches in both diameter and length, since with larger pellets the colour of the smoke issuing from within is degraded by the hot outside layer. In the limit, pellets can become small granules and the evolution of smoke will be brief and very dense. The production of such small pellets is costly and time-consuming and an alternative process which virtually achieves the same result is sometimes to be preferred.

In this process, the coloured smoke composition is made into a paste with a weak solution of gum arabic or other suitable adhesive, and the paste is forced through a $\frac{1}{4}$ -inch die to produce vermiform extrusions which are dried on trays in an oven and then broken up into suitable lengths. The material, when packed into the container, burns at rates satisfactory for the evolution of good dense smoke. This method of production has the advantage of producing a relatively clean product to handle in filling operations and thereby avoids creating a heavily dye-laden atmosphere in the filling shop. Its disadvantages are the space required for drying the composition on open trays and its low packing-density in the container.

Pellets of smoke composition need priming in order to ignite them satisfactorily. The usual priming compositions, sulphurless gunpowder and composition SR 252, are very hot and cause coloured smoke compositions to inflame. These compositions are therefore primed with the cooler composition SR 214, containing lactose and potassium nitrate, which gives sufficient heat to ensure satisfactory ignition. It is not necessary to prime every pellet

in a filling, for once combustion has begun it will quickly spread to other pellets. Up to a point, the rate of smoke evolution can be controlled within fairly narrow limits by the number of points of ignition, in the form of primed pellets, throughout the filling and the size of the pellets; Extruded fillings can be ignited by including a number of primed pellets.

The longest time of emission from a single coloured-smoke store, that can conveniently be achieved with high density smoke, is about one minute. When longer times are required it is usual to link two or more such containers together to burn in sequence.

CHAPTER 12

SCREENING SMOKE COMPOSITIONS

Screening Smokes, as the name implies, are used to hide fighting vehicles, troop movements, and local tactical operations from the eyes of the enemy for short periods of time. Generally, they are white or greyish white aerosols produced by chemical or pyrotechnic means, but it is also possible to produce efficient screening clouds by vapourising mineral oils which condense in the atmosphere in the form of tiny droplets.

Chemical screening smokes are produced by the rapid hydrolysis of certain liquid chemicals sprayed into the moist atmosphere. Chlorosulphonic acid, titanium tetrachloride or silicon tetrachloride are employed for this purpose. The first material produces a mixture of hydrochloric and sulphuric acids which absorb water vapour and form an aerosol of dilute acids, while the others produce a mixture of hydrochloric acid and solid particles of titanium hydroxide or silicon hydroxide.

The use of liquids for screening has the advantage of simplicity and flexibility of application, since they can be sprayed from moving vehicles or injected into the exhaust systems of vehicles or aircraft or scattered explosively from bombs. The liquids, however, are very unpleasant to handle and require special precautions. The smokes produced by them are toxic but do not appear to produce harmful effects over short periods of exposure.

PYROTECHNIC SCREENING SMOKES

The simplest screening smoke produced by pyrotechnic means is obtained by burning white phosphorus in air to form phosphorus pentoxide. The oxide, which is very hygroscopic, immediately absorbs moisture and forms an aerosol of phosphoric acid. It is a particularly useful filling for bombs, shell and grenades producing bursts of screening smoke, since it is readily melted, scattered and ignited by detonating explosives.

The most widely used pyrotechnic smoke compositions are those in which powdered zinc, zinc oxide or calcium silicide react with chlorinated hydrocarbons to produce, essentially, aerosols of zinc chloride, calcium chloride, silicon hydroxide and carbon. There are two main types of composition, one containing carbon tetrachloride, absorbed on some suitable material such as kieselguhr or magnesium carbonate, zinc powder and zinc oxide, and the other containing hexachloroethane, calcium silicide and zinc oxide.

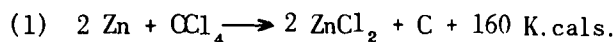
An example of the first type is composition SR 234 containing:-

Carbon tetrachloride	45 parts
Zinc powder	20 "
Zinc oxide	28 "
Kieselguhr	7 "

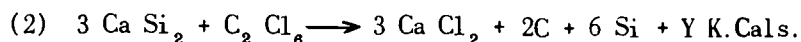
and one of the second types is composition SR 264A containing:-

Calcium silicide	10 parts
Hexachloroethane	45 "
Zinc oxide	45 "

The reactions that take place during combustion are very complicated, but the exothermic reactions responsible for the initiation and maintenance of combustion are respectively:-



and



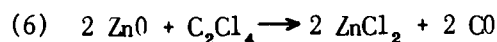
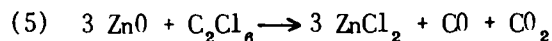
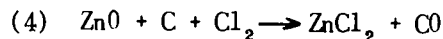
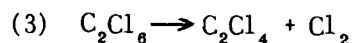
The value of Y in equation 2 is quite large, partly because of the excess silicon present in commercial calcium silicide.

Secondary reactions take place during combustion between the products of pyrolytic decomposition of the chlorinated hydrocarbons and the other components of the mixtures. The results of these reactions demonstrate the basic differences between the two types of composition.

When mixtures of zinc powder and carbon tetrachloride burn, the exothermic reaction generating the heat also generates the main smoke-producing material, zinc chloride. The results of the secondary reactions lead to the formation of other reactive chlorinated hydrocarbons, carbonyl chloride, carbon and chlorine, which combines with zinc to form more zinc chloride. The carbon produced gives the smoke a greyish colour.

When mixtures of calcium silicide, zinc oxide and hexachloroethane burn, the products of the primary exothermic reaction play only an insignificant part in the formation of the smoke, which is developed during the secondary reactions.

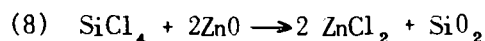
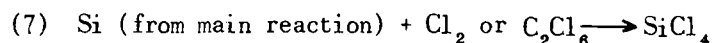
These are:-



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The rates of the reactions between zinc oxide and chlorine compounds are greatly increased by the presence of carbon produced in the main exothermic reaction.

Also, some silicon tetrachloride, which gives an aerosol in moist air, may be produced and may react with zinc oxide.



In both types of mixtures zinc chloride is the main smoke-producing product but it is derived from different sources.

The rate of burning of these mixtures is affected by a number of factors, including the chemical reactions outlined above. The reaction controlling the initiation of burning is the one that proceeds most rapidly at the temperature of initiation and is sufficiently exothermic. It will, in general, also control the rate of burning of the composition. The rate of burning increases with the reaction rate and with the amount of heat produced, and decreases with increase of thermal capacity and with decrease of thermal conductivity.

In mixtures of zinc powder and carbon tetrachloride, it is the primary reaction between the two that predominates, and the rate of this reaction is determined by the availability of zinc surface. The rate is decreased by increasing the size of the zinc particles, by the formation of agglomerates or by melting the metal. Also, the rate of reaction decreases with time, owing to an accumulation of layers of involatile products on the surface of the zinc.

In mixtures of calcium silicide, hexachloroethane and zinc oxide however, a different state of affairs exists, in so far as the reaction responsible for the maintenance of burning is not primarily responsible for smoke production. An increase in the amount of calcium silicide causes an increase in the rate of reaction by reason of the increase in the available area of silicide surface, and this increases the rate of burning. Potassium nitrate also increases the rate of burning, possibly by removing the carbon deposited on the surface of the silicide.

The rate of burning is affected by a change in thermal conductivity in the compositions, and changes in the proportions of zinc and of calcium silicide, which in respect of thermal conductivity behaves as a metal, affect the rate of burning. Zinc oxide and hexachloroethane have poor conductivities and produce the opposite effect. However, the increase in rate of burning brought about by increasing calcium silicide is out of all proportion to the increase in the available surface.

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THE STABILITY OF PYROTECHNIC SMOKE COMPOSITIONS

Both types of screening-smoke composition described in the previous section are subject to spontaneous heating and ignition in the presence of moisture. The speed with which this takes place depends to a large extent on the impurities, particularly metal chlorides, that may be present in the ingredients.

Carbon tetrachloride is reduced by zinc dust in the presence of water, producing hydrogen and zinc chloride. The reduction is probably brought about by nascent hydrogen generated in the zinc-water reaction and leads to the formation of hydrochloric acid which, in turn, reacts with more zinc or zinc oxide in the composition to produce zinc chloride. These reactions are exothermic and proceed until all the water is eliminated or the composition ignites. Sodium chromate is sometimes added to passify the zinc and thus prevent the initial generation of hydrogen, but it is effective with only small amounts of moisture and soluble zinc salts, present as impurities in the zinc oxide, tend to remove it by precipitating insoluble zinc chromate.

The reactions taking place in moist hexachloroethane-calcium silicide-zinc oxide compositions are somewhat similar in nature and are also affected by chloride impurities. Thus, water in the presence of chloride reacts exothermically with calcium silicide evolving nascent hydrogen, which, in turn, reacts with hexachloroethane to produce hydrochloric acid. The hydrochloric acid attacks fresh calcium silicide to generate more hydrogen and more heat. It also reacts with zinc oxide to produce zinc chloride. The zinc chloride effects an ion-exchange with calcium silicide, depositing metallic zinc thereon, and so forms a couple which increases the rate of decomposition of calcium silicide and the generation of heat. This acceleration continues until either the moisture is used up or the composition ignites. The compositions can be stabilised by the addition of sodium or potassium nitrate, which appear to inhibit the initial reaction between water and calcium silicide by preventing its initiation, rather than by absorbing the hydrogen generated by it.

THE EFFECTIVENESS OF SCREENING SMOKES

All the screening smokes described in the previous sections operate by interaction with the moisture in the atmosphere to produce aerosols of minute, highly reflecting particles or droplets that scatter the light. Their effectiveness is therefore governed by the relative humidity of the air during screening operations. They are not equally effective under identical conditions and, at 40 per cent relative humidity, white phosphorus is better than hexachloroethane-calcium silicide mixtures, which, in turn, are better than titanium tetrachloride. At 90 per cent relative humidity, the order is titanium tetrachloride, white phosphorus, hexachloroethane-calcium silicide mixture.

CHAPTER 13

SMOKE AND FLAME COMPOSITIONS

A number of pyrotechnic stores, used for marking positions at sea or for signalling purposes, must be visible by both day and night for extensive periods of time. All the stores include a float-chamber to enable them to remain on the surface of the water while functioning. Some are dropped from aircraft and are initiated by a percussion cap on hitting the surface, or by an electric igniter operated by a battery that functions in contact with sea water; others are ejected from submerged submarines to rise to the surface, and are initiated by a detonator after the hydrostatic pressure retaining a cocked striker has been sufficiently reduced, or by a seawater-operated battery.

The basis of the pyrotechnic filling of these stores is red amorphous phosphorus which, when ignited, burns with a lambent yellow flame and emits volumes of dense white smoke. Two compositions are available, namely, composition SR 414 containing 60 per cent red phosphorus coated with a small quantity of mineral oil, manganese dioxide, magnesium powder and calcium silicide, and composition SR 622 which contains about 50 parts of oil-coated red phosphorus, calcium sulphate and oxalic acid. The fillings are consolidated in the containers by hand - stemming or by light mechanically applied pressure.

When composition SR 414 is ignited, the magnesium, calcium silicide and some of the phosphorus react with the manganese dioxide and the heat generated vaporises the excess phosphorus which burns spontaneously in the atmosphere. The oxides of phosphorus so produced immediately react with moisture to produce minute droplets of phosphoric acid in the form of a dense white aerosol.

The reactions that take place between calcium sulphate and phosphorus when composition SR 622 is ignited are very complex and lead to the formation of phosphorus sulphide, which is emitted as a vapour with the excess phosphorus, and burns in air to produce phosphorus oxides and sulphur dioxide. The composition is rather less efficient than SR 414, largely because of the smaller proportion of phosphorus present. The rate of burning can be controlled by varying the proportions of the main ingredients, mixtures containing, say, 55 per cent of phosphorus burning slower than those containing 45 per cent. The slower burning mixtures are more difficult to ignite and hence the layer of composition immediately beneath the priming is usually composed of a faster burning mixture followed by the main charge.

Red phosphorus compositions are prone to extinction by water entering the flame-orifice of the store unless sufficient gas-pressure is maintained within. With composition SR 414, this defect is

partly overcome by the vigorous combustion of magnesium and calcium silicide, but the proportions of these ingredients cannot be increased too much or the composition burns too rapidly. Composition SR 622 burns less vigorously, and to provide sufficient gas, a small proportion (3 per cent) of oxalic acid is included. This substance takes no part in the main reaction but merely decomposes into water and carbon oxides.

Another type of filling for certain flame floats operating on the sea utilises the reaction between water and the phosphides of the lighter metals in which phosphine gas is generated. When calcium phosphide reacts with water, the gas evolved is mainly phosphine PH_3 , with a second hydride, P_2H_4 , as an impurity. The latter gas is spontaneously inflammable in air and hence the mixture ignites and burns as it is liberated. If the flame is extinguished by seawater it re-ignites immediately. The rate of evolution of gas is controlled by varying the size of the pellets of calcium phosphide used in the filling.

More efficient fillings utilize the phosphides of aluminium and magnesium, frequently mixed in equal proportions. Aluminium phosphide reacts only slowly with water, and magnesium phosphide reacts very vigorously, so that a balanced rate of evolution of gas can be obtained by using a mixture of the two. Unfortunately, the phosphine generated is purer than that from calcium phosphide and is not spontaneously inflammable. The addition of calcium phosphide to the mixture does not help. Re-ignition takes place if the issuing gas contains some nitric oxide generated by the interaction of potassium nitrate and potassium hydrogen sulphate which are included in the main filling. However, the proportion of nitric oxide necessary to render the phosphine inflammable is small and critical and is difficult to control.

CHAPTER 14

ELASTIC PYROTECHNIC COMPOSITIONS

The pyrotechnic compositions, that have been described in the foregoing chapters, are all composed of mixtures of powdered ingredients which are, for the most part, consolidated into containers so that they may burn cigarette-fashion from one end to the other at a steady rate. The preparation and filling of these compositions present many problems in manufacture which have to be surmounted by the rigid control of conditions and the use of specialised equipment. Some problems, such as the absorption of moisture, remain and cannot easily be solved, so that the service life of the store may suffer as a result.

The problems are two-fold in nature: those concerning the chemical and the physical aspects of the filling, the ingress of moisture, the stability of the composition, and the strength and rigidity of the consolidated powder, and those concerning the sensitiveness of the composition and the hazards involved in mixing and filling it into the store. The high loading-pressures required to consolidate powders involve the use of large air or hydraulic presses and of heavy moulds to contain the pyrotechnic during the consolidating process.

Much thought and effort has been given in recent years to the problem of reducing the labour and the hazards involved in this kind of filling by adapting moulding and extruding methods used in the plastics industry to the needs of pyrotechnics. To achieve this end, it has been necessary to consider pyrotechnic fillings from a point of view very different from that adopted for conventional powder fillings. These latter fillings can be considered as particles of dry powder with which the minimum of adhesive has been incorporated to ensure their bonding under pressure into rigid pellets. The adhesive can be oil, wax or resin and the proportion is adjusted to produce the desired pyrotechnic results. In the newer type of filling one starts with a medium of uncured, fluid plastic, and adds to it solid powdered ingredients in calculated proportions, thereby increasing the viscosity to a stage when the mixture can be satisfactorily moulded or extruded and then cured. The proportion of plastic present in the final mixture is necessarily much higher than that of the adhesive in the older type of mixture in order to maintain fluidity, and the pyrotechnic properties of the cured filling are correspondingly different. The problem, then, is how to modify the characteristics of the solid ingredients in such a manner as to bring the pyrotechnic properties of the plastic mixtures, after they had been cured, to match those of corresponding conventional fillings. In general, this has been achieved by using finer grades of the metallic fuels, increasing their proportions

and reducing the proportions of diluent materials. The basic ingredients are the same for both types of composition but particular characteristics may be achieved by varying the additives. Thus, organic diluents such as lactose and mannitol become unnecessary in plastic compositions and their place can be taken by oxalates and other metal salts.

The medium used in current plastic or elastic pyrotechnic compositions is thiokol liquid polymer, LP2 or LP33, which is converted to a polysulphide rubber by the addition of 7 per cent p-quinone dioxime and 3 per cent diphenyl guanidine and cured by heating it at 70°C for 12 to 18 hours. A small quantity (0.5 per cent) of carbon black is added to facilitate the incorporation of the pyrotechnic ingredients.

The manufacture of the composition takes place in an incorporator provided with a steam-heated jacket, a means of evacuating it and a mechanical stirrer, the blades of which are shaped to prevent sedimentation of the solid ingredients. The liquid polymer is first heated to 100°C under vacuum to remove moisture and air bubbles. Next, the magnesium powder is added and the mixture again stirred under vacuum for a further period. The remaining ingredients are then added in the same manner, the oxidant being added last. Before adding the oxidant it is mixed with the rubber-forming ingredients, the p-quinone dioxime, diphenyl guanidine and carbon black, so that it can act as a carrier for them and ensure uniform distribution of the small quantities involved. After mixing for a further period, the thick paste is ready for moulding or extruding into the container. The filled store is finally heated for 12 to 18 hours at 70°C to cure the filling and convert it into a rubber.

When cured, elastic pyrotechnic compositions are greyish black in colour and have the appearance and resilience of a hard rubber. They can be deformed within reason and recover their shape, but some mixtures are "shorter" in texture than others and break up more readily under stress. The nature of the product obviously depends upon the proportion of thiokol rubber present and the nature of the powdered ingredients.

The compositions are completely waterproof and ignite readily even after immersion in water for several hours. They have satisfactorily withstood the effects of temperature and humidity-cycling for a year or more with little change in their characteristics. One of the advantages of this type of composition is its insensitiveness to impact and friction and the safety with which it can be mixed and filled. The mixing takes place in a fluid medium under vacuum and the oxidant is added last so that the risk of ignition is reduced to a minimum. However, if ignition did occur combustion would be under considerable confinement and would almost certainly result in a violent explosion. This process lends itself to remote control and the consequences of such an explosion can be localised.

Most elastic compositions are sufficiently fluid before curing to be extruded under pressures varying between 400 and 1,000 lbs.

per square inch depending on the nature and proportions of the solid ingredients. Short mixtures containing the smallest proportion of thiokol require too high a pressure for convenience and are best moulded. Mixtures intended as fillings for delay cords, signal stars and flares of moderate diameter are extruded in the form of a cylindrical ribbon directly into the container and then cured. The container is precoated internally with thiokol rubber and partly cured to ensure good adhesion of the filling to the wall. Alternatively, plain extrusions of composition can be coated with thiokol rubber to inhibit combustion over the cylindrical surface, and so form caseless pyrotechnic stores. Compositions for priming pyrotechnic compositions are prepared in a similar manner and extruded as a flat ribbon which is rolled out to an appropriate thickness. The priming layer is pressed on to the surface of the main filling before curing or after partial curing, and when fully cured it remains firmly attached.

The types of pyrotechnic compositions that have been developed in an elastic form include illuminating, coloured signal, igniting, priming and screening-smoke compositions. Most of these compositions contain between 14 and 30 per cent thiokol rubber and the effect of this high proportion of pyrotechnically inert material tends to limit their usefulness. For example, the fastest-burning illuminating composition so far produced has a rate of burning of 6 seconds per inch, and any filling required to burn faster must be of the consolidated powder type. Elastic compositions produce copious volumes of gas when burnt because of the thiokol rubber, and their rates of burning are strongly affected by changes in ambient pressure. Combustion is therefore satisfactory at low or medium altitudes only. They are, however, not seriously affected by changes in ambient temperature and rates of burning of some flare compositions scarcely change over temperatures ranging from -30°C to $+65^{\circ}\text{C}$.

Illuminating and coloured signal compositions usually contain 14 to 18 per cent of thiokol rubber, and their pyrotechnic characteristics are determined by the proportions and the physical and chemical properties of the other ingredients. Illuminating compositions contain between 50 and 60 per cent blown magnesium powder, the remainder being sodium nitrate and possibly other additives. The rate of burning is determined by the proportion and the fineness of the magnesium powder, the slowest burning ones with a lower proportion of coarse powder and the fastest burning ones with a higher proportion of fine powder. Compositions with intermediate rates of burning may contain coarse and fine fuels mixed together in various proportions. Additives to control the rate of burning include metal oxalates and organic substances such as oxamide.

TABLE 20 TYPICAL ELASTIC ILLUMINATING COMPOSITIONS

	Slow burning	Fast burning
Thiokol Rubber L.P.2	15.0 parts	14.0 parts
Magnesium powder Grade 3	54.0 "	- "
Magnesium powder Grade 5	-	57.3 "
Sodium nitrate	27.0 "	28.7 "
Oxamide	4.0 "	- "
Rate of Burning, seconds/inch	19.8	6.2
Specific Intensity, candles/sq. inch	49,000	137,000
Specific Luminous Flux, Candles-seconds/gm.	33,600	35,900

Red and green signal compositions frequently contain fuel and oxidant in nearly equal proportions. Part of the oxidant consists of potassium perchlorate and part of barium or strontium nitrate according to the colour. The appropriate metal oxalates and amorphous boron are sometimes included to augment the flame-colour.

TABLE 21 TYPICAL ELASTIC SIGNAL FLAME COMPOSITIONS

	Red Signal	Green Signal
Thiokol Rubber	16.5 parts	18.0 parts
Magnesium powder Grade 0	41.5 "	-
Magnesium powder Grade 3	-	35.0 "
Potassium Perchlorate	21.0 "	11.0 "
Strontium nitrate	21.0 "	-
Barium nitrate	-	32.0 "
Boron	-	4.0 "
Rate of burning, seconds/inch	13.6	12.1
Specific Intensity candles/sq. inch	38,400	17,200
Specific Luminous Flux, candle-seconds/gm.	18,300	7,000

Elastic priming compositions contain thiokol rubber, potassium perchlorate and amorphous boron. The thiokol used is mainly LP.2 which produces a more fluid mix than other varieties and is better for extrusion into cords and strips. The proportion of thiokol varies from 21 to 29 per cent, that of potassium perchlorate from 58 to 69 per cent. A typical composition suitable for priming cord, sheet or granules contains 25 per cent thiokol rubber L.P.2, 55 per cent potassium perchlorate and 20 per cent boron. It is very ignitable from flash and burns in cord or sheet form similarly to quick-match or primed cotton cambric.

CHAPTER 15

THE CHEMICAL STABILITY OF PYROTECHNIC COMPOSITIONS

Military pyrotechnic stores, along with all other explosive stores, are expected to remain serviceable after years of storage in depots and to function satisfactorily. This requirement presents some serious problems to the pyrotechnist, since most of the fillings he uses are mixtures of fine chemically reactive powders that have absorbed a certain amount of moisture from the atmosphere during manufacture. Since more than two-thirds of the compositions listed in the SR composition book contain finely powdered metals and alloys whose electro-potential ensures that, given the right conditions, they will react with any moisture and salt solutions in their vicinity, it is apparent that corrosion can easily take place and lead to the deterioration of the composition. Magnesium is the commonest metal used and it is also one of the most reactive, so that the problem of stability becomes particularly acute where it is concerned. Other metals, such as aluminium, boron, manganese, zinc, iron and antimony, are used in various compositions and each has its own problems when mixed with other ingredients.

Magnesium reacts with water, especially in the presence of anions, to produce magnesium hydroxide and hydrogen gas thus:-



and each milligram of moisture present in a composition is capable of oxidising 0.67 milligrams of magnesium and of liberating 62 millilitres of hydrogen. This reaction takes place in the presence of chlorides, particularly in green signal compositions, and leads to a hard un-ignitable layer on the surface of the compressed composition. The gas evolved can exert dangerously high pressures in hermetically sealed stores or containers. When nitrates are present, however, secondary reactions lead to the formation of nitrites and ammonia, which is present in varying amounts in the liberated gases.

The rate of corrosion is rapid to begin with and then slows down as the layer of oxidation products covering the magnesium increases in thickness. When barium nitrate is present, the rate of corrosion is much faster than with sodium nitrate, owing to the peptising action of the barium ion on the surface film of magnesium hydroxide. Compositions exposed to the atmosphere absorb moisture according to the nature of the ingredients and to the relative humidity. As corrosion proceeds, the products, particularly those formed in magnesium - sodium nitrate mixtures, are usually more hygroscopic than the original ingredients because of the formation of hydroxides.

Corrosion of magnesium in the presence of chlorides proceeds much more rapidly than it does in the presence of nitrates but the rate can be very much reduced by alloying the metal with 1½ per cent of manganese. This method, however has little effect on the rate of corrosion with nitrates and any protection given to magnesium powder must be of the nature of external application rather than of internal chemical constitution.

The rate of corrosion is governed, other things being equal, by the degree of sub-division of the magnesium powder and by the shape of the particles. The flattened, irregularly shaped particles produced by milling processes are more readily attacked than the spherical particles produced by blowing. Blown powder, therefore, makes for more stable compositions.

Since corrosion occurs in the presence of moisture there are three courses open to improve the chemical stability of compositions. One is to protect magnesium particles with an external waterproof coating applied either by chemical or physical means. The second is to prevent moisture from entering the composition by using only non-hygroscopic ingredients and by carrying out all operations in a dry atmosphere, subsequently sealing the composition hermetically to prevent ingress of moisture during storage. The third course is to fill the stores with compositions containing the least practical amount of moisture and then to withdraw the moisture by drying techniques or by accelerated corrosion before hermetically sealing the stores.

THE PROTECTION OF MAGNESIUM POWDER

Among the various ingredients of illuminating and signal compositions those used to promote consolidation are also the most useful to protect the magnesium powder. These materials, described in Chapter 4, are mainly oils, waxes and resins, both natural and synthetic in origin, and are used in proportions varying between three and eight per cent by weight of the composition. They are usually coated on the surface of the magnesium powder before adding the other ingredients.

The degree of protection offered by this coating varies considerably with the nature of the material and the type of coating produced. Many waxes applied molten or in solution tend to crystallise and form discontinuous layers, so that moisture can still attack the metal beneath. In fact, with paraffin wax, corrosion appears to proceed as rapidly in its presence as when it is omitted. Oils derived from linseed oil offer reasonably good protection and many illuminating compositions containing lithographic varnish have a good shelf-life when properly filled and sealed. Resins, especially synthetic ones such as phenol-formaldehyde and polyester resins, applied as varnishes and dried, give good protection although their use may be undesirable for other reasons. Acaroid resin, applied in alcoholic solution, also gives good protection

in spite of the fact that it is a very hygroscopic substance. The protection may, in this case, be partly chemical in nature derived from one or more of the substances present in this very complex material. Silicones and thiokol rubber are also used with success.

Chemical methods of protecting magnesium powder by the acid chromate process have been successful although they cause some loss of powder by solution. If magnesium powder is exposed to a 5 per cent solution of nitric and chromic acids it turns golden brown in colour and, after washing and drying, it is found to be quite resistant to corrosion by nitrates. The losses during the chromatising process vary with the particle-size and amounts to 0.4 per cent for grade 0 powder and 0.8 per cent for grade 5 powder. Alkaline chromate and fluoride processes are not so successful.

The degree of protection can be estimated in a comparative manner by one of three methods, each of which supplies some distinctive information. In the first, the coated magnesium is mixed with an equal weight of barium nitrate, and the mixture is placed in a wide-mouthed Dewar vessel. There, the mixture is moistened with 5 per cent of its weight of distilled water, a thermometer inserted, the vessel closed with a plug of cotton wool and the rise in temperature recorded periodically. The test is repeated with unprotected magnesium powder for comparison.

There is usually a period of induction of variable length after which the temperature proceeds to rise. With mixtures containing finely divided (grade 5) unprotected magnesium powder the induction period is short and the temperature rises rapidly. It is always advisable to drown the contents in cold water should the temperature reach 80°C, to avoid possible inflammation of fine powders, although more often than not the excess water merely boils off. The ability of coatings to protect the metal powder is observed from the period of induction and the slope of the temperature - time curve. With good protection there is a long period of induction, the rise in temperature is gradual and frequently a maximum temperature is eventually reached. This method measures the initial onslaught of corrosion, but it is too insensitive, because of heat losses, to record the slower and more deep-seated processes that succeed it. Barium nitrate is preferred to alkali nitrates because it reacts more readily and results are obtained more quickly.

In the second method coated magnesium powder is immersed in a saturated solution of sodium nitrate and gently agitated by a slow stream of air bubbles drawn through the solution. The emerging gas is passed through a standard solution of sulphuric acid which is periodically titrated to estimate the ammonia absorbed. In this test the magnesium powder undergoes more rigorous treatment and corrosion is more severe and deep-seated. The results depend on the degree of agitation and on the temperature of the solution. It is a test that can yield results quickly and is flexible in application, since the temperature can be maintained at different levels and the solute can be varied to study the effect of different anions.

In the third method coated magnesium is incorporated in a suitable composition which is consolidated into pellets two or three grams in weight. The pellets are then stored in atmospheres of controlled humidity for long periods. By recording changes in weight, dimensions, appearance and chemical constitution at regular intervals the course of corrosion can be followed in detail.

Since mixtures of magnesium and sodium nitrate form such an important group of modern pyrotechnic compositions the reactions taking place between the two ingredients in the presence of moisture have been the subject of investigation over many years. The findings of these investigations are summarised as follows:-

All compositions containing magnesium powder slowly deteriorate as moisture gains access to the metal. The rate of deterioration depends partly on the degree of protection afforded by the coatings which are, in some compositions, applied to the surface of the particles of the powder, and partly on the nature of the other ingredients. Insoluble organic and inorganic ingredients have generally little effect on the corrosion of the metal, although zinc oxide and ferric oxide have been found to accelerate it; but the soluble ingredients, which are for the most part oxidising agents, have the most diverse effects. Potassium chlorate and perchlorate scarcely affect the normal rate of corrosion, but the nitrates of barium, strontium, potassium and sodium all increase it. Of the four nitrates, sodium nitrate is the most widely used and its effect on corrosion is the most difficult to control.

The products formed when magnesium reacts with sodium nitrate are sodium nitrite, hydrogen, ammonia and magnesium hydroxide. After a rapid initial attack the total corrosion curve of magnesium powder in a 2-molar sodium nitrate solution at 60°C. becomes approximately linear. The concentration of sodium nitrate becomes constant after a few days, whereas hydrogen and ammonia are evolved continuously. Hydrogen accounts for one-third of the corrosion. Increase in nitrate concentration has little effect at this temperature. At room temperature, the initial attack apparently leads to the formation of a protective film which delays but does not prevent further reactions.

A large number of substances have been tried as inhibitors but only two of them, potassium chromate and sodium fluoride, are very effective. The former inhibits the corrosive effect of a 2-molar sodium nitrate solution on magnesium powder at 60°C. for a week or two, and the latter for much longer periods. However, when solid sodium fluoride is added to a mixture of magnesium powder and sodium nitrate and pellets of this composition are stored in a moist atmosphere, it has little effect on the rate of corrosion. This is so even when the magnesium powder is coated with a film of sodium fluoride before mixing with sodium nitrate.

The rate of corrosion is unaffected by ambient air pressure although the rate of evolution of hydrogen is doubled in vacuo, no doubt because of the greater ease of bubble-formation under

reduced pressure. The rate of corrosion is also little affected by the concentration of the nitrate ion, a state of affairs which might arise if the controlling factor were the concentration of nitrate ions absorbed in the surface film of hydroxide and contact with the metal proceeded by diffusion through it.

When a magnesium electrode is immersed in a 2-molar solution of sodium nitrate its potential falls and approaches a more or less steady value of -1.37 volts. Soon, the liquid becomes opalescent with magnesium hydroxide separating out. Most of the metal surface remains bright but areas of film appear with gas bubbles attached and beneath which corrosion pits develop. Variations in temperature have little effect on the electrode potential but additions of fluoride or chromate ions cause it to rise to more positive values and the areas of pitting diminish whilst a hard layer forms over them. The addition of chromate ions has the greater effect.

In the light of these facts the reaction between magnesium and sodium nitrate can be summed up in this way:-

Magnesium reacts slowly with water because of the protective effect of a magnesium hydroxide film and the pH of the corroding medium becoming constant at about 11.0. The apparent temperature coefficient is about 1.6/10°C. rise, but this value is probably misleading for at the higher temperatures the increased rate of hydrogen evolution tends to strip off the film. In nitrate solution the reaction is probably the same but is complicated by the depolarising action of the nitrate ion. Hydrogen evolution still accounts for a large fraction of the total corrosion but sodium nitrite and ammonia also appear. They are probably secondary products formed by reduction of nitrate by hydrogen absorbed at the cathodic areas of the metal. The nitrite is probably formed by direct reduction of the nitrate in one stage independently of the formation of ammonia. That the formation of nitrite ceases after a few days at 60°C. may be due to the rise in current density by areas of the magnesium surface becoming covered with a film. The addition of chromate reinforces the hydroxide film over anodic areas with an insoluble product, probably chromium chromate. Some of the chromate is reduced, but this reduction tends to increase the corrosion by the establishment of centres of low hydrogen over-potential, and when it becomes the preponderating reaction the protection breaks down. This disadvantage does not apply to the addition of fluorides to the solution. Experiment shows that sodium fluoride is an excellent inhibitor when dissolved in the corroding medium. When, however, it is added to magnesium-sodium nitrate pellets, no positive effect is obtained doubtless because of the limited access to the metal. Magnesium, on which a fluoride film has been deposited, reacts with nitrate solution for one or two days after which protection is complete. Probably the film is stripped off and reformed, so that the protection is similar to that when fluoride is dissolved in the corroding medium. It seems clear

that protection by fluoride involves the constant repair of a film which is periodically being broken down. Magnesium covered with a fluoride film deteriorates readily in a pellet mixed with sodium nitrate.

The rapid fall in potential when magnesium is first immersed in nitrate solution indicates that the initial reaction is the passage of metal ions across the metal/solution boundary. A similar effect is seen in acid solutions, but it differs from that in potassium chloride or potassium sulphate solutions where the potential rises directly to the steady-state value. The steady-state value is considerably positive to the theoretical reversible potential and this cannot be determined by the anodic area of bare metal. The magnesium must therefore be in a state of high anodic polarisation. Two areas exist on the surface:- anodic areas covered by oxide film, and areas covered by hydride film. Since the latter are much larger than the anodic areas, the potential measured will be near to that of an unpolarised hydride film. Addition of fluoride or chromate increases the anodic polarisation by precipitation of an insoluble substance at the anode, or by repair of the oxide film. The potential is thus raised. This change in potential might be taken as a measure of the localisation of corrosion which is brought about by the inhibitor but does not necessarily indicate a reduced corrosion, since the pitting may be deeper. The films formed by the fluoride treatment are porous and hence can be expected to be effective only if a supply of inhibitor is maintained to repair damage at the anodic areas. This can be arranged in solution immersion tests but it is difficult to see how it can be applied to consolidated composition.

THE MOISTURE IN PYROTECHNIC COMPOSITIONS

The second course of action to be taken to prevent corrosion is to remove all traces of moisture and to seal compositions hermetically in metal containers until they are required to function.

A composition is as moist as its ingredients and the ambient conditions during handling permit, hence it is necessary to exert a tight control on both during manufacture. Extensive investigation of many pyrotechnic ingredients has shown that they can be arbitrarily grouped into three classes. Very good, absorbing less than 0.1 per cent moisture after three hours in atmospheres of up to 70 per cent relative humidity, good, those absorbing up to 0.14 per cent in three hours at 65 per cent relative humidity, and poor, those absorbing more than 0.14 per cent in three hours in 65 per cent relative humidity. The moisture absorbed during manufacture is very dependent on the humidity of the atmosphere and this must be maintained as low as possible consistent with safety.

The very good materials include metal powder fuels, most of the oxidants in common use, a number of organic materials and synthetic

resin moulding powders. The second group includes a number of strontium salts and some chlorinated materials, and the third includes naturally occurring materials such as starch and acaroid resin, cellulose derivatives and also amorphous boron. The last named material probably absorbs moisture because of its large surface.

One of the main problems in pyrotechny is to find suitable non-hygroscopic alternatives to the materials in group 3. This process is never easy since it is not always possible to match all the qualities of the substance to be replaced. Mannitol has most of the characteristics of starch, ivory-nut powder and cellulose acetate and absorbs very little moisture, and many compositions can be improved by merely substituting mannitol for the hygroscopic ingredient. Other compositions may require further minor adjustments to the proportions in order to maintain rates of burning and luminosity. Acaroid resin powder is also very hygroscopic but it is less easily replaceable because few of the possible alternatives are as readily ignitable.

Measurements of the moisture absorbed by SR pyrotechnic compositions show that they vary widely in this respect as would be expected from the variety of ingredients they contain. The percentage increase in weight after remaining for three hours in an atmosphere of 70 per cent relative humidity is given in Table 22. for a few selected compositions.

TABLE 22 THE ABSORPTION OF MOISTURE BY DRIED
SR COMPOSITIONS

Composition	Main Ingredients	Percentage of moisture after 3 hours in 70% R.H.
SR.812	Aluminium, Potassium Perchlorate	0.01
SR.60	Boron, silicon, Potassium dichromate	0.03
SR.57	Boron, Bismuth oxide	0.11
SR.112	Tetranitro-carbazole, potassium nitrate	0.19
SR.252	Silicon, potassium nitrate, mealed gunpowder	0.54
SR.428	Magnesium, Barium Chlorate, Potassium Perchlorate, starch	0.99
SR.414	Red phosphorus, manganese dioxide, calcium silicide, and magnesium	1.10
SR.232	Magnesium potassium Perchlorate, strontium oxalate, starch	1.60
SR.239	Mealed gunpowder, acaroid resin	2.20

In practice, of course, compositions would not be exposed to this extent, but it is apparent that, apart from certain photoflash and gasless delay compositions, few of them can escape absorbing some moisture during manufacture and filling, and the probability of achieving completely anhydrous fillings of the mixed powder type is remote.

OTHER PROBLEMS IN CHEMICAL STABILITY

Although aluminium is less readily attacked by water than magnesium because of the continuous film of oxide formed on its surface, moist compositions containing aluminium powder can become unstable especially at elevated temperatures. Mixtures of aluminium powder and water will remain quiescent for many hours before suddenly bursting into activity with a rapid rise in temperature. The excess water boils off, after which the temperature returns to normal as the reaction ceases. In a confined space such as in a sealed store, where the steam cannot escape, the reaction continues and the rising temperature accelerates it, leading possibly to the ignition of the filling and to explosion. This has happened to photoflash cartridges filled with an aluminium - potassium perchlorate mixture moistened with 0.75 per cent water and maintained at about 80°C. After an hour or two they exploded violently. With less moisture present the ignition temperature was not reached and no explosion occurred even after heating for 12 hours. Thermite incendiary compositions containing aluminium powder are frequently stabilised by the addition of boric acid.

Certain screening-smoke compositions containing zinc metal powder and chlorinated hydrocarbons become unstable when moistened with water and sometimes inflame spontaneously. (See Chapter 12). This was particularly true of some of the earlier compositions that contained zinc dust and hexachloroethane. Later developments changed the fuel to calcium silicide and retained the zinc in the form of its oxide, and so improved the stability.

Mixtures of aluminium powder and chlorinated hydrocarbons, especially the liquid ones, also react although not so vigorously as mixtures containing zinc. These mixtures can inflame, especially at elevated temperatures and particularly when mechanical work is done on the metal during milling operations or by a spark. The hazards are increased by confinement.

Since pyrotechny is still largely an empirical art in which the effects are produced by blending together specific ingredients, it is very important to remember at all times that the laws of chemistry apply, even to apparently innocuous substances, especially when moist. Magnesium is a very reactive alkaline metal and is capable of reducing heavy metal salts, cellulose nitrate and organic nitro-compounds, as well as other substances, and mixtures with these materials are liable to become unstable. Sulphur corrodes magnesium and light-producing compositions must therefore be primed with sulphurless gunpowder. On the other hand, mixtures of aluminium and sulphur are quite stable and sulphur is added to illuminating compositions containing aluminium and barium nitrate to improve their combustibility.

CHAPTER 16

THE SENSITIVENESS AND HAZARDS OF PYROTECHNIC EXPLOSIVES

Pyrotechnics are the oldest explosives known to man and they have been employed in warfare and in peaceful celebrations from very early times. Many of them can be manufactured from familiar everyday substances, and the ease with which they can be made, together with the spectacular effects that can be obtained with them, tends to obscure their dangerous nature and so leads to serious accidents when they are handled carelessly.

The diversity in the chemical and physical properties of the ingredients of pyrotechnic mixtures is reflected in a corresponding diversity in the ability of these mixtures to ignite from blows, friction or sparks, particularly when they are unconsolidated. Some compositions are as sensitive as initiators while others can only be ignited with difficulty by special means.

The ease of ignition of these mixtures is governed by many factors some of which are obvious and some more obscure. They include the following:-

1. The chemical reactivity of the ingredients. Strong oxidising and reducing materials tend to react with the rise in temperature brought about by local heating.
2. The proportions of the ingredients. Mixtures in stoichiometric proportions tend to be more sensitive than those that are not.
3. Particle size and shape. The larger surfaces presented by fine particles, particularly those with flattened or irregular shapes, increases the sensitiveness.
4. The intimacy of mixing.
5. The hardness of the ingredients. Many fuels are hard and gritty with angular particles that produce local hot-spots under pressure.
6. The air, that is always present in loose powders, can be heated adiabatically under local pressures and so initiate the decomposition of the oxidant.
7. The temperature of the mixture.
8. The atmospheric humidity plays an important role with electro-statically sensitive mixtures.
9. The presence of chemically inactive materials which protect the fuel particles or act as diluents, and which may absorb much of the heat generated by local friction or impact.
10. Melting points of the ingredients. An ingredient with a low melting point tends to absorb heat and decrease sensitivity.

There are other parameters whose effect on sensitiveness is less apparent but which may be just as important.

From this it can be seen that the sensitiveness of pyrotechnic compositions originates in many diverse causes, most of which can operate simultaneously in given circumstances. When it is realised that the number of ingredients in a mixture can be anything from two to eight or more, it is easier to appreciate the very wide range in sensitiveness that obtains, and the great difficulty in predicting the behaviour of mixtures in given circumstances. Even gunpowder, which is one of the oldest and best known pyrotechnic mixtures, has been known to ignite under most unlikely circumstances and no satisfactory explanation has been forthcoming.

In general, the greatest hazard with pyrotechnic mixtures, especially unconsolidated powders, is ignition by friction. Although many mixtures are very sensitive to impact they are also sensitive to friction and if they are accidentally ignited by a blow it is difficult to assess whether impact or friction has the greater effect.

Mixtures containing chlorates and peroxides are particularly readily ignited by friction, largely because of the low temperature of decomposition of the oxidant and the ease with which they oxidise organic matter. Hence their use in match composition. Their sensitiveness however, is considerably decreased by the addition of relatively inert material, as, for example, in coloured smoke compositions, which contain chlorate, lactose and large proportions of dyestuffs, and which are fairly insensitive to both friction and impact.

By far the most important group of pyrotechnic compositions are those containing powdered metals and oxidants, with or without the addition of other ingredients. Many of the fuels are among the most chemically reactive elements and liberate considerable energy and generate very high temperatures when they react. The simplest mixtures are the gasless delay compositions, which are mixtures of finely powdered silicon, boron, zirconium and other metals with metal oxides and oxysalts. The particles of such mixtures are extremely small, usually of the order of one or two microns, and they have large reacting interfaces. Moreover, the metal particles are hard and gritty and mixtures are generally very sensitive to friction and impact. Some mixtures of amorphous boron and bismuth oxide, for example, have a figure of insensitiveness of 20, similar to that of lead azide, and will also ignite with very little applied friction. In fact, they make excellent prick-sensitive igniting compositions. On the other hand, mixtures of boron and potassium dichromate, while being extremely sensitive to friction, are very difficult to ignite with blows.

The sensitiveness of metal powder - oxidant mixtures varies with the ratio of metal to oxidant, and mixtures containing ingredients in stoichiometric proportions are often the most sensitive, although this is not always true, since air occluded in the powder plays an important part in the igniting process. One of the serious hazards in mixing pyrotechnic compositions and which is frequently overlooked, originates in this variation of sensitiveness with proportions. The completely mixed composition may be relatively insensitive and safe to handle, but during the mixing process pockets

of partially mixed ingredients occur which can be far more sensitive than the finished product. If one of these sensitive pockets is subjected to local pressure or friction, ignition may occur in what is considered to be a relatively innocuous composition. This type of hazard is particularly associated with powders such as amorphous boron and heavy metal oxides, which have poor flow-properties and which are not easily dispersed throughout the mixture. It also applies when mixing fine magnesium and aluminium powders and oxysalts in the manufacture of photoflash compositions.

Flare and signal compositions invariably contain magnesium powder, a suitable oxidant and additives controlling the combustion characteristics. One of the additives is frequently a drying oil, wax or resin coated on to the surface of the metal powder to protect it from corrosion. The coating reduces the sensitiveness of the mixtures and allows them to be mixed and compressed safely. The degree of desensitisation achieved varies with the coating material and with the thoroughness of the coating process which, in turn, is governed by the proportion and the particle-size of the magnesium powder. Materials such as linseed oil products and waxes, which form soft adherent coatings, have the strongest desensitising effect, whereas resins, both natural and synthetic, which form hard, brittle coatings, are less effective. Furthermore, other additives, acting effectively as diluents, tend to decrease sensitiveness still further.

Thus, compositions containing magnesium powder exhibit a considerable range of sensitiveness. At one extreme, a binary mixture of uncoated magnesium powder and oxidant may have a figure of insensitiveness of 45 and ignite every time it is struck with a mallet on softwood, and at the other, mixtures may be so insensitive as to require special means of ignition.

The consequences of accidental ignition of uncompressed compositions containing magnesium and aluminium powders and oxysalts are usually more severe than those obtained from other pyrotechnic mixtures because the reactions liberate large volumes of gases and the burning metals generate temperatures ranging from 2000°C. to 3000°C. The radiated heat can produce severe burns in unprotected skin and the immediate explosive effect is similar to that produced by two-thirds the equivalent weight of high explosive, although the blast falls off more rapidly with distance.

The sensitiveness of pyrotechnic mixtures containing non-metallic fuels is mainly governed by the chemical activity of the oxidant. Mixtures containing chlorates and barium peroxide are much more sensitive to friction and impact than the corresponding mixtures with nitrates. This is demonstrated by the figures quoted in Table 23.

TABLE 25 COMPARISON OF THE SENSITIVENESS OF MIXTURES
CONTAINING CHLORATES, PEROXIDES AND NITRATES

S.R. Composition No.	Ingredients	Impact	Friction		
		Figure of Insensitiveness RDX = 80	% Ignitions with a boxwood mallet on		
			Stone	Hard Wood	Soft Wood
125	KClO ₃ charcoal	35	100	100	20
Sulphurless Gunpowder	KNO ₃ charcoal	120	0	0	0
451	Ba(ClO ₃) ₂ Lactose	51	100	0	0
208	Ba(NO ₃) ₂ Lactose	120	0	0	0
191	BaO ₂ Resin	80	100	0	0
239	KNO ₃ Resin	120	0	0	0

Table 24 shows a selection of pyrotechnic compositions arranged in descending order of sensitiveness to impact, as determined by the Rotter Falling Weight machine. The corresponding sensitiveness to friction is represented by the percentage ignitions obtained when a thin layer of the composition, spread on flat surfaces of stone, hardwood and softwood respectively, is struck ten glancing blows with a boxwood mallet. The values for normal lead styphnate and gunpowder are included for comparison.

In general, there is a fair correlation between the sensitiveness to friction and the sensitiveness to impact, except in the case of delay mixtures containing boron, silicon and potassium dichromate. These mixtures are very insensitive to blows but are very sensitive to friction, largely because of the gritty nature of the finely powdered fuels and the presence of a powerful oxidant.

The sensitiveness of pyrotechnic compositions to ignition by electric sparks is also varied and depends on the nature of the ingredients and the degree of sub-division of the powdered fuels. The most sensitive mixtures are delay compositions containing boron, silicon or zirconium and oxidants, and the least sensitive ones include flare and signal compositions containing coated magnesium powder, oxidants and inert ingredients. The energy required to ignite mixtures containing zirconium may be as little as 0.0001 joules, and that required to ignite delay compositions varies from 0.001 joules for mixtures of boron, silicon and barium peroxide, to 0.45 joules for those of boron, silicon and potassium dichromate. There is a definite risk of accidental ignition of some of these mixtures by electrostatic discharge from the human body and suitable grounding precautions must be taken. On the other hand, most flare and signal mixtures require more than 4 joules to cause ignition, and the chance of accidental ignition, except in a very dry atmosphere, is more remote.

TABLE 24 THE SENSITIVENESS OF SELECTED
PYROTECHNIC COMPOSITIONS

S. R. Compn. No.	Ingredients	Impact	Friction		
		Figure of Insensitive- ness RDX = 80	% Ignitions with a boxwood mallet on		
			Stone	Hard Wood	Soft Wood
	Normal lead Styphnate	18	100	100	100
57	B/Bi ₂ O ₃	20	100	100	60
458	Potassium dinitro phenate/ BaO ₂ /Resin	31	100	0	0
125	KClO ₃ /charcoal/sugar	35	100	100	20
450	Ba(ClO ₃) ₂ /Resin	48	100	0	0
371	Magnesium Gde. 5/KNO ₃ / Resin	50	80	0	0
399	Magnesium Gde. 4/BaO ₂ / Resin	55	100	100	100
463	Potassium dinitro phenate/ BaO ₂ /Resin	55	100	100	100
580	Magnesium Gde. 4/NaNO ₃ / Resin	64	50	0	0
110	Magnesium Gde. 5/BaSO ₄	65	0	0	0
541	Magnesium Gde. 6/NaNO ₃	83	100	10	0
	Gunpowder	90	0	0	0
562	Magnesium Gde. 0/oil/ NaNO ₃ /oxalate,	100	0	0	0
501	Magnesium Gde. 0/oil/ NaNO ₃ /oxalate	120	0	0	0
60	B/Si/K ₂ Cr ₂ O ₇	120	100	100	100
904	KClO ₃ /Lactose/dyestuff	120	0	0	0
	The magnesium powder used in the above compositions is the cut variety, Grade 0 being the coarsest powder and grade 6 the finest.				

The majority of pyrotechnic mixtures are consolidated under pressure into cylindrical containers in order to burn steadily layer by layer. The containers are made of paper, plastic materials or metals, and the consolidating ram of wood, brass or steel, according

to the technique employed and the applied pressure. The risk of ignition during pressing operations varies with the sensitiveness of the mixture, the materials of both containers and ram, the clearance between them, and the rate of movement of the ram. The risk is small in consolidating flare, signal and smoke compositions into paper or plastic containers, but it increases considerably when metal containers are used.

The principal danger arises from particles of metal becoming trapped between the metal surfaces of the container and the ram, and generating sufficient heat by grinding friction to ignite the bulk of the mixture. The usual method of diminishing this hazard is by facing the steel ram with softer bronze, but score marks in a worn or roughly treated ram of this nature can trap powder more effectively and so increase the danger of ignition.

Experience in the manufacture of bare pellets of pyrotechnic composition has shown that the safest tools are those made of hardened steel with polished working surfaces and the minimum practical clearance between them. The surfaces are not easily scored, and it is difficult for powder to be trapped. A similar practice is adopted in filling sensitive mixtures into steel delay units. The danger of nipping explosive dust between steel surfaces when inserting the ram is overcome by fitting a plastic collar to the mould.

TESTS OF SENSITIVENESS OF PYROTECHNIC COMPOSITIONS

The sensitiveness of pyrotechnic compositions to blows is determined by dropping a weight, either 2 Kgms, or 5 Kgms, from a measured height on to drifts beneath which a fixed volume of composition is confined between a steel anvil and a brass cap. The volume of gas liberated as a result of the impact on the explosive is measured.

Caps of the sample composition and caps of a standard explosive, R.D.X., with which it is compared, are struck alternately at heights that are varied in a manner known as the Bruceton Staircase Technique, in order to determine the height for a 50 per cent probability of ignition.

An ignition is considered to occur when one or more millilitres of gas are evolved. The median drop-heights for the sample and the standard are calculated from the results and the figure of insensitiveness of the sample is expressed as:-

$$F. \text{ of I. } = \frac{\text{Median drop-height of sample}}{\text{Median drop-height of standard}} \times F. \text{ of I of standard.}$$

The F. of I. of R.D.X. is taken as 80. Explosives with smaller values of F. of I. are more sensitive to impact than R.D.X. and those with larger values are less sensitive.

The test was originally devised and is used for high explosives and initiatory substances that produce large volumes of gas. It is

also applied to pyrotechnic compositions and, generally, the results obtained have agreed reasonably closely with the observed behaviour. However, with virtually gasless compositions, errors in measurement of the volume of gas liberated become greater and other tests of the completeness of the explosion have to be used.

The sensitiveness of explosives to sliding friction can be measured with a number of devices such as a "torpedo" with a rounded nose that slides down an inclined plane on to a thin layer of explosive spread over a flat plate. The materials of the torpedo and the plate are varied and the angle of elevation is adjusted to produce ignition of the explosive. Another machine is a pendulum fitted with a curved shoe that swings across the layers of explosive on the plate with the minimum clearance. The test normally carried out in Government Establishments relies on the skill and experience of the operator who delivers swinging, glancing blows on to a thin layer of explosive spread over a flat test-plate on the floor with a round-headed hammer or a mallet. The materials of the hammer-head, the mallet and the test-plate can be varied at will and the operator notes the number of ignitions in ten strikes and expresses them as a percentage. The usual implements for the test are a boxwood mallet with a chamfered edge, a slab of York paving-stone or concrete, and thick boards of hardwood (Oak or beech) and softwood (pine or deal).

A very sensitive explosive which ignites every time under this treatment on all three surfaces has its sensitiveness to friction expressed as 100-100-100, relating the stone, hardwood and softwood in that order. An insensitive explosive which does not ignite at all has figures of 0-0-0, and explosives intermediate in behaviour have figures of, say, 100-30-0, or 50-0-0, according to their relative sensitiveness to friction. The materials of the striker and the bed-plate are always specified.

In general, with all but the very sensitive pyrotechnic compositions the results obtained using a boxwood mallet on stone, hardwood and softwood are in descending order of magnitude, but occasionally an apparent anomaly may occur with mixtures containing peroxides, especially strontium peroxide, in which the value for softwood may be higher than one of the others. This has been attributed to oxidation of the wood itself during the striking operation.

Sensitiveness to electrical discharge is measured by discharging a condenser of suitable capacitance through a layer of the explosive lying between two electrodes. The type of discharge most frequently met with when handling explosives is closely simulated by using a pear-shaped electrode in close proximity to a cylindrical one, the flat surface of which is covered with a layer of conducting rubber on which the explosive is spread.

THE CLASSIFICATION OF PYROTECHNIC COMPOSITIONS INTO SAFETY-TYPES

Since loose pyrotechnic compositions vary so widely in their ability to ignite from blows, friction or sparks and in the effects produced thereby, it is necessary to separate them into types so that members of the same type can be stored and transported with precautions appropriate to their degree of sensitiveness and to the likely hazards resulting from ignition. The criteria used in this analysis are the figure of insensitiveness, the sensitivity to friction, the minimum spark-energy, and the effects produced by igniting several pounds of the composition, either as a loose heap or lightly confined in a container. Home Office regulations governing the manufacture of pyrotechnics in industry require all mixtures containing chlorates to be processed and stored separately from those that do not, hence the system of classification is duplicated, types A, F, C, H and K containing chlorates while types B, G, D, J and L do not. Each group is sub-divided into sensitive and insensitive sub-groups. The first includes all compositions which are as sensitive as, or are more sensitive than, gunpowder, (F. of I. 90, S to F 0-0-0), and which must be stored in mounded magazines with all the attendant precautions. The second sub-group includes compositions that are less sensitive than gunpowder, which may be stored in unmounded store-houses. Each type in a sub-group is further classified in respect to the probable results of ignition, i.e. whether the hazards are those of mass explosion, mass fire or of more controllable, localised effects. The complete analysis is shown in the Table 25.

SAFETY CERTIFICATES

Information concerning the sensitiveness of pyrotechnic compositions, their behaviour when ignited, their chemical stability, and many other properties that have a bearing on the precautions to be taken during mixing and filling operations, is summarised in safety certificates issued by the Director of Safety, Ministry of Defence, primarily for the guidance of staff of Royal Ordnance Filling Factories and of industrial firms handling pyrotechnics under Home Office licence. This information is acquired as a result of prescribed tests, such as those used to determine sensitiveness, and of experience gained with the compositions during their development and subsequent testing, and it includes the following data.

The designation of the composition, the ingredients and their proportions.

Its classification as a Government explosive.

Its sensitiveness to mechanical shock, friction and electric spark.

Its temperature of ignition.

The ease with which it ignites from a flash and how it behaves when ignited.

TABLE 25 THE CLASSIFICATION OF PYROTECHNIC COMPOSITIONS FOR STORAGE AND TRANSPORT

Home Office Classification	Type	E.S.T.C. Group	Sensitiveness	Storage	Safety Distance Category		Fire Fighting Category	Example SR No.
					Class	Risk		
Containing Chlorate	A	1	<u>Sensitive</u> F. of I. ≤ 90 or S. to F. $> 0-0-0$ or Spark $\leq 0.45J$	Magazine	ZZ	Mass Explosion	1	428
	F				Y	Mass Fire Moderate Explosion	2	99A
	K	9	<u>Insensitive</u> F. of I. > 90	Storehouse	ZZ	Mass Explosion	1	384
	H	11	S. to F. = $0-0-0$ Spark $> 0.45J$		Y	Mass Fire Moderate Explosion	2	None
	C				X	Localised Fire and Explosion	4	904
Not Containing Chlorate	B	1	<u>Sensitive</u> F. of I. ≤ 90 or S. to F. $> 0-0-0$ or Spark $\leq 0.45J$	Magazine	ZZ	Mass Explosion	1	399 580
	G				Y	Mass Fire Moderate Explosion	2	57 306
	L	9	<u>Insensitive</u> F. of I. > 90	Storehouse	ZZ	Mass Explosion	1	547 563
	J	11	S. to F. = $0-0-0$ Spark $> 0.45J$		Y	Mass Fire Moderate Explosion	2	349
	D				X	Localised Fire and Explosion	4	214 269

Its chemical stability, incompatibility with other materials, and the toxicity of its ingredients.

The recommended method of manufacture and filling, together with the type of containers and tools that should be used.

How it should be stored, or destroyed, and how fires involving the composition should be put out.

Other information required by a manufacturer includes the type of safety screen needed to protect operatives from the results of accidental ignition of the composition during manufacturing and filling operations.

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