

CHAPTER 14

PYROTECHNICS

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14 PYROTECHNICS

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14.1 AWARENESS SUMMARY

Pyrotechnic stores were evolved in the mid-19th century, a development of the already well established fireworks industry. The first use of such stores was for signalling, however, as equipment and ordnance became more complex, the need for a much wider range of pyrotechnic stores grew. It is understandable that such military stores are considered by some to be larger versions of commercial fireworks. This, however, is not the case since most military pyrotechnics are filled with high performance compositions with large energy outputs making them truly explosive materials.

Pyrotechnic compositions can be defined as materials which when correctly initiated, burn and produce a special effect. Thus in their designed use these compositions do not detonate, however, this does not mean that certain of the compositions are not capable of detonation. Under heavy confinement or by over-stimulus, highly energetic mixtures particularly when in powder form, can detonate or explode. The second point of importance in the definition is that the pyrotechnics are designed to provide a special effect. These effects are listed in **Error! Reference source not found.** Table 14-1, together with examples of each category.

Table 14-1 Special Effects Provided by Pyrotechnic Compositions

Effect	Examples
Heat	Priming, Igniters, Incendiaries
Light	Illumination (long and short period), Tracking, Signalling, Decoys
Smoke	Screening, Signalling, Riot-control, Target marking
Sound	Distraction, Signalling, Gunfire Simulators, Maroons
Gas	Pyromechanisms, Oxygen candles
Time Intervals	Delays

Since all compositions produce heat when they burn it could be said that heat was the primary driving force for all special effects. The output of light energy, for example, comes from the very high temperatures produced by illuminating compositions. More difficult to classify by effect is signalling or coloured smoke where a heated composition vaporises a dye. However, the effects listed in **Error! Reference source not found.** the Table are generally accepted as the most convenient method of classifying the special effects produced by pyrotechnic compositions.

The distinction between pyrotechnics and pyromechanisms is not clear. Though some pyromechanisms contain true pyrotechnic compositions, it is more common to use a single-base or double-base propellant powder. The gas produced by these can be used to operate a mechanical device. Other pyromechanisms contain detonating high explosives. The need for use of propellants rather than pyrotechnic compositions in pyromechanisms is that the latter may produce large amounts of unwanted solid slag in their combustion products. The subject of Pyromechanisms is covered in Chapter 15.

14.1.1 CHEMICAL COMPOSITIONS

Chemical compositions of pyrotechnics fall into three categories. The main category is fuel and oxidant mixture (see 4.2.1) where both components are themselves non-explosive. Other additives are often included as processing and performance modifiers.

The second category is that of fuel only compositions. The most important examples of this group are white and red phosphorus, used to provide screening smoke. Phosphorus fuel whether red or white burns in air therefore no oxidant is incorporated in the store but whereas white phosphorous will ignite spontaneously on contact with air, red phosphorus requires a source of ignition.

There is also the possibility of a fuel precursor filling, where a chemical reaction releases the fuel, again to burn in air. Naval smoke marker stores have been filled with calcium phosphide which reacts with water to form phosphine gas which spontaneously ignites in air and reacts with moisture to give smoke. These fillings with no oxidant content are still considered as pyrotechnics since the special effect, production of smoke, is considered a pyrotechnic effect.

The third group comprise materials which simply react with atmospheric moisture to produce a smoke on dissemination. These are smoke producers and are also considered as pyrotechnics. Examples are titanium tetrachloride and chlorosulphonic acid which hydrolyse forming acid droplets, which have corrosive properties.

14.1.1.1 Fuel-oxidant mixtures

Many materials found among pyrotechnic compositions are fuel-oxidant mixtures, which allow for the optimisation of output for a particular effect. The fuels are usually finely divided metal powders although some metal alloys, non-metals and organic materials are also utilised. Oxidisers cover a wide range of chemical species, most of which are sources of oxygen, used to oxidise the metal or non-metal fuel. One class, however, does not provide oxygen but contain chlorine or fluorine capable of reacting with elements to form metal chlorides or fluorides, which is classed as an oxidation reaction. For example, magnesium reacts with PTFE, $(-CF_2-)_n$, to form magnesium fluoride generating around 10 kJ g^{-1} of energy.

Table 14-2 lists the more important fuel elements and oxidant types. Intimate and uniform mixing of the fuel/oxidant mixtures is essential to ensure optimum-

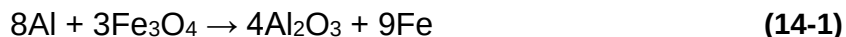
performance. To maximise shelf-life, ingredients should be non-hygroscopic and compatible.

Table 14-2 Fuel Elements and Oxidants

Fuel Elements			Oxidisers	
Metals	Aluminium	Al	Chlorates	NaClO ₃
	Iron	Fe	Chromates	PbCrO ₄
	Magnesium	Mg	Dichromates	K ₂ Cr ₂ O ₇
	Titanium	Ti	Halocarbons	C ₂ Cl ₆ , PTFE
	Tungsten	W	Metal Oxides	Pb ₃ O ₄ , BaO ₂
	Zirconium	Zr	Nitrates	KNO ₃ , NaNO ₃
Non-metals	Boron	B	Perchlorates	KClO ₄
	Carbon	C		
	Organic fuels	Lactose Hexamine		
	Silicon	Si		

14.1.1.1.1 Thermite compositions

One special group of fuel-oxidant mixtures comprises metal-metal oxide combinations. These are based on the original Goldschmidt reaction of aluminium with iron oxide as shown in Equation (14-1). Although the heat output is modest compared to the compositions described in Section 14.1.1.1, around 4 kJ g⁻¹ of mixture, the heat is held within the products and temperatures in excess of 2000 °C are obtained.



This provides molten iron in the products which has been used for onsite welding operations. This type of composition is nominally gasless.

14.1.1.2 Binders

Pyrotechnic compositions are sometimes filled into stores as loose powders particularly when very fast reaction is required. However, it is more common to find compositions consolidated into a single pellet known as a 'candle'. This consolidation may be achieved by pressing, usually with a binder included in the composition and often in increments, or by 'in-situ' polymerisation.

Table 14-3 details examples of both natural and man-made binders in use by the pyrotechnics industry. It should be noted that this list is not exhaustive

although as can be seen the range of binders is extensive. Part of the art of pyrotechnics lay in knowledge of natural binder materials; however, the move presently is towards man-made binders where quality control and availability can be more strictly governed.

Table 14-3 Pyrotechnic Binder Materials

Natural	Man-Made
Acaroid resin (Plant resin)	Carboxymethyl cellulose
Beeswax	Chlorinated natural rubber
Boiled linseed oil (Flax oil)	Epoxy resin
Carnauba wax (Palm wax)	Polyester resin
Lithographic varnish (From linseed oil)	Polytetrafluoroethylene (PTFE)
Paraffin wax (From hydrocarbon deposits)	Polyvinylacetate (PVA)
Shellac (Insect resin)	Polyvinylchloride (PVC)
	Silicone rubber
	Thiokol rubber
	Viton

Binders do more than just act as a consolidating agent. When present in significant amounts they can be considered as part of the fuel components. Also, the use of chlorinated binders can enhance the performance in certain cases, such as the production of coloured light.

The other major role of the binder is in the protection of reactive components. Metal powders such as those of magnesium and aluminium react with moisture which may be absorbed from the atmosphere. Coating these particles with a waterproof material can dramatically improve storage life. Thus, it is common practice to coat the metal powder by evaporation of an organic solution of a binder, such as lithographic varnish, before incorporation into the pyrotechnic mixture.

Other modifications which occur due to the presence of binders are reduction in burning rate and reduced sensitiveness (see 20.2.1) to initiation. This latter point is particularly true for polymer bound candles making them less susceptible to accidental initiation by friction or impact. However, it must be realised that purposeful initiation is also more difficult and that good ignition

methods are required. Finally, binders can aid powder flow in filling machines, reduce segregation and increase the waterproof properties of the composition.

14.1.1.3 Burning-rate moderators

Binders will normally reduce the burning rate of a composition. If further rate reduction is required, it may be achieved by incorporating inert materials such as clays or chemicals which decompose endothermically into the composition. Care must be taken that such moderators do not adversely affect the required output of the pyrotechnic, for example, flame colour.

14.1.2 MATERIAL PROPERTIES

The majority of pyrotechnic compositions used in military stores contain finely divided metal powders as fuel. These metals are usually highly reactive, such as magnesium or aluminium which, together with the large surface area available for reactions, makes these powders susceptible to degradation. The main problem is the reaction with moisture to form metal oxide and hydrogen. The presence of this extra metal oxide may well modify the output of the store. Also, the hydrogen produced may create a pressure build up making the device unsafe to handle. Thus the control of moisture content of a composition in manufacture and when filled in a store, is of great importance. As discussed in Section 14.1.1.2, metal powders are often coated with a binder such as lithographic varnish to give protection against moisture.

14.1.2.1 Sensitiveness

The diversity in the chemical and physical properties of the ingredients of pyrotechnic compositions is reflected in a corresponding diversity in the sensitiveness (see 20.2.1) of the compositions. The sensitiveness of the compositions depends on many factors which include:

- a. The proportions of the ingredients, compositions in stoichiometric proportions tend to have greater sensitiveness than those which are not.
- b. Particle size and shape; the larger surfaces presented by fine particles, particularly those with flattened or irregular shapes, increases sensitiveness.
- c. The intimacy of mixing
- d. The hardness of the ingredients as most pyrotechnic compositions contain metal or metalloid powders mixed with a crystalline salt or metal oxide powders and thus are gritty materials. These compositions show high sensitiveness to friction.
- e. The atmospheric humidity plays an important role with electrostatically sensitive mixtures. Pyrotechnics containing zirconium are especially sensitive to initiation by electric spark discharge.
- f. The presence of phlegmatizers which protect the fuel particles or act as diluents, and which may absorb much of the heat generated by local friction or impact, reduces composition sensitiveness.

14.1.2.2 Explosiveness

Since the early 1980s the explosiveness (see 20.2.1) of pyrotechnic compositions has given rise to great concern mainly due to incidents during the processing of MTV flare (see 14.4.6) compositions. Accidental ignitions may not be more common with these compositions than with any other compositions but the explosive response (explosiveness) has been very violent and led to fatalities at production plants. The use of remote control facilities, robotics and personal operator protection is now used when these compositions are processed.

14.1.2.3 Classification of pyrotechnic compositions

The classifications of the types of pyrotechnic composition with examples are given in Table 14-4.

PYROTECHNICS

BASIC CONSTITUENTS: FUEL + OXIDANT

REACTION INITIATED BY VARIOUS MEANS e.g. PERCUSSION CAP – ELECTRIC IGNITER
 SPECIFIC CHARACTERISTICS DEPEND ON PARTICULAR FUELS, OXIDANTS, ADDITIVES AND PHYSICAL FORM TO GIVE THE REQUIRED EFFECT
 PROPAGATES OVER ALL AVAILABLE SURFACE TO GIVE:

PRODUCTS + ENERGY OF REACTION

REQUIRED EFFECT: ENERGY USED AS

LIGHT

FOR ILLUMINATION

FLARES
HIGH INTENSITY. SECONDS TO MINUTES DURATION COMPOSITIONS CONTAIN MODERANTS AND ARE COMPRESSED
TYPICAL COMPOSITION
SR580
Mg
NaNO₃
Acaroid resin

PHOTOFLESHES
NOW OBSOLETE. VERY HIGH INTENSITY. SHORT DURATION. COMPOSITION LOOSE FOR RAPID BURNING.
TYPICAL COMPOSITION
SR541
Mg
NaNO₃

FOR SIGNALLING

COLOURED FLARES AND STARS SIMILAR TO ILLUMINATING FLARES BUT FLAME COLOURED BY SALTS
TYPICAL COMPOSITION
SR188 (RED) SR183 (GREEN)
Mg Mg
Sr(NO₃)₂ Ba(NO₃)₂
Chlorinated rubber Chlorinated rubber

FOR TRACKING FLARES

SIMILAR TO ILLUMINATING FLARES. MISSILE GUIDANCE. TRACERS FOR GUN PROJECTILES. MISSILE DECOYS
TYPICAL COMPOSITION
SR372sp
Mg
Beeswax
Sr(NO₃)₂
Shellac

HEAT

IGNITERS

FOR LIGHTING PROPELLANTS AND MISSILE ENGINES. PRODUCTS E.G. HOT SLAG SUITED TO GIVE APPROPRIATE HEAT TRANSFER TO ACCEPTOR
TYPICAL COMPOSITION
SR371c
Mg
KNO₃
Acaroid resin

PRIMING

FOR IGNITION OF PYROTECHNICS DIFFICULT TO IGNITE. PRODUCTS SUITED TO ACCEPTOR
TYPICAL COMPOSITION
SR44a
B
KNO₃
NC

GAS PRODUCTION

TYPICAL COMPOSITION
SR306
Al
Fe₂O₄
Ba(NO₃)₂

VAPORISERS

FOR COLOURED SMOKE
TYPICAL COMPOSITION
SR194
KClO₃
Lactose
Copper Oxide
Cereclor 70

DELAYS

IN IGNITION TRAIN TO TRANSFER IGNITION BETWEEN COMPONENTS AFTER A DESIRED INTERVAL

GASSY DELAYS

FOR VENTED CONDITIONS - LOW ALTITUDES
TYPICAL COMPOSITION
SR227
KNO₃
S
Charcoal

GASLESS DELAYS

FOR HIGH ALTITUDES AND CONFINED CONDITIONS WHERE PRESSURE CHANGES MUST NOT AFFECT PERFORMANCE
TYPICAL COMPOSITION
SR55
B
BaO₂

SOUND

WARNING

MARCON
TYPICAL COMPOSITION
SR541C
NaNO₃
Mg

WHISTLING COMPOSITION
SR135
KClO₃
Al

SIMULATOR

THUNDERFLASH
SR44a
KClO₃
Al

SMOKE SOURCE

WHITE AND GREY SMOKE

PRODUCTS FORM THE SMOKE
TYPICAL COMPOSITION
SR264AM
ZnO
CaSi₂
KNO₃
C₂Cl₆

KINETIC ENERGY

TO PROPEL ROCKETS

TYPICAL COMPOSITION
SR432
Al
TNT
KNO₃
H₃BO₃
Wax

TO EJECT COMPONENTS FROM STORES

TYPICAL COMPOSITION
Gunpowder

DETAILS OF COMPOSITIONS AND FORMULAE

Aluminium.....	Al	Nitrocellulose.....	NC
Barium oxide.....	BaO ₂	Potassium Chlorate.....	KClO ₃
Barium Nitrate.....	Ba(NO ₃) ₂	Potassium Nitrate.....	KNO ₃
Boron.....	B	Sodium Nitrate.....	NaNO ₃
Boric Acid.....	H ₃ BO ₃	Strontium Nitrate.....	Sr(NO ₃) ₂
Calcium Silicide.....	CaSi ₂	Sulphur.....	S
Hexachloroethane.....	C ₂ Cl ₆	Trinitrotoluene.....	TNT
Iron Oxide Magnetite.....	Fe ₂ O ₄	Zinc Oxide.....	ZnO
Magnesium.....	Mg		

14.2 FACTORS AFFECTING PERFORMANCE

When considering the performance of a particular pyrotechnic composition there are several factors which must be considered. The burning rate of a composition can be affected by the ratios of the ingredients (stoichiometry), by the chemical and physical characteristics of the ingredients (particle size and particle shape), presence of impurities, by the method of filling (consolidation pressure - compaction load) and the ambient temperature and pressure.

14.2.1 Effect of Ingredients – Stoichiometry

Once the particular chemical species to be used in a composition has been selected, there are many factors which can influence output. The first consideration is the ratio of reactants. If the products of the reaction are known, the optimum ratio of reactants can be chosen so that all ingredients are totally consumed. This is called the stoichiometric mix and weight percentages can be calculated from the balanced chemical equation. Stoichiometric mixtures are often the most sensitive and have the greatest heat output and for these reasons are not generally used.

The composition giving maximum heat output will also have the fastest rate of burning. This is measured in seconds per inch (s in^{-1}) and is usually the measured parameter when relating variations in composition with performance as shown in Figure 14-1. For any given grade of magnesium (0 to 5), as magnesium content increases, the luminosity and burning rate of the magnesium/sodium nitrate increase to maximum values at 60 % magnesium⁽¹⁾.

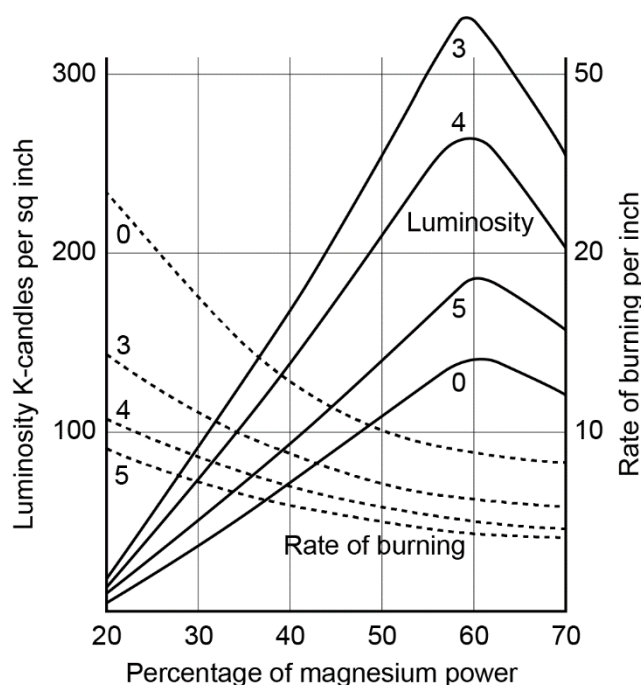


Figure 14-1 Variation of luminosity and rate of burning with grade and proportion of magnesium powder in magnesium - sodium nitrate compositions

It is of interest to note that since the maximum output occurs at 60 % magnesium, the reaction is not only between magnesium and sodium nitrate but also atmospheric oxygen. The stoichiometric mixture for the magnesium and sodium nitrate reaction would only contain 42 % magnesium based on the reaction shown in Equation (14-2).



The heat output and, therefore, rate of burning will always be of a lower value when the composition changes from the stoichiometric mixture, either to a fuel lean or fuel rich situation. As shown in Figure 14-2, this means that two compositions will have the same heat output either side of the maximum, therefore, the composition choice for, say, a delay, could be made on economic grounds, depending on the relative costs of fuel and oxidant⁽¹⁾.

On practical grounds, however, the fuel rich mixture is preferable, since the slope is less steep on the fuel rich side giving more tolerance to slight changes in composition due to inhomogeneity. Also, the fuel lean compositions may well have very small amounts of fuel, making mixing difficult.

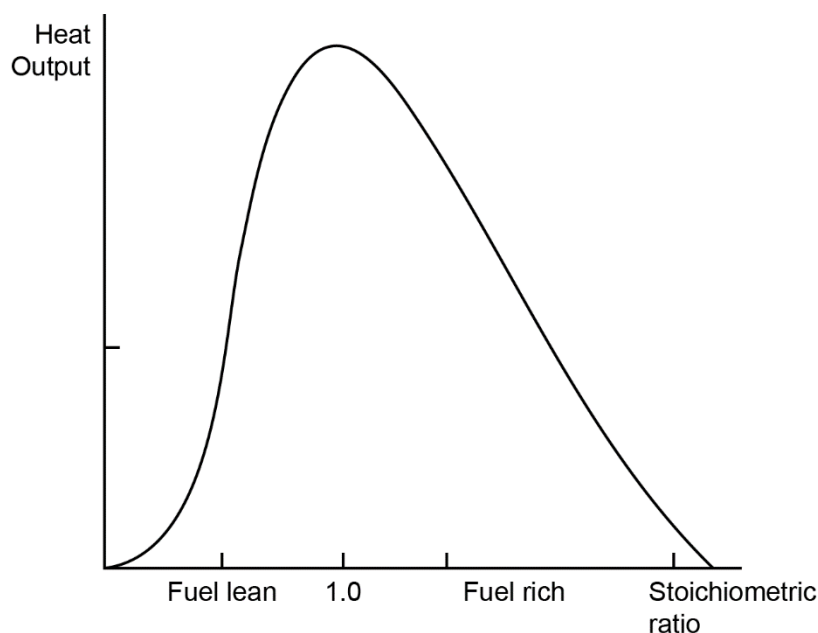


Figure 14-2 Stoichiometry versus heat output

The other method of obtaining a reduced heat output and rate of burning is to use the stoichiometric ratio or composition with the maximum values and add either an inert material or a coolant. This has the advantage that any slight change in the fuel oxidant mixture will have the least effect at this ratio being at the top of a curve. It must be remembered that the binder will probably act as a cooling moderator.

14.2.2 Effect of Particle Size and Particle Shape

Particle size and particle shape are of great importance since in most cases at least one if not all of the materials present are reacting as solids. Thus, the smaller the size of the particles, the larger the surface area per given weight at which reaction can occur. If the composition is held constant but the particle size distribution of one of the materials is changed, then performance can be modified to a large extent. Both rate of burning and luminosity of the flare composition shown in Figure 14-1 are altered markedly as the particle size changes. Metal powders can be obtained from sub-micron size called 'ultrafine', however, the usual range of practical use is from 5 μm to 100 μm .

For metal powders the particle shape is also very important. Metal powders are formed generally by one of two methods. Cut powder is manufactured by machining large pieces of metal whereas blown powder relies on the atomising of molten metal which is rapidly cooled and solidifies into spheres or pear-shaped particles. The cut powder being of a flake nature has a higher specific surface (area/wt) than blown metal powder. Therefore, a cut powder of apparently the same particle size distribution as a blown powder will have a larger surface area and thus react more readily. Some grades of metal powders are particularly reactive. For example, 'dark pyro' aluminium is much favoured by the pyrotechnician for its excellent performance in compositions. The shape of the particles can be assessed by measuring the apparent density, the less dense material being of the flake form whereas the higher density will be the near-spherical type.

The reactivity of solids is also controlled by strength of the intermolecular or interatomic forces that bind their crystal lattices together. These forces become weaker as the temperature is raised and atomic and molecular vibrations increase in amplitude. The strongest bonds are found in covalent lattices such as those of silicon; ionic bonds are next strongest and non-ionic lattices such as are found in organic compounds (e.g. hexachloroethane) are weakest.

Early work by Hedvall suggested that reactivity of a solid would be enhanced when the atoms or ions within the solid became more mobile. This occurs near the melting point (mpt) of the solid but also at phase changes, which occur for many solids at temperatures well below the melting point. Tammann quantified this with the coefficient α as shown in Equation (14-3).

$$\alpha = \frac{T_{\text{solid}} (\text{K})}{T_{\text{mpt}} (\text{K})} \quad (14-3)$$

Surface mobility becomes significant at $\alpha = 0.3$ and internal mobility at $\alpha = 0.5$. Thus, potassium perchlorate (mpt 588 °C) and potassium chlorate (mpt 364 °C) would have significant internal mobilities at 158 °C and 46 °C respectively.

14.2.3 Effect of Impurities

Small quantities of impurities or the presence of lattice defects due to the methods of preparation may also affect the reactivity of solids. Since pyrotechnics manufacturers are only small customers of large manufacturers it may be difficult for them to control specifications of ingredients and changes in suppliers may lead to changes in pyrotechnic composition performance.

14.2.4 Effect of Temperature

Pyrotechnics burn more slowly at low temperatures than at high temperatures, and the burning rates of the same system at two different temperatures can usually be related approximately:

$$r = r_0 \exp(bT/T_0) \quad (14-4)$$

Where r , r_0 are the burning rates at absolute temperature T, T_0 .

14.2.5 Effect of Ambient Pressure

Pyrotechnics are burning explosives and as such are affected in their performance by ambient pressure. Vieille's Law relates the rate of burning ($s\text{ in}^{-1}$) with pressure (atmospheres) as shown in Equation (14-5). The constants β and α (pressure index) differ from one composition to another.

$$r = a P^n \quad (14-5)$$

Where r is the burning rate at pressure P , a and n are constants for the chemical system. In general, the more gas that is produced by the pyrotechnic (how gassy) the greater the value of n (the greater the sensitivity to pressure).

If a composition's performance was independent of pressure, then n would be zero. This should occur for gasless mixtures, that is, those which produce no gas output at any stage of their combustion. This is never achieved completely and care should be taken when theoretical reactions seem gasless. The reaction between aluminium and potassium perchlorate, for example, should in principle form solid products only. However, during combustion large pressure increases can be measured.

Values of n , the pressure index, range from 0.5 for gas producing pyrotechnics such as gunpowder down to 0.05 for cool-burning 'gasless' compositions. It is important to consider that as pressure changes, the burning rate and thus performance can alter markedly. For example, gassy delays are unsuitable for delay elements in aircraft stores because of the dependence of the pressure index, and hence the burning rate, on the atmospheric pressure. At a height of 10 km the ambient pressure is 0.28 atmospheres and a pyrotechnic composition with an n value of 0.4 such as sulphurless gunpowder would have a burn 1.7 times slower than at sea level. Figure 14-3 shows the relationship between rate of burning and pressure, for five SR compositions. SR stands for 'Superintendent of Research', which was a numbering system for pyrotechnic

compositions developed at the Royal Armaments Research and Development Establishment, Fort Halstead, Kent.

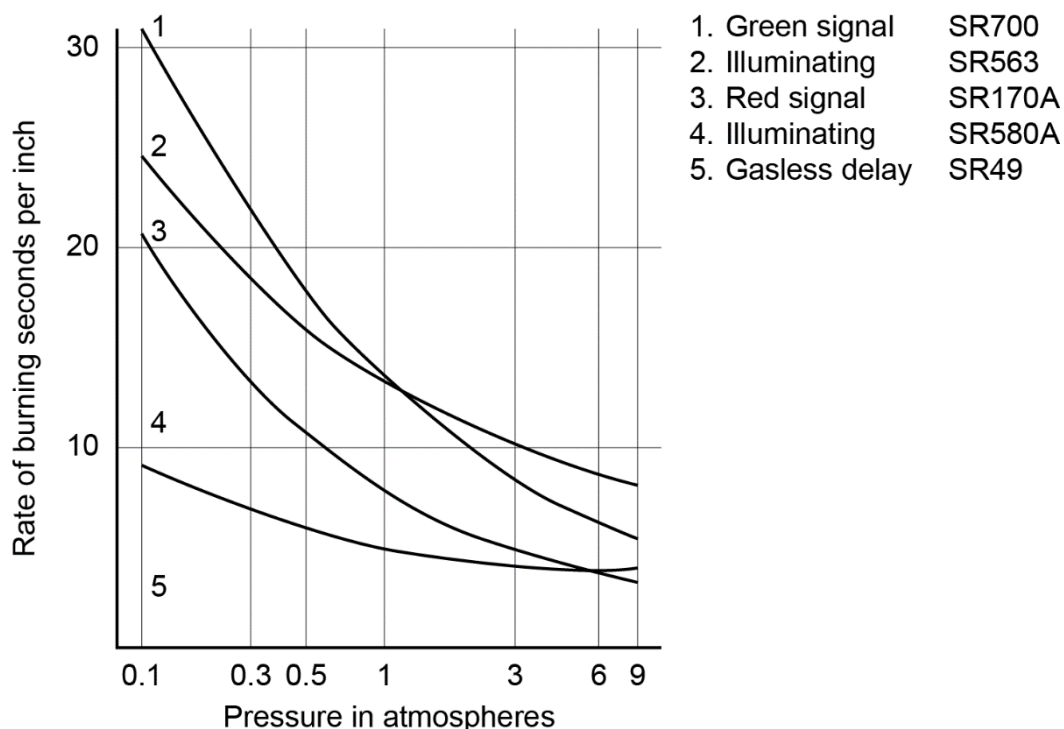


Figure 14-3 Variation in rate of burning with ambient pressure

14.2.6 Effect of Consolidation Pressure

The effect of consolidation pressure may markedly affect the burning rate, but its effect is often complex. If the combustion reaction is truly solid phase, that is no melting or vaporisation in the combustion zone, then increase in consolidation should allow better contact between the reactants, and the reaction rate should increase. If the reaction is not solid phase, then the effect is less predictable. Increasing the density decreases the porosity and thus may hinder hot gas penetrating the reactants and so reduce the burning rate. In most cases it is the linear burning rate of the pyrotechnic composition which is of interest to the designers, but the mass burning rate (kg s^{-1}) (see 7.2.2) is the real measure of the output from a pyrotechnic device. Many compositions have a lower linear burning rate at higher compaction loads, but the mass consumption rate decreases by less, or may even increase due to any increase in the density of the column.

It is unwise to attempt to predict the effect of consolidation on a new composition, as small changes in ingredient ratios and particle size can change the behaviour markedly. Except for pyrotechnic delay compositions, the effect of compaction on burning rate is usually of secondary importance, and the compaction load is adjusted to give optimum mechanical properties. Attention also must be paid to the ease of ignition, which often decreases at high compaction loads because the surface is smoother and less porous.

14.3 HEAT AS A SPECIAL EFFECT

In the following section priming, igniter, incendiary and delay compositions are considered.

14.3.1 Priming Compositions and Igniters

A priming composition is used to pick up the flash from an initiator such as an electric match-head or fuze-head and ignite the next component in the store, usually the main filling. Figure 14-4 gives an example of how a priming composition is used. In this case, two priming compositions are used, sulphurless fine grain (SFG) gunpowder composition picks up the flash from the ejection cartridge, ignites and then in turn, ignites the priming for the flare composition. This technique is used because the flare priming is not readily ignited by the cartridge flash. SFG is not suitable to ignite the flare but will readily ignite the flare priming layer.

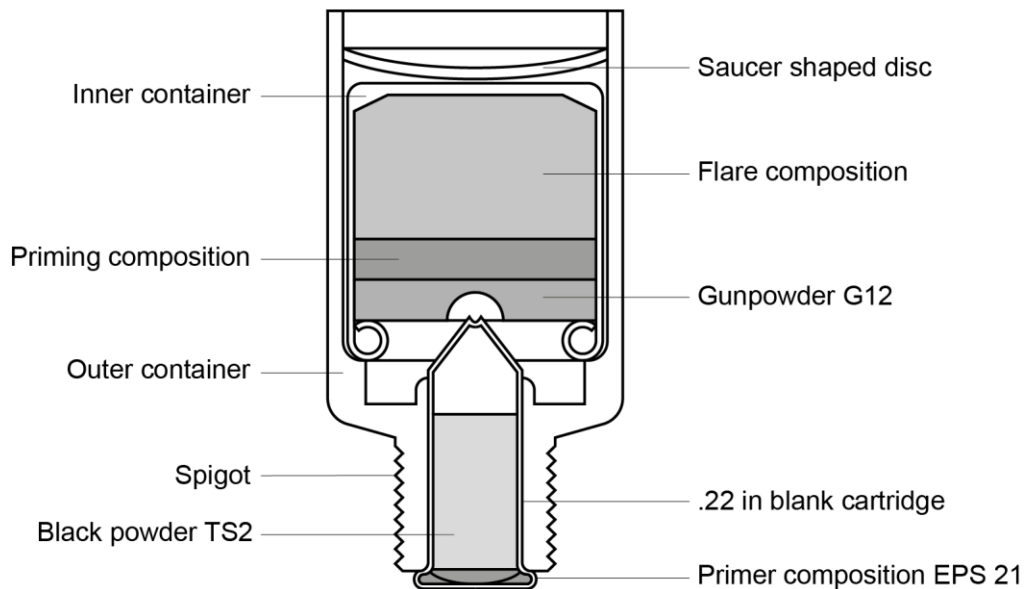


Figure 14-4 Example of a priming arrangement for a pyrotechnic store

Common terms for this type of composition are, priming composition, first fire, starter mixture and igniter. It is more usual to use the term igniter, for a store when it is used, for example to ignite rocket motors or flame-throwers. This type of igniter may well contain a pyrotechnic or propellant main filling and have an associated priming composition.

The role of a priming composition is essentially to act as a booster in a burning explosive train between the initiator and main charge. For such a composition to fulfil its role a number of requirements have to be met:

- It should be readily ignited by flash or flame.
- A large amount of heat must be generated but not too violently since that might throw the composition off the surface to be ignited.

- c. The output characteristics should match the ease of initiation of the filling to be ignited.
- d. Non-volatile products are desirable since a hot slag remains to enhance heat transfer.
- e. Sensitiveness (see 20.2.1) should be compatible with safe handling.
- f. The composition should be chemically compatible with the mixture to be ignited as often the priming composition is pressed directly onto the main filling and is in intimate contact.
- g. The use of gassy mixtures will ensure a pressure increase aiding the ignition process.

The most important group of priming compositions are based on gunpowder since gunpowder is readily ignited by flash. Gunpowder itself burns fiercely when compressed and a layer of this alone may not ignite an underlying layer due to the rapidity at which the gunpowder is consumed. Several approaches have been used to slow the burning rate. The addition of lactose or resins will give slower burning compositions; however, a more popular method is to mix with the gunpowder, an equal weight of the material to be ignited.

The most common priming composition is SR252 based on potassium nitrate/silicon/sulphurless mealed powder. An example of its use is shown in Figure 14-4 where a first layer of gunpowder (SFG12) is used to ignite the composition which primes the main filling. Composition SR252 is used as priming in signal and illuminating cartridges, most flares and many other stores.

Other modifications are made to gunpowder. The sulphur content is often omitted to increase compatibility with other compositions. When an adjacent layer contains magnesium this alteration is a necessity due to the corrosive action of sulphur on magnesium. These materials are known as sulphurless fine grain (SFG) or sulphurless mealed powder (SMP) depending on their form. Another modification is in the way the gunpowder is supported to give a layer for priming. Cambric is a woven material on which the gunpowder is supported giving a rigid or semi-rigid layer. This is used in the priming of most screening smoke stores.

Certain compositions require a cool-burning priming layer since over-ignition may well create an undesired burning regime. Coloured smoke compositions are prone to this problem and a second type of priming composition, organic fuel plus oxidant, provides suitable mixtures. For example, SR214 based on lactose/potassium nitrate provides suitable ignition.

If ignition is to occur at high altitude where pressure is very low, then special gasless compositions are required. Gasless mixtures are used such as SR44 (boron/potassium nitrate), which is readily ignitable and burns under near vacuum conditions. This is an example of a slag producing composition which leaves a hot solid residue to enhance thermal transfer. This is a particularly important condition if ignition conditions are difficult. Another difficult ignition condition, where this type of composition is used, is that of tracer compositions as in SR370 (magnesium/potassium nitrate/charcoal) and SR867 designed as a 'dark ignition' for small arms tracer rounds (see 14.4.4).

Igniters for rocket motors are normally based on high heat output compositions with large amounts of solid products. A popular composition for the ignition of solid propellants in rocket motors is SR371C (magnesium/potassium nitrate/acaroid resin). Data on the compositions used for priming and ignition are given in Appendix A, Table A-1.

14.3.2 Incendiary Compositions

Incendiary compositions are used for fire raising, physical destruction of flammable materials and for the physical penetration of metals. The requirements of an incendiary composition are quite stringent. To ignite a flammable material, it is necessary first to drive off the moisture content and then cause sufficient thermal decomposition to provide flammable gases which on burning propagate the combustion. The requirements are, therefore, a high temperature, large heat output and a relatively long burn-time. The burning time is very important since massive heat flashes will rarely cause ignition of all but the most flammable materials.

To obtain large heat outputs over long time periods it is usual to use a fuel burning in air as oxidant. These are not strictly pyrotechnics; however, the incendiary effect is normally linked historically to pyrotechnics and is considered here.

There are two types of material in this category, combustible metals or alloys and liquid fuels, usually as a gel. The two metals of most use are aluminium and magnesium having among the highest heats of combustion of any element. The values are 29 kJ g^{-1} for aluminium and 25 kJ g^{-1} for magnesium, compared with 12 kJ g^{-1} for typical pyrotechnic compositions without metallic constituents. It is important to note that pyrotechnic compositions with heats of combustion approaching this magnitude burn explosively and would not be suitable as an incendiary material.

The combustible metal can be fashioned into an outer container which is then filled with a suitable igniter composition. This was the basis for the incendiary bombs which caused extensive destruction during World War II. The igniter composition is based on Thermite type materials. The conventional aluminium/iron oxide composition being difficult to ignite is modified by the addition of barium nitrate to improve ignition as in composition SR306. This composition provides over 4 kJ g^{-1} and consists of both flake and blown magnesium, hammerscale a form of iron oxide produced by hammering hot iron in air, is the oxidant, barium nitrate aids ignition and boric acid which stabilises the composition chemically against reaction of aluminium with barium nitrate in the presence of traces of moisture. The composition does not itself ignite readily from a flame and is therefore primed normally with SR252 (potassium nitrate/charcoal/silicon), with an intermediate layer of SR252 + SR306.

The other type of fuel used as an incendiary is a liquid hydrocarbon, thickened to make it adhere to target material. Various thickeners or gelling agents have been used such as rubber, Perspex and soaps. The most widely known

example of the gelled liquid incendiary is called Napalm although strictly this is the thickener, a mixture of aluminium naphthenate and aluminium palmitate. The fuel is normally petrol or kerosene.

From the point of view of an adhering incendiary liquid the Napalm based materials are not particularly effective since a fast-burning fireball is produced. This occurs because the liquid is thixotropic and thins under shear stresses such as explosive dissemination. This property, however, makes it a very good flame-thrower fuel. As it passes through the nozzle it thins for easy passage, and on relaxing thickens to hold the stream together giving good range. More suitable thickeners for a burst munition are rubbers or man-made polymers. A composition developed in the United States of America uses partially esterified polyisobutylmethacrylate as thickener.

Incendiary composition CC466 (similar to SR306) is presently used in Destructor Incendiary (DI) EOD XL5E1 and L5A1 and is intended for use by EOD and other trained users to either initiate the explosive filling in target munitions or initiate combustible materials to assist in the bulk destruction of munitions or destroy materials by heat, flame and hot metal residue (slag).

Incendiary stores have also been used to destroy documentation in an emergency. An example of which is the Document Wallet Self Destruction Incendiary. This consisted of a PVC wallet (235 mm x 170 mm) inside which is a sheet of pyrotechnic composition SRE794 attached via a delay to a friction igniter. To aid destruction the document pages are interleaved with sheets of celluloid.

Incendiary bullets and cannon-shell fillings are based on magnesium-aluminium alloy fuel with barium nitrate oxidant such as SR365 composition. A short list of incendiary compositions is given in Appendix A, Table A-2.

14.3.3 Delay Compositions

A delay element is a device filled with a flame or heat producing composition which burns in 'cigarette fashion' at a known rate so that it can be used to control the time interval between two events. Timing accuracy in some cases need only be sufficient to allow for operator safety. In more sophisticated uses the timing accuracy may be critical and timings at the millisecond level are required such as in commercial delay detonators or for function operations within missiles. Military delays are often filled into lead sheaths or tubes to achieve the required burning rate and timing accuracy.

There are many factors to be considered in the design of a pyrotechnic delay and choice of composition. Of paramount importance is the required time interval and acceptable accuracy. Compositions are available which will burn from 0.01 s in^{-1} to 40 s in^{-1} .

The volume and shape of the space available to house the delay column may affect choice. In many simple munitions the delay column can be readily incorporated. However, in complex systems the physical form of the delay may

be dictated by the space available. Delay elements often consist of the composition filled into a lead sheath or tube. Small diameters are obtained by filling a large tube and then swaging down to the required diameter. This can be wound into a spiral to be accommodated in a restricted space. Other methods of incorporating a delay are to fill a channel cut into a metal or plastic plate or to have channels within the device such as in bomb and shell fuzes.

The operating temperature of a delay column will affect its rate of burning if the composition is either gasless or low gassing. In a crowded design, heat dissipation may be poor with associated large temperature rises. It is pertinent here to make note of the relevance of available heat sinks around the composition particularly the container. If the containment is a very good conductor of heat such as copper, the composition will have a slower rate of burning than if the heat cannot escape in this fashion. The designer of a delay munition must optimise these factors to suit the situation.

A choice must be made between a vented, semi-vented or obturated (closed) system. Vented systems are used when a gassy composition such as gunpowder is employed. For a delay a constant burn rate is required. The gaseous products must have, therefore, an unobstructed vent to atmosphere. A semi-vented system allows venting from the delay element into another closed system of finite volume. Obturated systems are used for the so-called gasless compositions and are particularly important at high altitude. It should be noted, however, that no system is truly gasless. For example, PbO/Si (80/20) burns at 2 s in^{-1} in the open but in a sealed tube at 1 s in^{-1} due to the formation of lead vapour. Compositions have been developed whose burning rates are essentially independent of pressure. These compositions, based on boron fuel with either barium or lead chromate as oxidant, are prepared by a co-precipitation process. One of these, boron/barium chromate, has a burning rate 15 % slower at 0.03 atmospheres compared to that at 1 atmosphere for a mechanical mixture whereas the co-precipitated mixture shows no change in rate.

The ignition source must be considered, since some compositions may be difficult to ignite. Delays are ignited in Service stores by several methods including burning propellant, percussion cap and electric fuze-head. The delay must pick up reliably from the ignition source.

The event to be initiated by the delay requires a consideration of suitability. The delay could be chosen to provide several different outputs such as flash, heat and pressure or heat only.

The simplest delays use gunpowder as the pyrotechnic composition. Fuse Instantaneous L1A1, used in Battlefield Noise Simulators, consists of a semi-fuse made from glazed Kraft Paper twisted yarn coated with sulphurless mealed gunpowder wound with yarn and protected by an outer light polyethylene covering and burns at not less than 33.5 m s^{-1} at 16°C . Gunpowder is the filling in Safety (Bickford) Fuze which consists of a gunpowder core enclosed in braided flax or jute and covered in rubber. Vent holes are provided to maintain an even pressure within the tube and the burning rate is 2 ft min^{-1} . The

variability of moisture content within the gunpowder due to the properties of charcoal precludes the use of the material for accurate timing although one such composition, SR227 based on potassium nitrate, charcoal and sulphur, was in Service use in the Fuze Nose Time No.390. Fuze timing for shells and bombs is now almost exclusively mechanical or electronic. However, as a safety delay as in demolition work, Safety Fuze is ideal.

To overcome the problems of moisture in the gunpowder other organic materials have been employed such as tetranitrocarbazole (TNC), nitroindene polymer and tetranitro-oxanilide. One such composition, SR12, based on TNC and potassium nitrate, is used in the Anti-riot Irritant CS Hand Grenade, L13 as delay composition. Another example of the use of organic fuel with barium and potassium nitrates, SR651, is used for the delay in some mortar systems where delay ignition is achieved from the burning propellant as the mortar bomb is fired.

Gasless delay compositions are based on metal or metalloid powders mixed either with oxidant salts or metal oxides, the latter oxidising agents giving Thermite type materials. For millisecond delays, very reactive combinations are required such as silicon or boron with an oxide of lead or bismuth, for example SR57. If the oxidant is a chromate or dichromate, the compositions will be slower giving second interval delays. One example of this type is co-precipitated barium chromate compositions with various fuels. One of these based on boron as fuel, RD1368, has been employed in the L25A5 Percussion Grenade Fuze. If lead chromate is employed the compositions become more reactive, and if the boron is replaced by titanium the burning rate is extremely rapid as in RD1370. If dichromate is used the compositions become slower as for SR67.

It should be noted that the rate of burning is dependent on exact compositions and also on pressing load. Compositions and their burning rates are given in Appendix A, Table A-3. Ambient pressure is one atmosphere and rate will alter even for the gasless mixtures, except for RD1368, as pressure changes. The factors which affect pyrotechnic performance are of particular importance in delay technology. Even small changes in stoichiometry or particle size will alter the rate of burning as will factors such as pressing load or container material (heat losses).

14.4 ILLUMINATING COMPOSITIONS (INCLUDING VISIBLE AND INFRARED EMISSIONS)

Some pyrotechnic compositions are designed to produce electromagnetic radiation. Depending on the region of the electromagnetic spectrum in which the radiation is produced, the special effect will be white or coloured light visible to the eye, or infrared radiation for wavelengths longer than 750 nm. The various regions and wavelengths of the electromagnetic spectrum are shown in Figure 14-5 and Table 14-5.

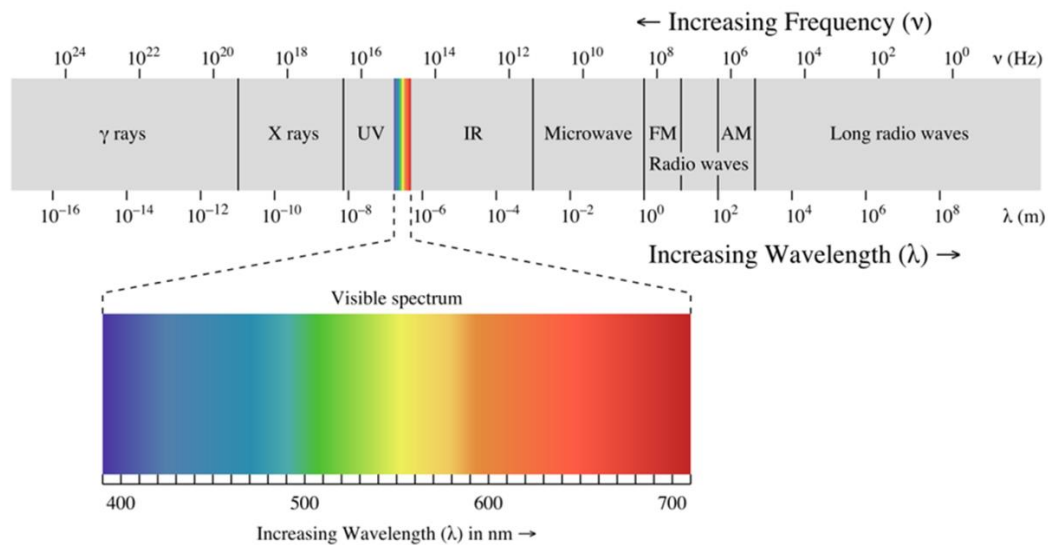


Figure 14-5 Electromagnetic Spectrum

Table 14-5 Regions of the Electromagnetic Spectrum

Region	Wavelength range
Ultraviolet	<380 nm
Violet light	380 – 440 nm
Blue light	440 – 495 nm
Green light	495 – 558 nm
Yellow light	580 – 640 nm
Red light	640 – 700 nm
Infrared	700 nm – 1 mm

The effects produced by the compositions considered in the following paragraphs are:

- Long duration illumination for target acquisition, reconnaissance, exposure of infiltrators and emergency landing
- Signalling with either white or coloured light
- Decoys emitting infrared radiation

14.4.1 Radiometric and Photometric Units

Radiometric units are concerned with the transfer of all radiant energy from or to a body. The total rate at which a body emits radiation energy is the *radiant flux* which has units of power (W). Emission in a particular direction as measured

radiometrically is the *radiant intensity* which is the radiant flux within unit solid angle measured in units of power per steradian (W sr^{-1}). If the body is not a point source, then the radiance is the radiant intensity per unit surface. If the body is receiving energy, its *irradiance* is the radiant flux that it receives per unit area. It is customary to report the values within a narrow waveband centred at a wavelength of interest with the results quoted per nanometre (the energy emitted at an infinitely narrow single wavelength is zero).

The sensitivity of the human eye to visible light depends on the wavelength. For example, two monochromatic sources of identical radiant intensity but different wavelengths appear to be of different brightness. Photometric units have been established that allow for this and the luminous intensity is related to the radiant flux by the sensitivity curve for a standard human eye.

The total rate at which light is emitted is the *luminous flux* from the source, measured in *lumens* (lm). The light emitted in a given direction is the *luminous intensity* measured in lumens per steradian, a unit usually known as *candela* (cd). The luminous intensity from unit area of the source (its brightness) is the *luminance* (cd m^{-2}) and the light falling on unit area of a surface is its *illuminance* (lm m^{-2}), also known as *lux*. If a light source emits with a luminous intensity of 1 candela in all directions, it provides a luminous flux of 4π lumens. Radiometric and photometric units are summarised and compared in Table 14-6.

Any radiating body radiates only part of its energy in the visible region of the spectrum. The fraction of the total radiation emitted as light is the luminous efficiency of the source, measured in lumens/Watt.

In pyrotechnic applications, a number of characteristics of a flare are important. Pyrotechnic nomenclature, synonyms, units and definitions often encountered are given in

Table 14-7.

Table 14-6 Radiometric and Photometric Units

	Radiometric Units		Photometric Units	
Rate of energy emission	radiant flux	W	luminous flux	lm
Radiation emitted in a specific direction	radiant intensity	W sr ⁻¹	luminous intensity	Lm sr ⁻¹ cd
Radiation emitted per unit surface area in a specific direction	radiance	W m ⁻² sr ⁻¹	luminance	cd m ⁻²
Radiation striking a unit area	irradiance	W m ⁻²	illuminance	Lm m ⁻² (or lux)

Table 14-7 Additional Units Used in Light Producing Pyrotechnics

Pyrotechnic Nomenclature	Synonym	Units	Definition
Specific intensity	luminance	cd m ⁻²	Luminous intensity per unit area of source.
Specific efficiency	specific light flux	cd s g ⁻¹	Total emitted light per gram of composition; compares compositions irrespective of burning rate.
Energy conversion	luminous efficiency	lm W ⁻¹	Compares luminous flux with the exothermicity of the composition.

14.4.2 White Light

The radiant or luminous energy emitted from a given source is very dependent upon the temperature of the source. A perfect radiator of electromagnetic radiation is called a black body (a condition rarely achieved and certainly not with pyrotechnics) whose energy emission is proportional to temperature to the fourth power. Thus high temperature compositions are required to provide large radiant outputs.

The production of white light, often with a yellow colouration, can be achieved by several methods. Foremost is the creation of very high temperatures to give thermal excitation and cause of broad continuous emission across the visible region. Secondly, the presence of sodium, particularly with a source of hydrogen gives another broad continuous emitter, NaH⁺, which emits from 550 nm - 700 nm providing the yellow colouration. The presence of organic material, as in the binder, is known to enhance luminous output of flares. Thirdly, the presence of species emitting in certain bands of the visible spectrum can further enhance performance. Examples of these species are, BaO⁺, BaCl⁺ and SrCl⁺, the latter two used together if white light is required. Such species are only stable at very high temperatures found in burning flare compositions.

The requirements of an illuminating store are that it burns for the required time interval, that it has an appropriate luminosity and that the flame colour is as desired. These factors are achieved by a judicious choice of composition, bringing in many of the factors, previously described, which affect pyrotechnic performance. Examples of illuminating compositions showing the effects of composition modification on flare performance are contained in Appendix A, Table A-4.

The fuel used in illuminating compositions is always magnesium and the preferred oxidant is sodium nitrate. With an organic binder, this provides the very high temperatures and emitting species such as NaH⁺. As shown

previously in Figure 14-1 the optimum magnesium content is 60 % in magnesium/sodium nitrate compositions such as SR580 which has by far the best performance of these compositions.

Particle size of the fuel is extremely important as shown by comparison of SR563 and SR563A compositions. Here the specific intensity is more than doubled by changing from grade 0 (coarse) to grade 5 (fine) magnesium. This is also exemplified in Figure 14-1. The burning rate of SR563A is about half that of SR563 and a smooth curve relationship exists between luminous performance of burning rate as shown in Figure 14-6.

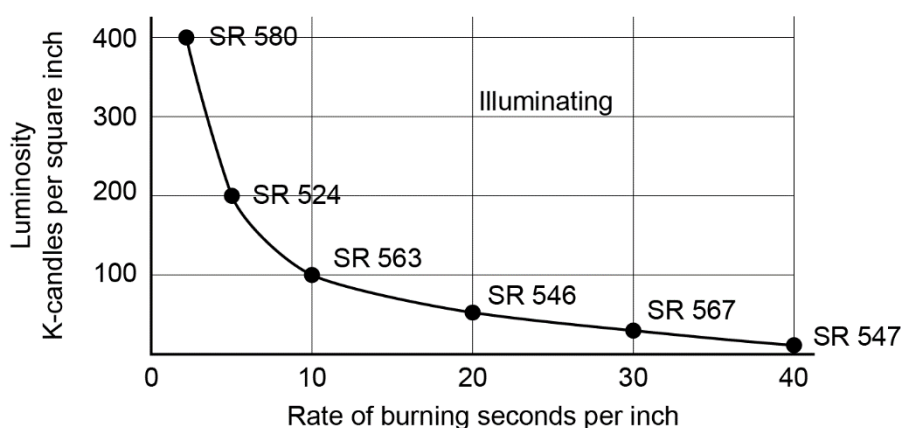


Figure 14-6 Luminosity versus rate of burning

Other modifications include the use of calcium oxalate to moderate and thus slow the rate of burning. Composition SR562 has almost the same fuel content as SR563, however, the presence of calcium oxalate (7 %) gives a rate of burning 1.5 times that of SR563 (17.8 s in^{-1} c.f. 12.0 s in^{-1}) and reduces luminous output to around 60 %. This type of modification is a useful method for increasing the endurance of a flare's illumination at the expense of luminous output.

Barium nitrate may also be employed in illuminating compositions. This increases the physical stability of the burning candle and consequently there is a lesser tendency for burning lumps to be ejected from the burning surface. The output of these compositions is less than sodium nitrate based materials, for example, compare SR343A with SR562 (see Table A-4 in Appendix A).

Choice of composition, therefore, depends on the requirements of the store. The tripwire flare, used to expose infiltrators, does not need the luminous intensity of a parachute flare operating at altitude; however, burn time is important. These needs are fulfilled by SR547. Parachute flares or stars require high intensities to provide ground illumination and thus, compositions such as SR576A in the anti-submarine aircraft flare and SR580 in the star for the 1.5 inch illuminating cartridge are utilised. Illuminating cartridges without parachutes need to produce high intensities and are relatively small since they only burn for a short time. The output from the compositions list above is given in Table A-4 of Appendix A.

14.4.3 Coloured Light

Coloured flares are known as signals and as such must be capable of being distinguished from considerable distances and against adverse backgrounds such as a bright sky. The requirements for such compositions are:

- a. A good luminosity
- b. A distinctive colour
- c. Colour which is highly saturated

Colour is produced by the emission from molecular species over wavebands appropriate to that colour. However, to attain the temperatures required to produce these species and to give a suitable luminosity for viewing at a distance the composition will also produce a continuum of white light achieved by using magnesium as fuel. This causes unsaturation of the colour and in some cases may give poor colour recognition. The luminous output of coloured flares is significantly lower than that from illuminating compositions.

14.4.3.1 Red light

The red part of the spectrum covers the range 640 nm – 750 nm and species which emit in this range include SrCl^+ (620 nm – 680 nm) and SrO^+ (600 nm - 690 nm). Red flames, therefore, require a source of strontium and chlorine in the composition. This has been achieved successfully using compositions consisting of magnesium fuel, strontium nitrate as oxidant and source of strontium with a chlorinated organic material, such as PVC or chlorinated rubber as the source of chlorine. These give good colour and have a relatively slow rate of burning. For example, commercial composition CC325 used in Signal Kit Pyrotechnic 16mm.

A further example is composition SR170A which consists of a mixture of magnesium fuel, potassium perchlorate as oxidant and source of chlorine and strontium oxalate as the source of strontium. This composition was used in the, now obsolete, 1.5 inch Signal Cartridge.

14.4.3.2 Green light

It is somewhat more difficult to produce a highly saturated green emission than it is red. The green part of the spectrum covers the range 495 nm – 558 nm and emission in this region is achieved from BaCl^+ having a spectral band from 505 nm – 535 nm. However, BaO^+ gives a broad band emission 400 nm - 800 nm which complements the high temperature continuum of white light, adding to the dilution of the green waveband emission.

The longest established compositions which produce green flames contain magnesium as a fuel with potassium perchlorate and barium chlorate as oxidants. Barium chlorate provides the barium and potassium perchlorate the chlorine as in SR429. The presence of barium chlorate, however, makes these compositions rather unstable in the presence of moisture. A second type of composition which is much more stable in storage is based on magnesium and potassium perchlorate. In this case the barium is introduced as barium nitrate

and additional chlorine as a chlorinated organic material such as PVC. The luminous output of this second group is generally much less than those containing barium chlorate, for example SR700 used in the, now obsolete, 1.5 inch Signal Cartridge. However, the increased stability is an important factor in military stores. For green signal flares such as those used in the Signal Kit Pyrotechnic 16 mm it is more common to use commercial composition CC326 which consists of magnesium fuel, barium nitrate as oxidant and source of barium with a chlorinated organic material, such as PVC or chlorinated rubber as the source of chlorine.

14.4.3.3 Yellow and white light

The production of yellow flames requires emission in the range 580 nm - 640 nm and this is provided by the presence of NaH^+ giving a broad band emission over the range 550 nm - 700 nm. Yellow signals rely on sodium to produce the colour and use sodium nitrate as the oxidant. Sometimes they also contain barium nitrate to counter the tendency of a yellow flame to appear orange through atmospheric haze. Coolants such as sodium or calcium oxalate which decomposes endothermically producing carbon dioxide may be added to reduce desaturation of the colour whilst maintaining a sufficiently high burning rate. The emission spectra for yellow light compositions are generally similar to those of an illuminating composition. Flare Ground Indicating No.1 Yellow used during conditions of poor visibility to indicate the position of an airfield runway in use contains composition SR562H.

White light signal flares such as those used in the Signal Kit Pyrotechnic 16 mm consist of commercial pyrotechnic compositions such as CC327. These compositions contain magnesium fuel, barium nitrate and strontium nitrate as oxidant and source of barium and strontium with a chlorinated organic material, such as PVC or chlorinated rubber as the source of chlorine

14.4.3.4 Blue light

Blue signal flares are rarely used since the emission in the blue region of the spectrum 440 nm – 496 nm from pyrotechnics is weak. Furthermore, the human eye does not register blue wavelengths as readily as other colours such as red and green. The presence of a strong white continuum will “wash out” blue emissions, therefore any blue flare must be of low intensity. Blue wavebands are produced by CuCl^+ over the region 420 nm – 460 nm. The compositions usually have lactose as fuel with potassium perchlorate as oxidant, producing much less energetic mixtures than the magnesium fuelled systems. A copper salt and source of chlorine is then added. The luminous intensity is an order of magnitude less than for red, green or yellow flares as shown for SR405 in

Table 14-8. Blue signal flares cannot be used in daylight which restricts their use.

Table 14-8 Coloured Signal Compositions – Luminous Intensity

Designation	Luminous Intensity (cd in⁻²)
SR170A Red	92500
SR700 Green	16500
SR560 Yellow	152500
SR405 Blue	200

Typical compositions used across the spectral range are given in Appendix A, Table A-5.

14.4.4 Tracer Compositions, Tracking Flares and Target Flares

Tracer ammunition (tracers) are bullets or artillery projectiles that contain a small pyrotechnic composition contained in the base of bullets or shells. When the weapon is fired, a priming composition is ignited by hot propellant gases which in turn ignite the tracer composition. The pyrotechnic composition burns very brightly (cf. bright and subdued tracers), making the trajectory of the projectile visible to the naked eye during daylight, and very bright during night time firing. This enables the firer to make aiming corrections without observing the impact of the rounds fired and without using the sights of the weapon.

Tracer compositions must function under very demanding conditions and provide sufficient luminous output to be observed throughout the flight of the projectile. A small arms round, for example, will be spun at about 400,000 rpm and be subjected to an acceleration of 200,000 g. To provide the necessary burn time, the filling must burn 'cigarette fashion inside the container and must not crack or allow the flame front to travel down the side of the filling. This would significantly reduce the functioning time.

In flight there will be a low pressure area behind the projectile where the composition is burning. Tracer compositions must be as gasless as possible to minimise pressure effects on the rate of burning. It is usual to use a priming layer pressed onto the tracer composition which is ignited from the heat of the burning propellant. This composition must maintain combustion on the large pressure drop as the projectile leaves the barrel of the gun.

There are three types of tracer; Bright, Subdued and IR/Dim. Bright Tracers sometimes known as “Red Tracers” start burning immediately after exiting the muzzle. This has the disadvantage that the firer's location can be given away. An example of a red tracer is composition SR390A (magnesium, linseed oil, strontium nitrate, strontium peroxide, talc). A priming composition SR370

(magnesium fuel and barium peroxide oxidant) is used with this tracer composition.

Subdued Tracers sometimes known as “Dark Tracers” burn at full brightness after a few hundred yards and avoid giving away the fire’s position or dazzling the firer during night firings. For tracers of this type there is a requirement for 'dark ignition', a priming layer which emits little light. This has been achieved by using SFG12 gunpowder which ignites an intermediate dark ignition priming layer which in turn ignites the tracer composition. Direct dark ignition priming is obtained by composition SR867.

Both bright and subdued tracer ammunition can create excessive illumination or visual interference known as the blooming effect when viewed through night-vision devices (NVDs). To counter this effect, IR/Dim tracers have been developed which emit in the near infrared region of the spectrum, which prevents the tracer from being detected by the naked eye. To meet this requirement, tracer compositions have been developed which emit in the near infrared region of the spectrum. Tracers of this type are invisible to the naked eye, but visible through NVDs and do not cause the blooming effect. Dark Ignition priming composition is used with IR/Dim tracers. Examples of typical priming compositions used with tracers are given in Appendix A, Table A-6.

Red provides good contrast against blue sky and green fields, and bright red compositions are readily made. Most visible NATO tracer compositions are red however, most visible Russian and Chinese tracer compositions are green, the reason for this is unclear but one possible explanation is that green tracer is more effective in an urban environment. Tracers are required for projectiles of all calibres, SAA (i.e. 5.56 mm) to anti-tank rounds (i.e. 120 mm). Different compositions are required for small arms and artillery ammunition.

Tracking flares for missiles have constraints similar to tracers; that is, high velocities which reduce luminosity, and low pressure behind the flare. Compositions used both for tracking flares and target flares are often based on magnesium and sodium nitrate, such as SR568A a typical white illumination mixture. The performance may be enhanced by additional components such as barium and strontium salts (both required for white light) and a source of chlorine such as chlorinated rubber. For high altitude uses the composition should be as gasless as possible. This is achieved by the use of barium peroxide as oxidant with the minimum binder. An example of this is SR399 where the rate of burning at an altitude of 60,000 ft is 5.4 s in^{-1} compared with 4.6 s in^{-1} at sea level. While for SR568A there is a change in burning rate from 6.0 s in^{-1} burning at sea level, to 12.1 s in^{-1} at 35,000 ft.

For missile tracking flares, the smoke produced by the flare may cause unacceptable levels of obscuration. This can be remedied by the use of titanium as fuel instead of magnesium. One such composition is SR699 using strontium nitrate as oxidant. Compositions that have been used for tracers, tracking flares and target flares are given in Appendix A, Table A-7.

14.4.5 Infrared Decoys

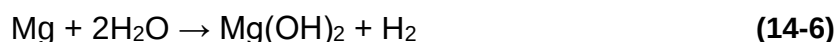
One of the most important developments in the pyrotechnics field is that of infrared decoys. As the name suggests the decoys act to protect targets which emit in the infrared region of the electromagnetic spectrum. The main use is to protect aircraft, from heat-seeking missiles. To be effective the decoy thermal output must be greater than that from the exhaust of the jet engine. Three types of pyrotechnic devices have been evaluated for Service use - pyrotechnic flares, spectral flares and pyrophoric flares.

14.4.6 Pyrotechnic Flares (MTV)

The pyrotechnic flares are based on magnesium, PTFE and Viton formulations commonly referred to as MTV compositions. These flares in essentially the same form have provided standard self-protection for all military aircraft since the 1970s. The combustion products, mainly incandescent carbon, emit grey body radiation in both the infrared and visual region of the electromagnetic spectrum. Flares of this type work by generating a heat signature in excess of the platform signature. The effect is to seduce any heat seeking missile's homing system into locking on to the flares' instead of the heat signature of the target platform. The required output is in excess of 8 kJ g^{-1} and achieved by formulating a fast burning composition with high calorific value which burns over the whole surface of the candle. It must also reach the required decoy energy output in the shortest time possible after deployment. Performance achievable from these flares is for example, time to effective output $< 0.5 \text{ s}$ and burning time 2.5 s to 3.5 s with intensities up to 35 kW sr^{-1} . Compositions of this type of flare are classified.

14.4.6.1 Hydrogen outgassing and mitigation

A major problem with pyrotechnic flares containing MTV compositions and all pyrotechnic compositions containing magnesium is that during storage they can evolve hydrogen. This is generally brought about as a result of reaction between magnesium and water:



This raised serious safety concerns with reported increased pressures and high levels of hydrogen in ammunition container assemblies housing MTV type flares. This resulted in the development of a suitable hydrogen scavenger, referred to as a "Hydrogen Getter" which is now used extensively in ammunition container assemblies housing MTV countermeasure flares.

14.4.7 Spectral Flares

Traditional MTV flare composition spectral distribution does not match that of a typical aerial target, whose spectral output is mainly created by burning kerosene as shown in Figure 14-7 **Error! Reference source not found..**

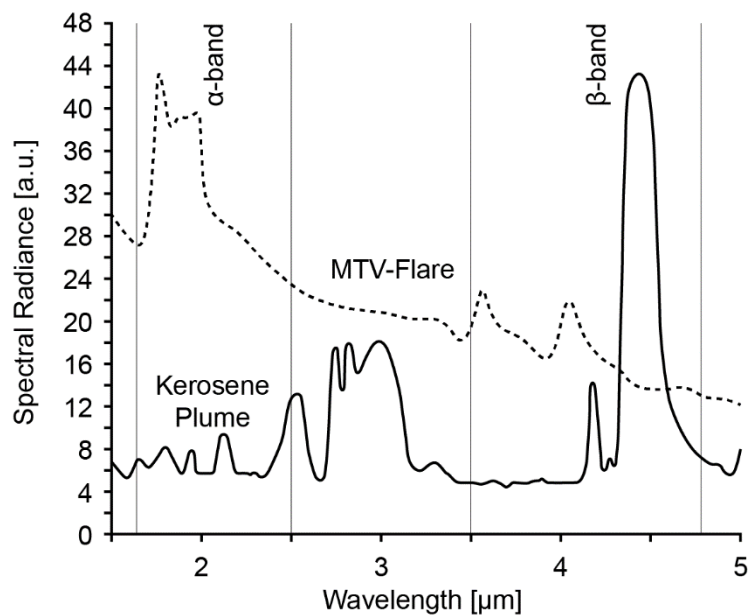


Figure 14-7 Spectral intensity of MTV flare and Kerosene plume⁽⁸⁾

IR missiles search out the hotter flame provided by the MTV flare which burns at around 2000 °C whereas the aircraft jet engine temperature is in the range 600-800 °C. Newer generation missile seekers can spectrally discriminate between the decoy and the aircraft exhaust plume and can compare the energy levels in two different parts of the IR waveband simultaneously. If the flare does not match certain criteria it will be rejected as a non-target.

To mitigate this problem, spectrally matched flares have been developed. The flare provides large amounts of hot H₂O and CO₂ on combustion, similar to burning kerosene aviation fuel and effectively matches the exhaust of jet engines.

Spectral flare compositions are usually based on propellant and/or high explosive rather than pyrotechnic compositions such as MTV. Compositions of this type of flare are classified.

14.4.8 Pyrophoric Flares

Pyrophoric substances ignite spontaneously in air. The main advantage of these is that they produce CO₂ and H₂O vapour as the main constituents of their combustion products and therefore match spectrally the exhaust of jet engines. The materials can be solid, e.g. iron platelets coated with ultrafine aluminium, or liquid, often organometallic compounds such as alkyl aluminium compounds, such as triethylaluminium and ignite on contact with the oxygen enriched airstream providing an alternative IR source for the missile to target. Pyrophoric decoy flares exist in various shapes and sizes to suit the appropriate flare dispenser. Pyrophoric materials have low intensity power output levels, partly due to dilution in the wind stream in which they must function. As a result, they are generally used as a pre-emptive countermeasure prior to lock on.

Some flares work on the principle of ejecting a special pyrophoric material out of an airtight cartridge. The material then self-ignites in contact with air. The main advantage of pyrophoric flares is that they are covert in nature due to the fact that only a faint glow, not a ball of flame, is produced. They are also effectively invisible to the naked eye during the day.

14.5 SMOKE COMPOSITIONS

All smokes are aerosols, suspensions of small particles in air which settle very slowly under gravity. Typical sizes for these particles which may be solids or liquids are between 0.1 μm and 5 μm . The types of smoke covered in this section are:

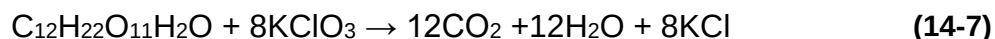
- a. Coloured smoke for signalling
- b. Smoke and flame signals
- c. Irritant smoke for crowd control
- d. Screening smoke

14.5.1 Signal Smokes

Coloured smokes are produced for military use by the vaporisation of an organic dyestuff, heated by a pyrotechnic composition. These smokes are used for signalling, screening and for visual displays. The main colours are red, orange, green, yellow, violet and blue. Smokes are produced by the vaporisation of an organic dyestuff, heated by a pyrotechnic composition. When the vapour leaves the exit hole of the store, it is cooled as it enters the air and condenses back to solid particles of the required particle size distribution to be a smoke aerosol. The organic dyestuff is intimately mixed with the pyrotechnic composition and ideally it should vaporise or sublime below 350 °C and have good thermal stability.

For effective smokes, chemical reactions during smoke formation should cause only minimal thermal decomposition. In order to achieve this the fuel-oxidant system must fulfil some demanding requirements. The temperature produced must be sufficient to give efficient vaporisation of the dye. However, since the dyestuff is an organic compound it can pyrolyse and the composition must, therefore, be cool enough to prevent or minimise this degradation. There should be a minimum of solid residue from the fuel-oxidant reaction because reactions can occur between the dyestuff and char. Any smoke formed other than by dyestuff vaporisation will dilute the colour and should not occur. Particle size of these components plays a very important role in determining smoke quality.

The composition of choice is lactose monohydrate as fuel and potassium chlorate as oxidant. The general reaction that occurs between the ingredients is shown in Equation (14-7).



The stoichiometric mixture, 26 % w/w lactose, 74 % w/w chlorate, burns too hot and would decompose the dyestuff therefore; the mixture normally employed will be near a 50/50 mix (i.e. lactose 25 % w/w, chlorate 25 % w/w, dyestuff 50 % w/w). The excess fuel may lead to char formation which includes elemental carbon. At the temperatures present in the char, water may react with the carbon forming hydrogen gas. This is the 'water-gas' reaction shown in Equation (14-8). The hydrogen thus formed can react with double bonds in the dyestuff necessary to produce their colour.



This additional reaction can alter the colour of the dye, possibly making it colourless. Design of munitions which enhance dyestuff-char contact should be avoided. Examples of UK service signal smokes and smoke compositions are detailed in Appendix A, Table A-8.

14.5.2 Marine Markers

Marine markers are stores designed to produce a visible signal both day and night for prolonged periods of time. They may be dropped by aircraft, usually on a parachute, or released from submarines at depth. Stores include, Marine Marker No.4 Mk N11, Float Smoke and Flame No.1 Mk5 and N2 Mk4, Candle Smoke White N6 MOD5 and Candle Smoke Yellow N7 MOD4.

On functioning these stores provide smoke and flame, usually from burning red phosphorus or occasionally a phosphorus compound such as phosphine (PH_3). The smoke produced is based on phosphorus oxide hydrolysis products as described in Section 14.5.5. The luminous output comes from a yellow lambent flame. Being a marker the burn time is more important than smoke density; however, the density must be sufficient for visual recognition at some distance.

To obtain the necessary burn times, pyrotechnic reactions are used to vaporise excess phosphorus in the composition which burns in the air as it exits the store. For example, SR414 uses calcium silicide and magnesium as fuel with manganese dioxide as oxidant. The heat these produce on reaction vaporises the red phosphorus. This is quite a vigorous reaction which maintains pressure inside the store to counteract ingress of seawater which might extinguish the burning phosphorus flame.

A newer composition used in the Marine A/C Marker, No. 4, is SR622, and variations, based on calcium sulphate and red phosphorus. These react to produce heat to vaporise excess phosphorus plus phosphorus sulphide. This composition, which includes oxalic acid, has a very slow burning rate (240 s in^{-1}). This gives one hour of functioning from a 4.5 kg charge. The oxalic acid is present to maintain pressure inside the store by thermally decomposing to give gaseous products.

One other type of composition, not strictly a pyrotechnic, has been used. This utilises the reaction between water and calcium phosphide which releases phosphine (PH_3) and a diphosphine impurity (P_2H_4) the latter being spontaneously flammable in air. Both hydrides burn to produce a 'phosphorus' smoke. Examples of UK service Marine marker smokes and smoke compositions are detailed in Appendix A, Table A-9. A typical marine marker, Float Smoke and Flame N.2 Mk4 is shown in Figure 14-8.



Figure 14-8 Float Smoke and Flame N2 Mk4

14.5.3 Irritant Smoke

Irritant smoke used for riot control purposes can be generated pyrotechnically in a manner identical to coloured smokes. Lactose monohydrate is used as fuel with potassium chlorate as oxidant and these are intimately mixed with the chemical agent CS (o-chlorobenzalmalononitrile). A typical composition is PN700 consisting of:

- CS (25 % w/w)
- Potassium chlorate (30 % w/w)
- Lactose monohydrate (30 % w/w)
- Kaolin (15 % w/w)

PN stands for 'Porton Number', which was a numbering system for pyrotechnic compositions developed at the then Chemical Defence Establishment, Porton Down, Wiltshire.

14.5.4 Screening Smoke

The purpose of screening smoke is to obscure a target from an observer. This is achieved by reducing the contrast, that is the difference between irradiance falling on the detector from target and background, to a level below the threshold of the detector. This is shown in Equation (14-9) where R is irradiance falling on the detector and τ the transmission having a value between 1 (no smoke or atmospheric interference) and 0.

$$\text{Contrast} = \tau [R(\text{target}) - R(\text{background})] \quad (14-9)$$

Transmission can be reduced by two processes, absorption or scattering of electromagnetic radiation. All smokes cause scattering, but absorption may or may not occur. Both depend upon type of aerosol produced and the wavelength or region under consideration. The effects of scatter plus absorption are called

attenuation or extinction equal to $(1 - \tau)$. The attenuation is a function of aerosol concentration, path length through the aerosol and smoke particle properties.

The screening effectiveness of a smoke cloud can be expressed by its mass extinction coefficient, α , which can be calculated from the Beer-Lambert law, Equation (14-10).

$$\alpha_{\lambda} = [-(\ln \tau)_{\lambda}] / CL \text{ m}^2 \text{ g}^{-1} \quad (14-10)$$

Where: τ_{λ} = transmission through a smoke cloud at wavelength λ ; α_{λ} = mass extinction coefficient at wavelength λ ; C = smoke mass concentration; L = optical path length through smoke cloud.

As can be seen, the mass extinction values relate to a specific wavelength (λ), however, average values across spectral bands such as the visible region may be used. The mass extinction coefficient is a measure of how strongly a chemical species or substance absorbs or scatters light at a given wavelength per unit mass. Therefore, the higher the mass extinction coefficient, the more effective the material is as an attenuator.

There are five basic methods by which a visual screening smoke may be generated:

- Vaporised materials which recondense unchanged
- Partially combusted organic materials
- Materials which react directly with atmospheric moisture
- Materials which burn in atmospheric oxygen
- Pyrotechnic compositions

Type (a) includes fog oil, a liquid hydrocarbon such as diesel injected into vehicle exhausts. Type (b) is typified by stack smoke as used by large ships. Type (c) includes titanium tetrachloride (TiCl_4) and chlorosulphonic acid (ClSO_3H) which react to form acid gases which are themselves hygroscopic forming liquid droplets. These water types of smoke are not used currently in British Service.

14.5.5 Phosphorus Smokes

Phosphorus (White and Red) can be used to provide visual screening smoke and is a type (d) material. The phosphorus burns in air to produce oxides of phosphorus particularly phosphorus pentoxide (P_4O_{10}) a very strong hydrating agent. This then reacts further with atmospheric moisture, forming a mixture of phosphorus acids including H_3PO_4 as detailed in the reactions shown in Equations (14-11 to 14-14) below.



The acids produced are hygroscopic and absorb further moisture from the atmosphere producing sub- μm sized droplets of an aqueous solution of orthophosphoric acid (H_3PO_4). It is this acid mist which constitutes the white smoke cloud and scatters both visible and near infrared electromagnetic radiation.

Atmospheric moisture is required for the formation of the droplets with the amount of smoke formed being dependent upon the relative humidity of the atmosphere. Because the composition is only a fuel with no oxidant, it is usual for the weight of smoke material produced to be greater than the weight of the filling. Under high humidity conditions it is possible to achieve "Yield Factors" of 4 or higher (i.e. for every gram of phosphorus burnt, four grams of sub-micron sized droplets are produced). Typical Indicative Yield Factors for a range of munition smokes are shown in Table 14-9 and highlight the effect of atmospheric moisture on the yield factor.

Table 14-9 Indicative Yield Factors

Munition	Composition	Indicative Yield Factor
Grenade Coloured Smoke, Training Smoke, Anti-Riot Smoke	Pyrotechnic Heater Composition + Volatile Material	0.5
Tube Launched HCE	ZnO/HCE	1.4 (60 %RH)
WP	White Phosphorus	2.3 (0 %RH) 16 (90 % RH)
Tube Launched RP	Red Phosphorus, NaNO_3 , Mg, Binder	1.5 (0 %RH) 12 (90 %RH)

The mass extinction coefficient is a measure of how strongly a chemical species or substance absorbs or scatters light at a given wavelength per unit mass. Therefore, the higher the mass extinction coefficient, the more effective the material is as an attenuator. Figure 14-9 shows a typical mass extinction coefficient for a phosphorus smoke across a range of wavelengths.

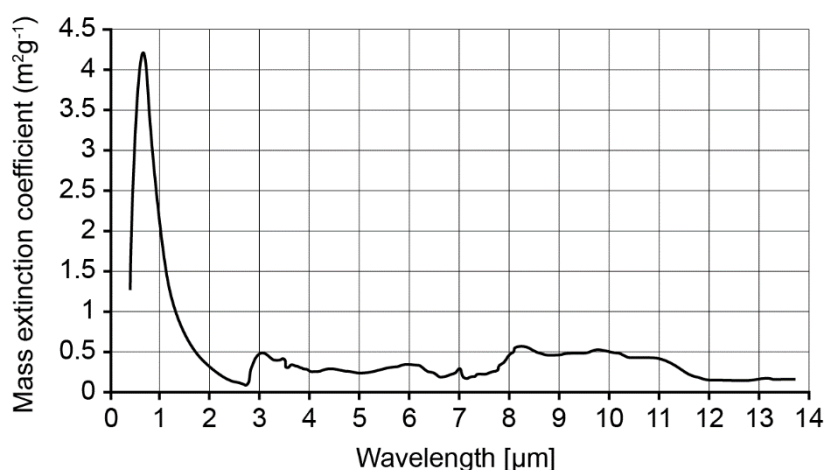


Figure 14-9 Mass extinction coefficient of a phosphorus smoke

The value of α peaks at $\sim 0.6 \mu\text{m}$ and drops off in the far infrared region of the electromagnetic spectrum. Therefore, it is possible for high concentrations of phosphorus smoke to provide effective infrared screening.

There are two types of filling which can be used to give a phosphorus smoke. One is simply white phosphorus (WP) which spontaneously ignites on contact with air and is employed as a filling with a central high explosive burster charge to disperse burning phosphorus which continues to burn once on the ground. This method can be used in stores ranging from hand grenades through to mortars and large artillery shells.

The other phosphorus filling used consists of red phosphorus (RP). An example of a filling is composition PN841 consisting of red phosphorus and butyl rubber binder (95/5 % w/w). This composition is used in the Grenade Discharge Smoke Screening L84A4 used for vehicle screening. Examples of red phosphorus compositions and stores are detailed in Appendix A, Table A-9.

The use of red phosphorus is preferred on safety grounds since white phosphorus is relatively toxic compared to the red form. White phosphorus presently is not employed in UK Screening Grenades. However, it does have applications in UK mortar and artillery munitions. Red phosphorus is a versatile material which is used for many military applications. The chemical reactivity of red phosphorus can be altered depending on its intended application. Slow burning pellets are used to produce long duration smokes, it can be mixed with metal fuels and oxidants to accelerate its burning to produce rapidly formed dense smoke clouds, granular and thin films which burn rapidly to form a highly emissive infrared signature can be used.

The high mass extinction coefficient of a red phosphorus smoke cloud coupled with its high yield factor has resulted in it being used as the screening smoke for the complete range of smoke screening munitions (i.e. grenades, mortars and artillery shells).

Red phosphorus infrared decoys are used for the protection of slow moving military platforms, such as naval vessels, against modern heat seeking missiles.

An infrared emission profile for a red phosphorus/rubber composition is shown in Figure 14-10 and shows significant emission in the 8 – 12 µm waveband which is used by many IR surveillance and target acquisition devices.

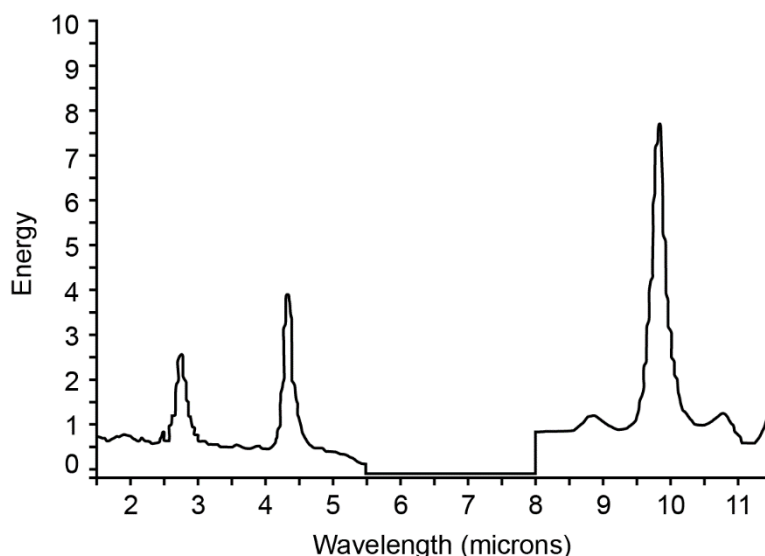
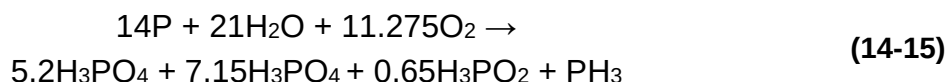


Figure 14-10 IR emission profile for a RP/Rubber composition

14.5.5.1 Phosphine outgassing and mitigation

A major issue associated with munitions containing red phosphorus is that during storage, red phosphorus can react with moisture and air, to form a mixture of corrosive phosphorus acids and the toxic gas phosphine, as detailed in Equation (14-15) below.



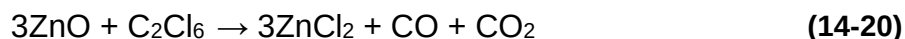
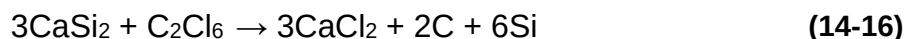
This has raised serious concerns relating to the Health and Safety of personnel handling these munitions and resulted in the development of a suitable phosphine adsorbing material referred to as a “Phosphine Getter”. The phosphine getter consists of an activated carbon cloth impregnated with chemicals which react with phosphine to produce less benign reaction products. The getters are now being used successfully to mitigate phosphine evolution in both ammunition container assemblies housing munitions containing red phosphorus and in the main body of certain munitions.

14.5.6 Pyrotechnic Smokes

Pyrotechnic compositions used to create screening smoke are designed to produce hygroscopic metal salts essentially forming aqueous droplets of these salts. This is achieved by the use of halocarbons as a source of chlorine, acting as oxidant and a metal fuel. Zinc oxide is also present in these compositions and this takes part in some complex chemistry associated with the combustion

of these mixtures. Early compositions used zinc powder and carbon tetrachloride, however, for more stable fillings the fuel became calcium silicide (CaSi_2), and the oxidant, hexachloroethane (C_2Cl_6).

The main composition of this type developed in the UK was PN800, details of which are shown in Appendix A, Table A-10. Some of the reactions shown in the following equations, (14-16 to 14-20), are occurring when this composition is burning together with some minor reactions.



Because this smoke is white, reaction (14-19) is important as this is the only way carbon can be removed. This reaction is significant above 1000 °C.

To increase storage stability, it is necessary to replace calcium silicide since it readily reacts with moisture to form hydrogen gas. The fuel of choice in aluminium powder and work in the United States of America has shown that the chemistry occurring with this mixture is driven by the Thermite reaction between aluminium and zinc oxide as shown in Equation (14-21).



The reactions shown in Equations (14-18) and (14-19) then follow. It has been shown that a constant ratio of zinc oxide to hexachloroethane of 51/49 % w/w can be employed. The burn time for the composition is altered by changing aluminium content.

Some HCE smokes are used in large calibre artillery shells. However, due to the potential health hazards of lung damage associated with inhalation of HCE smokes, these types of composition are presently being phased out of British service. The intention being to replace the HCE smoke compositions with red phosphorus based smoke compositions.

14.5.7 Training Smokes

Training smokes are needed to reproduce the characteristics of tactical smokes without their toxicity problems. The UK standard training smoke (L83A1 and L83A2) used in training screening smoke grenades are based on cinnamic acid. US formulations are based on terephthalic acid and these compositions are detailed in Appendix A, Table-11.

Kaolin, an inert material is used in UK compositions to moderate the heat of combustion and to act as a buffer to prevent the acid catalysed decomposition

of the potassium chlorate oxidant, present in the smoke composition, which can cause premature ignition of the composition. Sodium bicarbonate can be used as an alternative to kaolin.

Grenade Hand Smoke Screening Training L83A1, Figure 14-11, used as a replacement for white phosphorus, consists of two smoke pellets (lower and upper pellets). The lower pellet consists of a pressed pellet of composition CC265 whilst the upper pellet consists of a pellet of composition CC264. Both pellet compositions are based on cinnamic acid. Composition CC265 in the lower pellet burns at a faster rate than composition CC264 and this provides a rapid build-up of smoke on initiation.

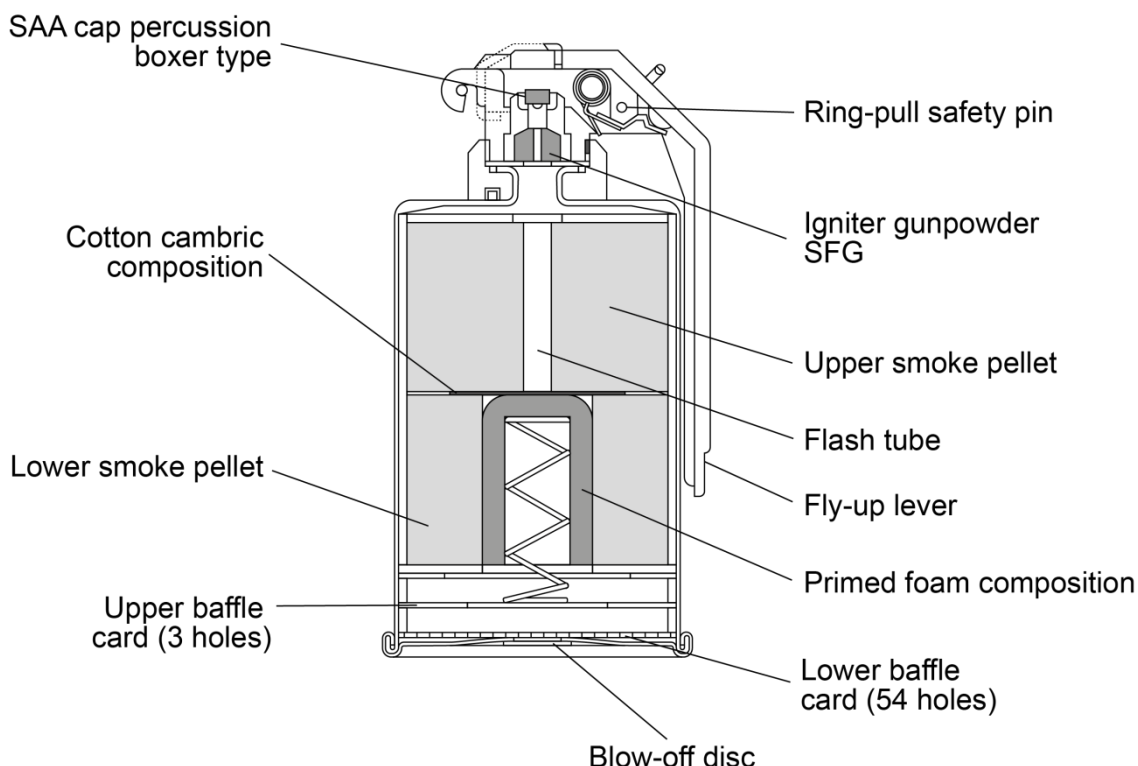


Figure 14-11 Grenade Hand Smoke Screening Training L83A1

The pyrotechnic smoke compositions used in both Generator Smoke 120/W6 Mk2 used by both the UK Royal Navy and the Royal Air Force for fire and ground defence training and Generator Smoke L4A1 used by UK land forces to produce a smoke screen in training are based on a composition consisting of Gum rosin, potassium chlorate and ammonium chloride. Examples of compositions and stores are detailed in Appendix A, Table A-12.

For comparison typical indicative mass extinction coefficients (m^2g^{-1}) of phosphorus smoke, Zn/HCE smoke and training smokes containing cinnamic acid and terephthalic acid are given in

Table 14-10.

Table 14-10 Indicative Mass Extinction Coefficients

Smoke	α (visible)	Mid IR α (3-5 μm)	Far IR α (8-12 μm)
Phosphorus	4.6	0.3	<0.3
Zn/HCE	5.0	-	<0.1
Cinnamic Acid (UK)	4.8	-	<0.1
Terephthalic Acid (USA)	4.8	<0.1	<0.1

14.6 NOISE, FLASH and PYROTECHNIC WHISTLES

14.6.1 Noise and Flash

Noise in this context is produced by a pressure wave which can be achieved by confining a composition, even a slow burning one, in a container which bursts due to increased internal pressure or with a composition sufficiently fast burning to produce the pressure wave with no, or minimum confinement. The sound representation produced depends upon choice of composition, type of confinement and method of initiation.

Compositions producing various types of noise or sound outputs are used in battlefield simulator stores for training purposes such as ground burst simulator, booby traps, rifle fire simulators, etc.. Invariably the bang is accompanied by a flash and this can be advantageous particularly in stun grenades. The usual fuels used in noise and flash compositions are magnesium and aluminium which have high heats of reaction. Although aluminium is well protected by its oxide coat to the extent that it is relatively ineffective in a flare composition, it reacts violently when subjected to the temperatures of a flash and bang composition.

Burning pyrotechnic compositions including gunpowder are used in confinement. Gunpowder is used for a simple explosion simulator and also to represent small-arms strikes. Composition SR371C is the filling for the Gunfire Flash and Sound AFV Simulator.

The high energy noise and flash compositions, which burn very rapidly, are probably the most sensitive and most dangerous of the pyrotechnic mixtures. The Thunderflash device, which contained composition SR801B, caused many injuries in training and through misuse such that it has been removed from the inventory of Service pyrotechnics. Great care must be taken if noise/flash type pyrotechnics are used in confined spaces and underwater where the damage

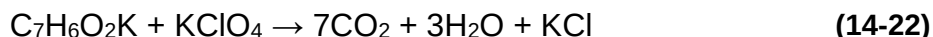
potential is enhanced. Examples of noise and flash compositions are given in Appendix A, Table A-12.

Heavy gun-fire and mortar fire can be simulated by the use of ammonium nitrate based materials, some containing TNT and all initiated by detonator. Examples of simulator compositions initiated by a detonator are given in Appendix A, Table A-13.

14.6.2 Pyrotechnic Whistles

Certain pyrotechnic compositions, when pressed into candles, contained within a case, which on ignition burn cigarette fashion can produce an ear splitting whistle. These have been used as disorienting devices for example, riot control and for military training providing simulated effects of incoming artillery or bombs.

Compositions usually consist of aromatic hydrocarbons such as potassium benzoate, sodium salicylate, potassium 2,4-dinitrophenate or gallic acid as the fuel and a strong oxidant such as potassium perchlorate. The maximum frequency (critical frequency) obtained is dependent upon the composition. A mixture of potassium benzoate/potassium perchlorate (30/70 % w/w) has a critical frequency of around 500Hz. The potassium benzoate/potassium perchlorate whistle reaction is shown in Equation (14-22).



The whistling sound is produced when composition burns in a tube and is produced by a combination of oscillating burning of the composition plus sound reflecting up and down the length of the tube with the characteristic frequency varying with ingredients used, ratio and geometry. Burn rates are faster for mixtures emitting at high frequency with superior whistles obtained with finely ground ingredients. Whistle compositions are extremely sensitive and candles are prone to explode when burning.

14.7 OXYGEN GAS PRODUCTION

Gases are produced by all pyrotechnic compositions with the carbon dioxide produced from the combustion of organic fuels the most copious produced. However, its manufacture by this method is of little interest. The most important gas production by pyrotechnics is that of oxygen which can provide a safe supply for critical life support and revitalisation in submarines.

Most oxygen producing reactions rely on the thermal decomposition of chlorates or perchlorates as shown in Equation (14-23).



The decomposition requires a significant amount of energy input to drive the chlorate decomposition with the source of the energy being the oxidation of iron powder which is formulated with the sodium chlorate. A typical oxygen producing composition consists of a mixture of sodium chlorate, powdered iron and barium peroxide. When the mixture is ignited the iron burns at around 600°C which supplies the heat required for the reaction. The sodium chlorate breaks down into sodium chloride and oxygen equation (14-23) with some of the oxygen combining with iron to form iron oxide. During the decomposition of chlorates and perchlorates chlorine gas often several hundreds of ppm is produced. Chlorine is highly toxic and even ppm levels must be removed to ensure that the oxygen is breathable. To remove any chlorine, barium peroxide is added as shown in Equation (14-24).



Sodium chlorate is often chosen as it has a very high oxygen storage capacity (i.e. 784 dm³ oxygen/dm³ which is similar to the volume/volume capacity for liquid oxygen (798 dm³ oxygen dm⁻³). A typical oxygen generator, based on sodium chlorate can be formulated to produce 3300 dm³ of oxygen over a period of 40 to 60 minutes. A typical Self Contained Oxygen Generator (SCOG) is shown in Figure 14-12.

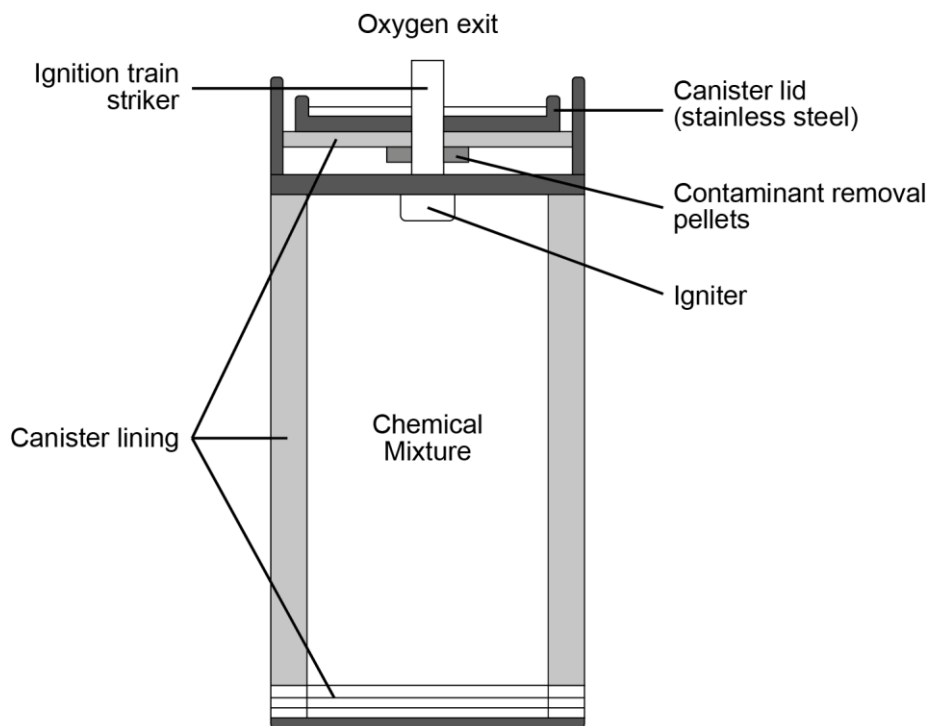


Figure 14-12 Typical self-contained oxygen generator

14.8 THERMAL BATTERIES

Many missile systems contain thermal batteries as energy sources. A typical battery consists of a stack of electrical cells each consisting of an anode and a cathode in the form of discs separated by a solid electrolyte and pyrotechnic heater composition (pellet).

When operated, an electrical current is applied to the battery to ignite a suitable igniter such as a fusehead or squib and an ignition strip which causes the pyrotechnic heater material to ignite and begin to heat. Heat produced from the pyrotechnic heater material causes the solid electrolyte to melt and become conductive. When the electrolyte melts current can flow and the battery discharges. Whilst the electrolyte remains in a solid state it is an electrical non-conductor hence, no current flows. In this state, the battery may remain without deterioration for decades.

The essential arrangement consists of an anode and cathode pair (typically lithium alloy and iron sulphide respectively), separated by the electrolyte (typically a eutectic of potassium chloride and lithium chloride). Ignition of the heater pellets can be achieved by the use of strips of heat paper (woven silica impregnated with fast burning zirconium and barium chromate) running the length of the battery. The pyrotechnic 'Heat Pellet' composition used, almost universally, is a fuel rich mixture of iron powder and potassium perchlorate. Because the reaction products are not electrically conducting, the preferred heat mixture contains a large excess of iron powder (i.e. 80 % in the mixture). This also has the benefit of moderating the reaction which is violent near stoichiometry. The burn rate achieved with a suitable mixture is around 100 mm s^{-1} . Heat paper is very readily ignited and burns around 200 mm s^{-1} .

The requirements placed on the pyrotechnic heat composition are somewhat severe. They must not deteriorate over decades; combustion products of the pyrotechnic reaction must form a good electrical conductor because they are part of the electrical circuit; pellets are required to be very thin to reduce battery weight. Their total heat output, rate of heat output and ignition time must be carefully controlled and the combustion should generate little gas to guarantee that the entire battery remains hermetically sealed. Compacted composition should not melt at any stage of the combustion because the cells must maintain their physical shape. The temperature should not be so high that other components in the battery are damaged and the pyrotechnic reaction should initiate and propagate very rapidly to minimise time taken to melt the electrolyte and activate current generation. Typical advantages and disadvantages of thermal batteries are summarised in Table 14-11.

14.9 SOLAS STORES

To meet the requirements of the "International Maritime Organisation (IMO) Convention for the Safety of Life at Sea (SOLAS) chapter III" and the "Maritime

and Coastguard Agency (MCA) Marine Guidance Note 280 (M) - Small Vessels in Commercial Use for Sport or Pleasure, Workboats and Pilot Boats” that require vessels and craft to carry distress pyrotechnics on-board a range of Distress sets are available. These sets are made up from a variety of stores to meet the relevant SOLAS/MCA regulation.

Warships are exempt from the SOLAS legislation, however to meet the Secretary of State requirements to produce outcomes that are at least as good as those required by UK legalisation they will carry the required SOLAS stores.

All SOLAS stores are commercial of the shelf items and are not required to undertake Safety and Suitability for Service Use testing. The stores are accepted in to service having passed the SOLAS testing requirements. Typical stores are detailed Appendix A, Table A-14.

Table 14-11 Thermal Battery Advantages and Disadvantages

Advantages	Disadvantages
Very long storage life (>20 years)	Short activated life
No maintenance requirements	High surface temperatures (>200 °C)
High reliability	Non-linear output voltage
Instantaneous activation	One-time use
High power output (0.1 – 2 KW)	
Rapid power availability (<1 sec ⁻¹ hour or more)	
Able to withstand severe mechanical stresses of acceleration, shock, vibration and spin	
Wide operating temperature range (-54 °C - +74 °C)	
Safe operation	

14.10 REFERENCES

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Appendix A Pyrotechnic Compositions

Pyrotechnic composition designations

The following pyrotechnic composition designations are referred to in this chapter and in the Tables shown in Appendix A:

Original Compositions:

SR	Superintendent of Research Composition
SRE	Superintendent of Research Elastic Composition
PN	Porton Composition
RD	Research and Development Composition

Commercial Compositions:

NE	Nobel Energetics (Now Chemring Energetics UK)
CC	Chemring Composition
WI	Wallop Industries Composition

Note: Due to the commercial confidentiality of the commercial pyrotechnic compositions referred to in the Tables shown in Appendix A, composition ingredient mix ratios and percentages for formulations are not given.

Table A - 1 Priming and ignition compositions

Designation	Composition Material	% w/w	Use
SFG	Potassium nitrate Charcoal	70.0 30.0	Flash pick-up
SR252	Potassium nitrate Silicon Sulphurless mealed powder	40.0 40.0 20.0	General purpose priming
SR214	Potassium nitrate Lactose	60.0 40.0	Cool priming for coloured smokes etc.
SR370	Magnesium Barium peroxide Charcoal	11.0 87.7 1.3	Shell-tracer priming
SR867	Magnesium Acaroid resin Strontium peroxide Bitumen Zinc stearate	6.9 0.6 80.0 12.5 1.0	Dark ignition for small arms tracer rounds
SR371C	Magnesium (grade 3) Magnesium (grade 5) Acaroid resin Potassium nitrate	32.0 10.0 8.0 50.0	Solid propellant igniter

Table A - 2 Incendiary compositions

Designation	Composition Material	% w/w	Use
SR306	Aluminium (size 25) Aluminium (size 120) Hammerscale Barium nitrate Boric acid	10.0 10.0 40.0 35.0 5.0	Thermite for ignition of bulk aluminium, magnesium or their alloys
SRE794	Boron Potassium nitrate Thiokol S.101 Magnesium oxide Curing agent	20.0 55.0 22.2 0.3 0.5 2.0	Paper incendiary for document destruction
SR365	Magnesium-aluminium alloy (50/50) Barium nitrate	50.0 50.0	Incendiary bullets and cannon-shell
CC466	Thermite Composition (similar to SR306)	---	Initiation of explosive filling in target munitions or initiate combustible materials to assist in the bulk destruction of munitions

Table A - 3 Delay compositions

Designation	Composition Material	% w/w	Rate of burning (s in ⁻¹)	Use
Gunpowder	Potassium nitrate Charcoal Sulphur	75.0 15.0 10.0	2.5	Safety fuze
SR57	Boron Bismuth oxide	10.0 90.0	0.5	Airburst AP mine
SR67	Boron Silicon Potassium dichromate	10.0 20.0 70.0	0.9	Ejector seat delay
SR112	Potassium nitrate Tetranitrocarbazole	60.0 40.0	2.9	Grenade fuze
SR149A	Gunpowder Potassium nitrate Sulphur	55.2 33.3 11.5	---	Marine marker / Surface signal
SR227A	Potassium nitrate Charcoal Sulphur	72.0 21.0 7.0	---	Shell fuze
SR651	Potassium nitrate Barium nitrate Purpurin	52.0 18.0 30.0	7.1	Mortar fuze
RD1368	Boron Barium chromate	4.5 95.5	4.2	L25A5 fuze
RD1370	Titanium Lead chromate	50.0 50.0	0.2	---

Table A - 4 Illuminating compositions (White Light)

	DESIGNATION							
	SR547	SR562	SR563	SR563A	SR576A	SRS80	SR343A	SR502
Magnesium (% w/w) (Grade)	26(0)	49(0)	50(0)	50(4)	60(0)	60(4)	50(0)	35(4)
Lithographic Varnish (% w/w)	4	5	4	4	3	4	-	4
Oxidant	NaNO ₃	NaNO ₃	NaNO ₃	NaNO ₃	NaNO ₃	NaNO ₃	Ba(NO ₃) ₂	NaNO ₃ / Ba(NO ₃) ₂
Oxidant (% w/w)	42	39	46	46	37	36	40	41 & 12
Calcium Oxalate (% w/w)	16	7	-	-	-	-	5	-
Other	PVC	-	-	-	-	-	Wax	Mannitol
Other (% w/w)	12	-	-	-	-	-	5	8
Rate of Burning (s in ⁻¹)	39	17.8	12.0	5.2	6.1	2.3	11.0	15.5
Specific Intensity (cd in ⁻²) (000s)	7.6	63	100	240	184	365	360	385

NOTE: Figure in parentheses after percentage of magnesium represents the grade of magnesium, ranging from coarse (0) to fine (5).

Table A - 5 Coloured signal compositions

Designation	Composition	% w/w	Rate of Burnining (s in-1)	Use
SR170A Red	Magnesium (4) Boiled linseed oil Potassium perchlorate Strontium oxalate	48 4 38 10	7.2	Cartridge Signal 1.5-inch Red (Obsolete)
SR700 Green	Magnesium (4) Boiled linseed oil Barium nitrate Potassium perchlorate PVC	42 6 17 27 8	13.0	Cartridge Signal 1.5-inch Green (Obsolete)
SR560 Yellow	Magnesium (3) Lithographic varnish Sodium nitrate Sodium oxalate	45 4 46 5	7.4	Cartridge Signal 1.5-inch Yellow (Obsolete)
SR405 Blue	Lactose Potassium perchlorate Basic copper carbonate Mercurous chloride	48 22 8 22	33.0	
CC325 Red	Magnesium (0 and 4) Boiled linseed oil Chlorinated rubber Strontium nitrate	---	---	Signal Kit Pyrotechnic 16 mm
CC326 Green	Magnesium (3 and 4) Boiled linseed oil Chlorinated rubber Barium nitrate	---	---	Signal Kit Pyrotechnic 16 mm
CC327 White	Magnesium (3) Boiled linseed oil Barium nitrate Strontium nitrate Chlorinated rubber	---	---	Signal Kit Pyrotechnic 16 mm

NOTE: Figure in parentheses after percentage of magnesium represents the grade of magnesium, ranging from coarse (0) to fine (5).

Table A - 6 Tracer priming compositions

Designation	Type	Composition	% w/w	Use
SR867	Dark Ignition	Magnesium Bitumen Strontium peroxide Acaroid resin Zinc stearate	6.3 11.0 81.0 0.5 1.2	Small arms ammunition (5.56 mm, 7.62 mm)
SR390B	Bright	Magnesium Strontium peroxide Strontium nitrate Boiled linseed oil Talc	28.6 50.4 4.8 11.4 4.8	Small arms ammunition Spotter tracer (9 mm)
SR399	Bright	Magnesium Barium peroxide Acaroid resin	12.0 86.0 2.0	Artillery (40 mm)
SR372ABS	Bright	Magnesium Strontium nitrate Beeswax Chlorinated rubber Shellac Magnesium carbonate Zinc stearate	40.0 45.0 4.8 5.0 5.0 5.0 0.3	Artillery (30 mm)

Table A - 7 Tracer, tracking flare and target flare compositions

Designation	Composition Material	% w/w	Use
SR390A	Magnesium (4) Polymerised linseed oil Strontium nitrate Strontium peroxide Talc	29.3 11.7 51.7 4.9 2.4	Small arms ammunition
Commercial Composition	Strontium peroxide Barium peroxide Calcium resinate Barium nitrate	---	IR/Dim Tracer
Commercial Composition	Boron Potassium perchlorate Sodium salicylate Iron or magnesium carbonate Calcium resinate	---	IR/Dim Tracer
SR568A	Magnesium (3) Lithographic varnish Sodium nitrate	55.0 4.0 41.0	Tracking flare
SR399	Magnesium (4) Acaroid resin Barium peroxide	12.0 2.0 86.0	High altitude tracking flare
SR699	Titanium (powder 8µm) Boiled linseed oil Strontium nitrate Chlorinated rubber	48.0 4.0 45.0 3.0	Low smoke tracking flare

NOTE: Figure in parentheses after percentage of magnesium represents the grade of magnesium, ranging from coarse (0) to fine (5).

Table A - 8 Signal smoke and smoke compositions

Designation	Smoke Colour	Composition Dyestuff	Use
CC204	Green	Dye Solvent Green 3A Dye Solvent Yellow 33	Grenade hand signal smoke L152A1
CC147	Red	Dye Disperse Red 9	Grenade hand signal smoke L154A1
CC146	Blue	Dye Disperse Blue 180	Grenade hand signal smoke L71A1
CC168	Yellow	Dye Solvent Yellow 33 Dye Solvent Orange 86	Grenade hand signal smoke L156A1
CC486	Orange	Dye Solvent Orange 86 Dye Disperse Red 9	Grenade hand signal smoke L153A1 Grenade hand arctic smoke L145A1
CC271	Purple	Dye Disperse Blue 180 Dye Disperse Red 9	Grenade hand signal smoke L158A1 Grenade hand arctic smoke L145A1
CC428	Turquoise	Dye Solvent Green 3A	Grenade hand signal smoke L158A1 Grenade hand arctic smoke L146A1
CC355	Orange	Dye Solvent Orange 86 Dye Solvent Orange 7 Dye Disperse Red 9	Signal distress day and night Mk4/Mk5
PN739	Yellow	Dye Solvent Yellow 33 Dye Disperse Orange 11	Candle smoke yellow Mk N7

Note: All compositions contain potassium chlorate, lactose, kaolin, zinc oxide

Table A - 8 Marine marker and smoke compositions

Designation	Material	% w/w	Use
SR414	Calcium silicide	6	Candle Smoke White (Early Mk5)
	Magnesium powder	6	
	Manganese dioxide	28	
	Oiled red phosphorus	60	
SR622B	Oiled red phosphorus	52.0	Marker Marine No.4 Mk11
	Calcium sulphate	45.1	
	Oxalic acid dihydrate	2.9	
WIC227	Amorphous red phosphorus (encapsulated)	---	Float Smoke and Flame Mk5
	Manganese dioxide		
	Calcium silicide		Candle Smoke White Mk N6
	Magnesium		
	Acaroid resin		

Table A - 9 Phosphorus screening smoke compositions

Designation	Material	% w/w	Use
Commercial Composition (Pellets)	Red phosphorus (encapsulated)	---	Grenade Discharge Visual and IR L131A1
	Potassium nitrate		
	Magnesium		
	Ferric oxide Binder		
Commercial Composition (Leaflets)	Red phosphorus (encapsulated) Potassium nitrate Binder	---	Grenade Hand Smoke L84A3
Commercial Composition	Red phosphorus (encapsulated) Potassium nitrate Binder	---	

Table A - 10 Pyrotechnic visual screening smoke composition

Designation	Material	% w/w	Use
PN800	Hexachloroethane	44	Shell
	Potassium nitrate	2	
	Zinc oxide	47-32	
	Calcium silicide	7-22	

Table A - 11 Training smokes and smoke compositions

Designation	Material	% w/w	Use	Country
CC264 (Slow Burning)	Cinammic acid Potassium chlorate Lactose Kaolin	--	Grenade hand smoke screening training L83A1/L83A2	UK
CC265 (Fast burning)	Cinammic acid Potassium chlorate Lactose Kaolin	---		UK
UK Composition	Cinammic acid Potassium chlorate Lactose Kaolin	33 26 26 15	---	UK
USA Composition	Terephthalic acid Potassium chlorate Sucrose Magnesium carbonate Stearic acid PVA	56 23 14 3 3 1	---	USA

Table A - 12 Noise and flash compositions

Designation	Material	% w/w	Simulation
SR371C	Magnesium (Gd 3) Magnesium (Gd 5) Potassium nitrate Acaroid resin	32 10 50 8	Gunfire
Commercial Composition	Magnesium Potassium nitrate Strontium nitrate Iron oxide Sodium bicarbonate Silicic acid	---	Cartridge flash bang smoke
Commercial Composition	Potassium chlorate Charcoal Acaroid resin	---	Small arms fire
SR801B	Magnesium Potassium perchlorate Graphite	57 37 6	Explosion (bombs, shells etc.) Thunderflash

Table A - 13 Simulator compositions initiated by detonator

Designation	Material	% w/w	Simulation
NE 1243	Ammonium nitrate	91	81 mm mortar
	Charcoal	3.5	
	Aluminium (paint fine)	2.75	
	Cork dust	2.75	
	TNT	-	
NE1244	Ammonium nitrate	80	Heavy mortar
	Charcoal	3	
	Aluminium (paint fine)	2.4	
	Cork dust	2.4	
	TNT	12.2	
NE1245	Ammonium nitrate	73.6	120 mm BAT
	Charcoal	2.8	
	Aluminium (paint fine)	7	
	Cork dust	2.2	
	TNT	14.4	

Table A - 14 SOLAS stores

Item	Variant
Rocket Hand Fired Para Red Distress	Mk8A
Rocket Hand Fired Para White Distress	Mk8
Hand Flare Red Distress	Mk8
Hand Flare White	Mk8
Lifesmoke	Mk9
Marker Man Overboard	Mk9
Line Thrower L1A1	-
Signal Set Submarine	L1A2
Signal Set Diver Supervisor	L5A1