

The Chemistry of Fireworks

Michael S Russell
2nd Edition



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Preface

This book does not claim to be a definitive text on fireworks and the fireworks industry. It is primarily an introduction to the basic science of fireworks with particular emphasis on the underlying chemistry and physics.

The historical material – stemming from several well known sources – is valuable for its technical content. The subject matter then advances to a presentation on the characteristics of gunpowder, whose unique properties cause it to be the mainstay of the fireworks industry, even today.

Succeeding chapters describe the manufacture and functioning of the most popular fireworks, including rockets, shells, fountains, roman candles, bangers, gerbs and wheels in what is hoped is a stimulating and easily assimilated way for those approaching the subject for the first time.

Whilst the book is aimed at students with A-level qualifications, or equivalent, it is also intended to be useful background material and a source of reference for anybody engaged in a study of pyrotechnics as applied to fireworks. Chapters on fireworks safety and legislation complete the book and deserve special mention.

None of this book could have appeared – at least as a commercial project – without the enthusiastic advice and very willing co-operation of Mr John Stone and the late Gordon Curtis of Pains-Wessex Ltd. I am also indebted to Bill Deeker of Pains Fireworks for permission to reproduce the black and white photographs, and to David Cox who gave advice on their selection and indeed took many of the pictures.

Probably the most comprehensive general text on fireworks is the book by the Rev. Ronald Lancaster and co-contributors (*Fireworks – Principles and Practice*, 3rd Edition) and I am grateful to him for discussing my book with me and for giving permission to quote some of his formulae.

I must also acknowledge the many friends and display operators with whom I have enjoyed sharing my passion for fireworks over the years. These include Ray Harrison, Henry Dunlop, Campbell Wilson, Chris Wilson, Ken Norton, Dave Laurence, Andy Goodwin and Debbie, Jonathon Webb, Steve Cornall, Dale Sullivan, Roly Harrison, the late Wally Betts, Kevin Russell, Robert Stevens and my number two daughter, Jane.

My grateful acknowledgements also go to Kay, Carol and Peter who worked wonders on the computer.

Finally, I would like to thank my dear wife, Lyn, who sat through countless evenings of researching, writing and re-writing.

But having a degree in chemistry and a birthday on the 5th November, what else could a person choose to write about?

Michael S. Russell

Preface to Second Edition

This Second Edition of *The Chemistry of Fireworks* has been compiled at the behest of The Royal Society of Chemistry.

As with the First Edition, the aim has been to provide a text that will hopefully prove stimulating to those who are considering a career in science or to anybody engaged in a study of the science of pyrotechnics.

Where possible, each chapter has been enlarged to include further subject matter and up-to-date material. Once again, special emphasis has been placed on the important subjects of Safety and Fireworks Legislation.

I have enjoyed preparing this Second Edition and am especially indebted to Robert Pallant, who was volunteered as Information Scientist, and to David Cox of Pains Fireworks who provided valuable advice and archive material together with some of his splendid photographs. Grateful thanks are also due to Mr. John Deeker who kindly agreed to check and give his seal of approval on the finished work.

Family-wise, I must thank my daughters Jane and Claire who enjoy fireworks (at a distance) and who added a touch of glamour to Chapter 11; and my dear wife Lyn, who again tolerated months of writing and researching, even allowing me to convert a bedroom into an office!

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Glossary

AFTERGLOW The glowing remains produced by the firing of gunpowder-based products such as quickmatch. It is very important that any afterglow is extinguished, especially when reloading shells or mines into mortar tubes.

AMORCE A toy cap that consists of a paper envelope containing explosive composition and which forms part of a roll.

APOGEE The point at which a projectile, such as a rocket, is at its greatest height above the Earth.

BALLISTICS (INTERNAL) The science of internal ballistics is concerned with the propulsion of a projectile such as a shell along the tube of a mortar by gas pressure acting on the base of the shell, or, in the case of rockets, by the backward exhaust of the gas jet.

BALLISTICS (EXTERNAL) External ballistics deals with the science of the motion of bodies such as shells and rockets in the earth's atmosphere and under the effect of the earth's gravitational field.

BANGER A small tube containing gunpowder (or any other powder, *e.g.* flash powder) that is ignited from a simple fuse.

BATTERY A group of Roman candles or a set of similar or connected fireworks.

BINDER A substance such as varnish, shellac or gum arabic that is used to bind together the components of a pressed composition.

BLACK POWDER (synonymous with Gunpowder) An intimately milled mixture of potassium nitrate, sulfur and charcoal that has propellant or explosive properties.

BOMBETTE A combination of candles and/or shells packed in a box and fired by interconnecting fuse or a mini shell found as a component of a Roman candle, mine or shell.

BOUQUET Simultaneously ejected coloured stars from rockets or shells.

BRITISH STANDARD (Fireworks) BS7114: Part 1 Classification of Fireworks, Part 2 Specification for Fireworks, Part 3 Methods of Test for Fireworks (BSI Sales Dept, Linford Wood, Milton Keynes MK14 6SL, UK).

BURNING RATE The regression of a reaction zone of a pressed composition or fuse, usually expressed in millimetres per second. The volume burning rate is expressed in cubic centimetres per second while the mass burning rate, which is the product of the composition density and the volume burning rate, is expressed in grams per second.

BURSTER OR BURST CHARGE Explosive composition which will burn to evolve gas which in turn is intended to burst open the firework case in order to expel one or more pyrotechnic units.

CAP Small amount of impact-sensitive explosive composition contained in a non-metallic envelope.

CATEGORY 1 FIREWORKS Fireworks which are suitable for use inside houses (*e.g.* toy caps, party poppers and cracker snaps).

CATEGORY 2 FIREWORKS Fireworks intended for use in confined areas such as small gardens (*e.g.* small fountains, Roman candles and rockets).

CATEGORY 3 FIREWORKS Larger fireworks designed for use in outdoor use in open spaces with spectators at least 25 metres away.

CATEGORY 4 FIREWORKS Fireworks of such effects that they are not intended for use by the general public.

CATHERINE WHEEL A firework consisting of a spiral of pyrotechnic composition in a paper case that rotates on a pin.

CHINESE FIRE A pyrotechnic composition based on meal powder, iron filings and charcoal which is designed to produce visual effects including sparks.

CLER The Classification and Labelling of Explosives Regulations 1983.
HMSO, HS(R)17, ISBN 0 11 88 37060.

CLOVE HITCH A knot which is used (or should be used) by fireworks operators in order to effectively secure stakes to posts, *etc.* It is affected by looping the cord around the timber so that the loop crosses over at the front. The top section of cord is then looped again around the timber, but this time passed **underneath** the cross to form a double loop. The knot is then pulled taut and secured with a half-granny knot or similar.

COMET A single large star expelled from a firework such as a mine.

COMPOSITION (Explosive) An intimate mixture of fuels, oxidisers and additives of such particle size that, when pressed, it is capable of producing pyrotechnic effects.

CONTINUUM THERMAL RADIATION Radiation which involves the transfer of heat by electromagnetic waves, confined to the relatively narrow “window” of the electromagnetic spectrum (*i.e.* visible light around 400 nm to infrared light around 1000 nm). The hot particles in and above firework flames contribute to this type of radiation.

CRACKER SNAP Two overlapping strips of paper or card with a friction-sensitive explosive composition in contact with an abrasive surface.

CROWN WHEEL A circular firework with a central pivot that rests upon a nail or spike to give the effect of spinning like a wheel and then rising into the sky.

DEBRIS Any part of a firework that remains after the firework has finished functioning.

DEFLAGRATION A pyrotechnic event in which the flame front proceeds at less than the speed of sound in the material; the velocity of deflagration being related to the thermal conductivity of the material.

DELAY TRAIN A combination of igniters and fuses that burn for a predetermined time before igniting the main explosive composition.

DETONATION An event in which the speed of the reaction front exceeds the speed of sound in a material. In this event the velocity of

detonation is related to the transfer of shockwaves through the material.

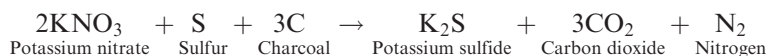
DEVICE An assembly consisting of various types of fireworks, linked together, each producing specific pyrotechnic effects, with a single point of ignition.

DIFFUSION FLAMES The flames seen in pyrotechnics are classified as vapour phase diffusion flames. The principal characteristic is that the fuel and oxidiser are initially separate (as finely powdered components). Combustion takes place when fuel and oxidiser crystals are subjected to high temperatures (from an igniter flame); the finely powdered components decompose, giving off columns of gas which mix by diffusion. The diffusion flame takes place in the zone where the gases mix.

ELECTRIC FUSE (see Wirebridge Fusehead).

ENDOTHERMIC A term used to describe a chemical reaction in which energy in the form of heat is absorbed.

EQUATION (chemical) A representation of a chemical reaction, using the symbols of the elements to represent the actual atoms and molecules taking part in a reaction. For example, a classical, but simplified, overall reaction for the deflagration of gunpowder is as follows:



EXOTHERMIC A term used to describe a chemical reaction in which energy in the form of heat is released.

EXPLOSION A very rapid release of energy and/or matter from an item such as a firework.

EXPLOSIVE Substances which undergo rapid chemical changes, with the **(chemical)** production of gases, on being heated or otherwise initiated.

EXPLOSIVES ACTS Acts of Parliament whose objectives are to control the manufacture, keeping, sale, conveyance, importation and criminal use of explosives (largely superseded by MSER).

FIRECRACKER An early form of banger using gunpowder and paper cases commonly tied into bundles or strips.

FIREWORK An article containing a pyrotechnic composition which, upon functioning, will burn and/or explode to produce visual and/or aural effects which are used for entertainment or signalling.

FIREWORKS REGULATIONS The Fireworks Regulations 2004 (Published by The Stationery Office Limited London).

FIREWORKS SAFETY REGULATIONS The Fireworks (Safety) Regulations 1997. SI No. 2294.

FLASH POWDER A mixture of fuels, oxidisers and other additives that is capable of being initiated to undergo fast deflagration which is usually accompanied by smoke and a bright flash.

FLITTER (colloquial) A spark that gives a transient but twinkling effect.

FOUNTAIN A long, tubular firework from which a jet or spray of sparks issues, sometimes accompanied by stars.

FUEL Any substance capable of reacting with oxygen and oxygen carriers (oxidisers) with the evolution of heat.

FUSE An item with pyrotechnic or explosive components that is intended to be ignited in order to start the firework functioning or to transmit ignition from one part of a firework to another.

FUSEE An article resembling a safety match but which has additional pyrotechnic composition that glows after ignition and is essentially wind-proof and weather-proof. Used for lighting fuses.

GERB A small tubular firework from which a jet or spray issues.

GRAIN The particulate matter of a granulated composition, or a charge of solid rocket propellant, or a unit of mass, where one grain = 0.0648 g.

GUNPOWDER See BLACK POWDER.

HANG FIRE (Of a firework or firearm). To be slow in going off.

HSE Health and Safety Executive. (Explosives Inspectorate. Redgrave Court, 1,2 Merton Road, Bootle, Merseyside, L20 7HS, UK, www.hse.gov.uk).

IGNITION Initiating combustion by raising the temperature of the reactants to the ignition temperature.

INCANDESCENCE The emission of light caused by high temperatures; white or bright red heat.

INITIATOR The first component in a pyrotechnic or explosive train.

LANCE Small, tubular firework designed to emit a coloured flame for about 90 seconds. Used for a visual effect in set-pieces.

LATTICE A framework of crossed laths used for supporting lances or other fireworks.

LOCAE List of Classified and Authorised Explosives, 1994. (HSE Books, PO Box 1999, Sudbury, Suffolk, CO10 6FS, UK).

MALTESE WHEEL A firework wheel which, when lit, shows the pattern of the Maltese Cross and other visual effects.

MAROON A firework that is fired from a mortar, or on the ground, and explodes with a loud report. Usually used to signal the start of a display.

MEAL POWDER A very fine particle-size gunpowder that is used for priming and making quickmatch.

MILL The apparatus for reducing the particle size of pyrotechnic ingredients and/or intimately mixing the said ingredients.

MINE A firework that is fired from a mortar and which contains a single propellant charge and pyrotechnic units or a firework in which the case of the firework serves as the mortar.

MISFIRE The failure of any firework or pyrotechnic unit to function. In the event of a misfire, at least 20 minutes should be allowed before approaching the firework.

MORTAR A tube from which a mine or shell may be fired.

MSER The Manufacture and Storage of Explosives Regulations 2005 (Published by HSE Books Sudbury).

NEC Net Explosive Content. The mass of explosive composition within a firework.

OPERATOR A person who operates fireworks or pyrotechnic displays (usually in conditions of darkness, cold and damp, with little financial reward, but inestimable dedication).

PARTY POPPER Small hand-held firework operated by a pull-string.

PAYLOAD The total mass of pyrotechnic effects carried by a rocket, *etc.*

PEC The Packing of Explosives for Carriage Regulations 1991 (SI 1991/2097) HMSO, ISBN 0 11 015 197 X (now obsolete).

PIC Plastic Igniter Cord. A fuse burning with an intense flame progressively along its length. Used for igniting the match attached to shells, *etc.* Different burning speeds are available from 49 s m^{-1} to 3.3 s m^{-1} .

PIPED MATCH A fuse consisting of quickmatch enclosed in a paper pipe that serves to increase the burning speed.

PORTFIRE A hand-held tubular appliance containing slow-burning explosive composition which will emit a small flame. Commonly used for lighting fuses.

PRIME A layer of readily ignited explosive composition that is applied to the surface of the main composition in order to facilitate ignition.

PROPELLANT An explosive composition that burns with the characteristics necessary for propelling shells and rockets, *etc.*

PYROCLOCK A modular system of vented delays with a range of burn times which form robust fuses. May be used for connecting to piped match or similar for the timed firing of shells *etc.*

PYROTECHNIC Of, like, or relating to fireworks.

PYROTECHNIC COMPOSITION Can be a substance or a mixture of substances used to produce effects (*e.g.* light, sound or smoke) as a result of non-detonative, self-sustaining exothermic chemical reactions.

PYROTECHNIST A person skilled in the art of making or using fireworks.

QUICKMATCH A fuse consisting of gunpowder coated onto cotton yarn using an adhesive such as gum arabic.

RAD HAZ OR RF HAZ Radio Hazard. The hazard associated with the use of electro-explosive devices (EEDs) such as wirebridge fuseheads in the vicinity of radio-frequency transmitting equipment (BS 6657: Prevention of Inadvertent Initiation of Electro-explosive Devices by Radio-frequency Radiation).

ROCKET A self-propelled firework with stick, or other mechanism, *e.g.* fins, for stabilisation of flight.

ROCKET LAUNCHER A tube, frame, box or base from which rockets may be launched.

ROMAN CANDLE A tubular firework usually containing a plurality of alternate pyrotechnic units and propellant charges.

SAFETY FUSE (BICKFORD FUSE) A pyrotechnic fuse in which the composition is enclosed in a flexible casing such that no sparks or flame are seen whilst the fuse burns internally.

This type of fuse was invented and patented in the U.K. in 1836 by William Bickford and subsequently became known as 'Bickford Fuse'.

SAXON A tubular firework containing a pair of opposing nozzles that is designed to rotate by virtue of a central pivot.

SERIES CIRCUIT A method of firing fireworks electrically by connecting wirebridge fusehead igniters in series, *i.e.* one after the other, so that the current flows through each in turn.

SNAKE A small tube filled with explosive composition or an integral container of explosive composition that is fired en mass from mines or shells to fly in a random manner before bursting.

SET-PIECE An assembly consisting of lances, gerbs, and other fireworks linked together to form images and other pyrotechnic effects with a single point of ignition.

SHELL A firework designed to be projected from a mortar tube and containing propellant charge, delay fuse, burster and pyrotechnic units.

SOUND WAVE A disturbance in air, from any sound source (including a functioning firework) which travels through the air *via* the vibration of layers of air particles. The disturbance is more appropriately described as a wave, and the layers of air are moving when a wave passes along it. The intensity of the sound is quantified by measuring overpressures in the vicinity of the blast (or bang).

SPARKLER Wire coated along one end with explosive composition, and designed either to be non-hand held (*i.e.* free-standing or fixed to a support) or to be held in the hand.

SQUIB A small tubular firework, containing gunpowder, that makes a hissing sound and then explodes.

STAR A compressed pellet of explosive composition designed to be projected as a pyrotechnic unit, with visual effects. Used in mines, shells, rockets and Roman candles.

STOICHIOMETRIC MIXTURE A balanced mixture which, on reaction, will yield a stoichiometric compound. For example, two molecules of hydrogen and one molecule of oxygen constitute a stoichiometric mixture because they yield exactly two molecules of water on combustion. Such a balance is important when formulating pyrotechnic compositions.

SULFURLESS GUNPOWDER A grade of gunpowder in which the sulfur is omitted and the proportion of charcoal is increased to maintain the correct fuel balance against the potassium nitrate. Mainly used in fireworks where there may be compatibility issues due to sulfur (*e.g.* in the proximity of chlorates).

THERMODYNAMICS This branch of science is the study of the quantitative relationships between heat and other forms of energy. The application of certain laws of Thermodynamics enables an

explanation or prediction to be made on many physico-chemical systems including those operating in pyrotechnic reactions.

THROWDOWN An article containing an impact-sensitive explosive composition.

TOURBILLIONS Fireworks designed to revolve on the ground and then ascend. They consist of tubes with opposing nozzles and small wings. They used to be known as ‘aeroplanes’ in the UK during the 1950s.

WATERFALL A firework assembly consisting of a row of fountains suspended in the inverted position or fired horizontally on a rope such that simultaneous ignition of the fountains produces a cascade of silver (or coloured) sparks.

WHEEL Any firework that is designed to rotate about a fixed point.

WHISTLER A firework designed to whistle by virtue of an explosive composition containing potassium benzoate or similar.

WIREBRIDGE FUSEHEAD An electric igniter containing a bridgewire surrounded by a small bead of explosive composition designed to emit a short burst of gas and flame.

CHAPTER 1

Historical Introduction

EARLY INCENDIARY DEVICES

Working with fire probably began about half a million years ago when patriarchal cavemen realised that they felt the cold and began rubbing pieces of wood together until the friction caused an ignition. In fact, it is none too easy to generate fire in this way but we have all seen contrivances driven by coils of leather that spin a pointed stick against a wooden notch until it smokes and eventually bursts into flame.

Now it was originally thought that fire was a kind of substance and that this substance generated flames when it met the air. It is only within the last 200 years or so that fire was correctly interpreted as being a form of energy where the flames are defined as regions of luminous hot gas.

To find evidence of the first application of fire in the creation of ‘special effects’ it is necessary to go back some 1400 years when the naturally-occurring substances petroleum and naphtha were employed by the Greeks as an early form of napalm. In the characteristically unfriendly practices of those times, one Kallinikos from Heliopolis of Syria set forth in armed conflict against the Arabs. He had equipped fast-sailing galleys with cauldrons of what amounted to burning crude oil and proceeded to set the boats of the enemy ablaze, with the men still aboard. The incendiary was called ‘Greek Fire’.

The ploy must have worked because the subsequent narrative tells us that the Byzantines then capitalised on their secret weapon by the wholesale destruction of the Moslem fleet at Cyzicus and continued to win naval battles in this way for several centuries afterwards.

DEVELOPMENT OF BLACK POWDER

By about the eighth century AD, Chinese alchemists, amongst others, were preoccupied with discovering the elixir of life. Concoctions were made containing all manner of substances including oils, honey and beeswax, but among the most significant, so far as future firework makers were concerned, were the ingredients sulfur and saltpetre. Unbeknown to the ancients, their brew of honey, sulfur and saltpetre (potassium nitrate) was special in that, on evaporation over heat, the contents would suddenly erupt into a wall of flame. By chance, the experimenters had produced the exact proportions by which the molten sulfur and what was left of the honey were acting as fuels that were subsequently oxidised by the oxygen from the potassium nitrate in what is now known as an ‘exothermic chemical reaction’, and a fairly vigorous one at that! In purified form, the chemicals sulfur and saltpetre are used to this day in what is without doubt the most important tool of the firework makers, *i.e.* gunpowder.

These dangerous early experiments led to many secret or banned recipes, but enough information was disseminated to enable the details of the discovery to be brought to Europe. However, the place and date of the invention of true gunpowder are still unknown and have been the subject of extensive but inconclusive investigation.

Once the reactive tendencies of potassium nitrate were unleashed it was simply a matter of time before the third vital ingredient, charcoal, was added to complete the famous gunpowder recipe of charcoal, sulfur and potassium nitrate. Needless to say, much time and effort were expended before the alchemists produced a successful product.

As with many notable inventions, the credit for the discovery is usually coloured by patriotism, each country putting forward its own ‘inventor’. What is significant, however, is that by about 1000 AD the Chinese were using a propellant similar to gunpowder in crude forms of rockets (Flying Fire), together with grenades and even toxic smokes. For example, a recipe in the Wu Ching Tsung Yao dated 1044 describes a mixture containing sulfur, saltpetre, arsenic salts, lead salts, oils and waxes to give a toxic incendiary that could be launched from a catapult.

More peaceful uses of these crude articles appeared in the form of ‘fire crackers’ – the first fireworks? One mixture corresponded quite closely to modern gunpowder in that it contained saltpetre, sulfur and willow charcoal. The ‘fire cracker’ was said to consist of a loosely-filled parchment tube tied tightly at both ends and with the introduction of a small hole to accept a match or fuse. All of these incendiary mixtures, presumably containing saltpetre, are mentioned in Chinese work dating

from the eleventh century AD. Thus, in theory at least, the Battle of Hastings could have been one of 'Greek Fire', incendiary rockets and grenades.

Skipping about two centuries, the activities of one experimenter typify the development of early black powder. His work took place between about 1235 and 1290 AD and he is reputed to have been the first scholar in Northern Europe who was skilled in the use of black powder. In essence, his work provided the backbone of all early chemical purification and formulation, without which the development of true gunpowders would not have been possible. His name was Roger Bacon (Figure 1.1).

Born in about 1214, Bacon became a monk but was educated at Oxford before gaining a doctorate in Paris. His subjects included philosophy, divinity, mathematics, physics, chemistry and even cosmology. He carefully purified potassium nitrate (by recrystallisation from water) and went on to experiment with different proportions of the other two ingredients (sulfur and willow charcoal) until he was satisfied that,

By the flash and combustion of fires, and by the horror of sounds, wonders can be wrought, and at any distance that we wish, so that a man can hardly protect himself or endure it.



Figure 1.1 Roger Bacon.

Of course, ‘The Church’ was not wildly enthusiastic with the prospect of one of its disciples practising such fiendish alchemy, and Bacon served ten years’ imprisonment. But he preserved his most famous recipe of *ca.* 1252 AD in the form of an anagram, which on deciphering reads ‘of saltpetre take six parts, five of young hazel (charcoal) and five of sulfur and so you will make thunder and lightning’. In percentage terms, the 6:5:5 formula translates as saltpetre 37.50 parts by weight, charcoal 31.25 and sulfur 31.25 parts.

In fact, Roger Bacon’s formula was not too dissimilar from early Chinese recipes. But being natural products, all three ingredients were of variable purity. For example, the crude Indian or Chinese saltpetre was richer in true saltpetre than the European material, but all required recrystallisation. The preferred process seems to have involved wood ashes, containing potassium carbonate, which precipitated deliquescent calcium salts from the saltpetre solution. The solution was then passed through a filter, boiled to reduce the volume of water and then left until the transparent plates of purified saltpetre were formed.

Sulfur occurs widely in nature as the element and was thus easily obtainable by the ancients. The Chinese had rich natural deposits, and the substance is readily purified by sublimation, a process in which the native sulfur is heated and the evolved vapour collected directly as a pure solid.

Charcoal was made from common deciduous woods such as birch, willow or alder, the last two being preferred.

The wood is simply carbonised at relatively low temperatures in a restricted air supply to form an amorphous, quasi-graphitic carbon of very fine particle size. Although of reasonably high purity, it is the enormous surface area per unit mass of the charcoal which makes it very adsorbent to water vapour, and this property is conferred to the black powder mix, as Roger Bacon would have soon realised.

Guns were invented shortly after Bacon’s death in about 1292 and so he never used the term ‘gunpowder’. However, he had certainly had experience of fireworks for which his early black powder recipe would have been perfectly suitable. In the *Opus Majus* he wrote:

We have an example of this in that toy of children which is made in many parts of the world, namely an instrument as large as the human thumb. From the force of the salt called saltpetre so horrible a sound is produced at the bursting of so small a thing, namely a small piece of parchment that we perceive it exceeds the roar of sharp thunder, and the flash exceeds the greatest brilliancy of the lightning accompanying the thunder.

In experimenting with fireworks, Roger Bacon and other medieval chemists discovered that a loose, open tray of powder was all that was needed to produce a flash, but in order to produce the bang the powder needed to be confined, and this has great significance. And even with his unbalanced 6:5:5 formula, Bacon was able to deduce these fundamental ballistic effects.

This short introduction to gunpowder would not be complete without reference to its final development and one or two subsequent events that were to change the course of history.

In lighting a firework we are going back at least 1000 years. The potassium nitrate in the blue touch-paper or the match burns in much the same way as it did when the Arabs or the Chinese played with their fire crackers. The smell of the sulfur when it forms hydrogen sulfide on combustion would have been much the same, as would the dense white smoke that is so characteristic of gunpowder. But modern fireworks are reliable products. The gunpowder has a consistent burning rate and is less affected by moisture than it would have been in the eleventh century. Obviously it was in the interests of the future markets that the experimenters persevered, and their pioneering work was by no means trivial.

First, true gunpowder is not just a 'loose' mixture of unground potassium nitrate, sulfur and charcoal. Indeed, if the three ingredients are mixed in this way then a greyish powder results that is almost impossible to light. If ignition does occur the burning is fitful and prone to extinguishment. In order to overcome these deficiencies the ingredients must be brought into intimate contact. The charcoal and sulfur are milled together with 2–3% of water in a tumbling barrel, then the potassium nitrate is added and the damp mixture is further milled under rollers before being pressed into a cake using a hydraulic press at a pressure of about 2 tonnes.

As with the modern fireworks industry, pressing is preferred over more forceful techniques, but even so, fires regularly break out in presses. Milling is not without hazard either, especially when the large wheel mills weigh several tonnes and the powder batch is around 150 kg.

After pressing, the gunpowder cake is broken and this corning or granulating is the most dangerous of all manufacturing operations.

It is necessary to crack the cake between crusher rolls to form the grains (see Figure 1.2) which are subsequently graded by sieving. The 'finishing' process involves tumbling and drying the granulated powder in wooden barrels in the presence of graphite to give a polished or glazed appearance. The granulated and glazed gunpowders were found to be more moisture-resistant than the early fine powders and the ignition and burning consistency was also much improved. It is the 'fines' or corning mill dust that is used in fuse powder and by the makers of fireworks.

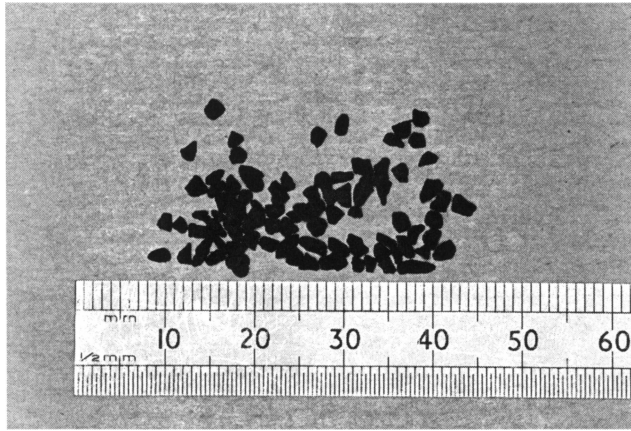


Figure 1.2 Gunpowder.

Of course, in the Middle Ages the emerging gunpowder industry relied on mortars and pestles to do the mixing, and the recipes were changed in what was, in reality, an enrichment of the saltpetre content to give faster burning and ever more powerful powders for yet another historically important invention – the gun.

Thus, in Arabic work dating between perhaps 1300 and 1350 AD, gunpowder is described as a propellant. Cannon were also known in Europe by that time and were used in the defence of castles and villages. In 1338, cannon and powder were provided for the protection of the ports of Harfleur and L'Heure against Edward III. From about 1340 onwards there is frequent mention of the use of guns, and by 1400 the Crown in England possessed a stock of guns and gunpowder.

Rocketry was also developed and early in the nineteenth century an Englishman by the name of William Congreve commenced experiments to produce a large war-rocket for use against the French. The object was to provide the rocket with an incendiary or explosive charge and a range of up to 3500 metres where both the propellant and the explosive charge would have been based on gunpowder.

In 1807 Congreve is said to have personally directed the firing of his rockets at the siege of Copenhagen where they are reported to have been effective and by the middle of the nineteenth century all the leading powers in Europe were manufacturing war-rockets.

Although the generic term 'Congreve rocket' remains current, the form of the weapon varied considerably and its evolution was gradual. Thus the documented improvements included an iron case, a balancing weight and chain as a substitute for the stick and various methods of imparting spin to the rocket as a means of attaining stability in flight.

Table 1.1 Examples of gunpowder compositions.^a

<i>Date</i>	<i>ca. 1252</i>	<i>ca. 1350</i>	<i>ca. 1560</i>	<i>ca. 1635</i>	<i>ca. 1781</i>
<i>Saltpetre</i>	37.50	66.6	50.0	75.0	75.0
<i>Charcoal</i>	31.25	22.2	33.3	12.5	15.0
<i>Sulfur</i>	31.25	11.1	16.6	12.5	10.0

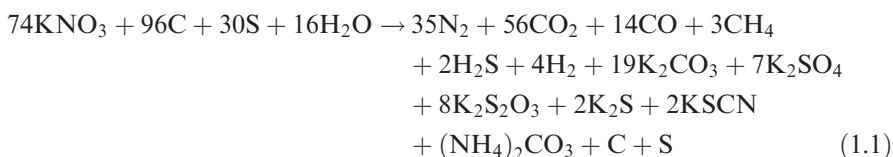
^aCompositions given in parts by weight.

And even as recently as 1979, gunpowder remained the propellant of choice for the production of large (70 mm) line carrying rockets. These devices typically weighed some 5 kg of which about 2 kg was propellant pressed inside a metal case. An 8 mm diameter hemp line could be projected to a distance approaching 300 metres while the line also provided flight stability. A wire bridle connecting the rocket to the line ensured that the latter was not burnt by the hot exhaust gases.

It is interesting to record how the composition of gunpowder changed as history progressed (Table 1.1) and how the 75:15:10 mix of 1781 remains in use to the present day.

In fact, most of the improvements to gunpowders after about 1600 AD concerned the methods of manufacture, there being no question that the proportions of the three components were correctly balanced for chemical reaction, that is to say ‘stoichiometric’.

An approximate equation for the burning of black powder has been given as in reaction (1.1).



The above reaction corresponds to a composition containing saltpetre (75.7%), charcoal (11.7%), sulfur (9.7%) and moisture (2.9%).

APPLICATION OF BLACK POWDER TO FIREWORKS

The fireworks industry also benefited from these improvements, which was reflected in the growing popularity of organised displays and the diversity of the pyrotechnic effects so presented.

Historically, it is generally accepted that the first fireworks were developed in far-eastern countries, notably India or China, for display at

religious festivals, and that knowledge of the art subsequently spread to Europe, probably *via* the Arab kingdom. The Italians are credited with introducing the firework industry in Europe, again promoting their use for public occasions before the manufacture was adopted by neighbouring countries such as France and Germany. By the sixteenth century, fireworks displays were being given in England, and it is documented that Elizabeth I witnessed such an event in August 1572.

Although the early displays in England were enthusiastically received, it must be admitted that most of the pyrotechnic art, and indeed the operators and equipment, originated from Europe – foreign workers were still giving displays in England as late as 1775. It may also be noted, in passing, that in the early seventeenth century the making, purchasing or keeping of fireworks was ruled to be illegal; this was due, in no small measure to the famous (or infamous) attempt to blow up the Houses of Parliament in 1605 by a certain Mr Guy Fawkes using 36 barrels of gunpowder.

The conspiracy is alleged to have begun in 1604 during the second year of the reign of James I, when a group of Catholic fanatics decided that the Establishment must go. Five conspirators, including Guy Fawkes, commenced digging under the main parliamentary building in an attempt to undermine it, and in doing so came across a cellar which was being used by a coal dealer. This they duly filled with ‘powder, faggots and billets’. Timing the event to coincide with the State Opening of Parliament on the 5th of November 1605 meant that the conspirators could also claim the life of the King. However, a warning letter was sent to some members of parliament beforehand, and this was read not only by the Secretary of State but also by James I who, with amazing insight, correctly interpreted it as meaning an explosion on November 5th.

The vaults under the main chamber were visited by the Lord Chamberlain on the 4th November and there they found ‘a tall and desperate looking fellow’ who identified himself as Guido Fawkes. On the 5th of November, magistrates examined the neighbouring house and cellar where they arrested Fawkes who was ‘just leaving’.

Guy Fawkes was tortured and his accomplices arrested, tried and executed. The Establishment was clearly not ecstatic about the fact that the plot had so nearly succeeded, and Fawkes was tried at Westminster on 27 January and ceremoniously executed on 30 January 1606.

All of this was subsequently of great benefit to the British fireworks industry, of course, which has capitalised on the 5th of November celebrations ever since. However, any other country in the world might have bent the truth a little and claimed in the history books that the plot

took place on a nice, warm day in August rather than in cold and damp November – even if only for the sakes of the fireworks operators!

By the nineteenth century, English firework makers including Brock, Pain and Wells had established themselves in the London area to be later followed by Standard Fireworks and others in the North. Thus the availability of locally-produced gunpowder and fireworks was enough to eschew any drift towards European suppliers.

The Brock company originated in the early eighteenth Century in London and was soon firmly established as the producer of innovative fireworks to satisfy the increasing demand for public and private displays.

Run as a family business, John Brock established his premises in North London at a time when ‘Pleasure Gardens’ were growing in popularity and provided ideal venues for the erection of tall frames on which to effect the pyrotechnic displays.

By the nineteenth century London had grown significantly in area, and the Brock company was moved to larger premises reflecting the scale of its products, with set-pieces depicting famous victories or battle scenes typically extending to many hundreds of feet.

Some of the most highly acclaimed displays commenced around 1865 at the Crystal Palace where Mr C. T. Brock set a standard for brilliance and colour which was said to defy competition. This improvement was due, in no small part, to the introduction of metal powders and chlorates into the pyrotechnic mixes, an innovation which is used even today.

The twentieth century saw the continuation of the company’s influence on fireworks, now worldwide, with Roy Brock organising displays during Princess Elizabeth’s twenty-first birthday celebrations in South Africa in April 1947 while Christopher Brock directed a centenary display for the city of Dunedin, New Zealand in 1948. The Brock name enjoyed an association with pyrotechnics until well into the second half of the twentieth century, eventually specialising in defence related products such as simulators and smokes.

The history of Pains Fireworks began in about 1593 when John Pain established his business as a gunpowder manufacturer and armourer near Bow Bridge in East London. It is also documented that twelve years later, in 1605, he had the dubious distinction of being the supplier of the one tonne of powder required by Mr Guy Fawkes for reasons mentioned previously!

Later in the seventeenth Century Peter Pain, a French descendant of the Pain Family, moved to Bow Bridge to join the London arm of the family. During this period customers for Pains gunpowder included Charles II and James II.

It was during the 1700's that Firework Masters from Europe came to England to meet the demand for ever more spectacular displays for members of the Royal Family. Many labourers were employed locally to erect the huge frames and platforms from which to display the fireworks, and amongst the locals were members of the Pain (and Brock) families. In this way William Pain acquired enough knowledge from 'the Masters' to present his own displays in London's Parks and Gardens in the late 1700's.

By the early nineteenth century William Pain had passed his skills on to his son James and to a nephew called Joseph Wells, but in 1837 Joseph left to establish Wells Fireworks, a company that also survived into the twentieth Century.

In 1872 James Pain established a fireworks factory near Mitcham in Surrey before setting off to America in 1878 in the company of his son Henry to form the leading firework company in the USA. On returning to England, James expanded the business to the extent that Pains Fireworks became renowned throughout the world.

James Pain died in 1923 and the running of the Company became the responsibility of his other son, Philip, who died 3 years later (Figures 1.3 and 1.4).

The intervention of two World Wars together with the economic depression of the 1920s and 1930s saw a rise and fall in the fortunes of Pains Fireworks, to the extent that take-overs became inevitable.

In 1963 Pains was amalgamated with the Wessex Aircraft Engineering Company (WAECO) who were based at High Post near Salisbury and who were, in turn, owned by the British Match Company. Within two years Pains Fireworks had relocated from Mitcham to High Post in a move that extended the Factory's product base from fireworks to distress flares, signalling smokes, line carrying rockets and munitions simulators trading under the name of Pains-Wessex.

The picture became even more complicated in 1968 when Wells Fireworks was acquired by Schermuly who operated out of the SPRA (Schermuly Pistol Rocket Apparatus) works at Newdigate near Dorking (Figures 1.5 and 1.6).

In the 1970's Schermuly was, in turn, taken over by British Match and the latter then merged with Wilkinson Sword Limited to form the Wilkinson Match Group.

Thus it was that Pains-Wessex/Schermuly had access to the extensive Wilkinson Sword Research facilities (which resulted in many new and improved military pyrotechnics) while Pains Fireworks gave up shop goods to concentrate on display fireworks, moving back to the old Wells factory in Dartford in 1976 (Figures 1.7 and 1.8).



Figure 1.3 Pains Mitcham girls plus spaniel guard the Pyro aboard a 1920's MG.
(Courtesy of Pains Fireworks Ltd.)

By now Pains was owned by John Deeker who had spent most of his life working for Pains Fireworks and then Pains–Wessex both as a director and an accountant.

In 1982 Pains moved again, this time to the site of an old chalkpit in Whiteparish near Salisbury where the Deeker family continue to own and promote the business and where Wilf Wells, a former Wells director, spent his remaining years.

Although the Explosives Act of 1875 expressly forbids the manufacture of gunpowder or of fireworks outside a licensed factory there have been tales of the Yorkshire miners who, amongst others, produced squibs (small exploding fireworks) by packing gunpowder into rolled paper cases. These were used for blasting but were also said to be effective in clearing the soot from the flues of domestic homes. Under these circumstances it is not difficult to imagine a cottage industry springing up whereby the squibs were turned into crackers or any other simple form of fireworks which were then sold locally.



Figure 1.4 Somewhere in England *ca.* 1930.
(Courtesy of Pains Fireworks Ltd.)



Figure 1.5 The Dartford Factory *ca.* 1975.
(Courtesy of Pains Fireworks Ltd.)

And so on to the twentieth century when the emergence of free trading between nations once again meant that fireworks, and more importantly, gunpowder, were available from around the world. Gunpowder is no longer manufactured in the United Kingdom and supplies are procured from Spain, Germany, South America and the Far East, as are fireworks. Of the original esteemed group of factories, few survive today and even fewer make any fireworks, relying instead on the magazine storage of imported products to effect their displays, just as they did 300 years ago.



Figure 1.6 Wilfred Wells *ca.* 1984.
(Courtesy of Pains Fireworks Ltd.)



Figure 1.7 The Dartford Factory *ca.* 1985.
(Courtesy of Pains Fireworks Ltd.)

Clearly gunpowder has played a prominent role in the construction of early fireworks but, unless it was used in conjunction with other pyrotechnic mixtures, the range of effects was very limited. However, it continued to be the main performer in fireworks until the introduction



Figure 1.8 The Dartford Workforce *ca.* 1976.
(Courtesy of Pains Fireworks Ltd.)

of potassium chlorate some years after the first preparation of this substance by the French chemist Berthollet in 1786.

Even earlier, in the seventeenth Century, John Bate recorded the use of antimony sulfide “to produce a blue flame” in his *Book of Fireworks* in 1635. The same author also used iron scale in some of his compositions to give rockets a more luminous tail.

In 1801 the French pyrotechnist Claude-Fortuné Ruggieri described the use of metal salts in the production of coloured flames. By the early nineteenth century the firework maker had at his disposal a diverse arsenal of materials, many of which are still in use today. The following substances were documented by Audot and others at around that time:

POTASSIUM CHLORATE, KClO_3 : Used to enhance the colour of flames produced by other metal salts *e.g.* strontium nitrate, $\text{Sr}(\text{NO}_3)_2$ (red flame).

ANTIMONY SULFIDE, Sb_2S_3 : Gives a blue flame.

IRON AND STEEL FILINGS: Give white and red sparks.

RED COPPER FILINGS: Give greenish sparks.

ZINC FILINGS: Produce blue sparks.

YELLOW AMBER (Organic resin): Gives a yellow flame.

LAMP BLACK: (Soot) Gives a reddish flame.

COPPER NITRATE, $\text{Cu}(\text{NO}_3)_2$: Gives a blue flame.

BARIUM NITRATE, $\text{Ba}(\text{NO}_3)_2$: Gives a green flame.

And finally it is gratifying to be able to report that, for the 5th of November's Guy Fawkes Night celebrations in London in 2007, free firework displays were held at Clapham Common, Alexandra Palace, Blackheath, Streatham Common and Brockwell Park, with crowds of up to 40,000. Long may it continue!

FURTHER USES OF BLACK POWDER

Of gunpowder itself, although it has a long and colourful history, its use as an explosive dwindled into insignificance after the domination enjoyed by the much more powerful high explosives that succeeded it. But besides fireworks, there are still a few 'niche' applications where the unusual burning properties of gunpowder and kindred substances may be exploited. For example, as a 'low explosive' it is suitable for controlled blasting in which the treatment of the stone must be mild. It is therefore used in the manufacture of roofing slates and in quarrying for paving stones, the powder grains being freely poured into boreholes.

Whilst the 75:15:10 formula corresponds to one of the quickest and most vigorous of the gunpowder compositions, a slower form is required for blasting (as detailed in Table 1.2).

This criterion is satisfied by a reduction in the potassium nitrate content, which also results in a slight reduction in cost.

A significant amount of blasting powder is also made using sodium nitrate in place of the potassium salt. Although hygroscopic, the sodium salt is said to give good performance over a range of climatic conditions provided that a heavy graphite glaze is used to coat the gunpowder grains.

And as well as being used to demolish buildings, gunpowder has assisted in their construction; the Royal Observatory at Greenwich being paid for by the sale of surplus stocks of military powder during the reign of King Charles II.

Table 1.2 Examples of application of black powder.

<i>Application</i>	<i>Composition</i>		
	<i>KNO₃</i>	<i>Charcoal</i>	<i>Sulfur</i>
1 Lift charge or burst charge	75	15	10
2 Priming powder	70	30	0
3 Blasting powder	68	18	14
4 Rocket propellant	62	28	10
5 Delay fire	62	18	20
6 Sparking composition	60	12	28
7 White smoke	50	0	50
8 Fire extinguishing smoke	85	15	0

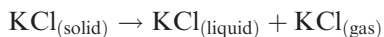
Gunpowder is also employed by the military in making priming charges for smokeless powders. In the largest calibres the gunpowder grains are sewn into quilted silk bags that fit over the ends of the cordite charges to promote ignition. It also finds use in the production of fuses, pyrotechnic stores, 'special effects', bird-scaring cartridges, cartridge actuators and small-arms 'blanks'.

Apart from its unique property of burning quickly at relatively low confinement it is not prone to detonation. Under normal conditions the maximum rate of explosion is about 500 ms^{-1} . In the absence of moisture, gunpowder is also extremely stable. It has been documented that until World War I it was the practice of the French Army to preserve any batches of gunpowder that had proved especially good. These were used in time train fuses and it was claimed that some batches so preserved dated from Napoleonic times.

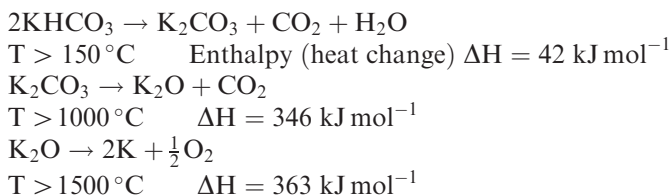
Perhaps the most unusual modern application of potassium nitrate-based powders is in the fire protection industry. The white smoke mainly consists of potassium carbonate and this has been found to have fire extinguishing properties due to the way in which the potassium salt in the smoke interferes with the combustion chemistry of a fire.

The generally accepted mechanisms for the suppression of fires and explosions by alkali metal salts such as potassium chloride, KCl ; potassium bicarbonate, KHCO_3 and potassium carbonate, K_2CO_3 in the form of dry powders or aerosols (smokes) involve heat absorption, endothermic decomposition and radical recombination.

Heat absorption occurs by virtue of the intrinsic thermal mass of the cool material injected into the flame, and by endothermic phase changes, *e.g.*

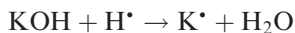


The cooling effect is enhanced by endothermic decomposition reactions, *e.g.*



The heat absorbed due to the decompositions listed above amounts to 5.6 kJ g^{-1} .

Free radicals are atoms or groups of atoms possessing an odd (unpaired) electron. Radical recombination occurs when active flame propagating species (O^\bullet , H^\bullet and $\bullet\text{OH}$) recombine (heterogeneously) on particle surfaces or (homogeneously) as a result of gas phase reactions catalysed by alkali metal atoms in the flame, *e.g.*



Also, the water vapour and carbon dioxide produced in the reactions act as inertants.

Finally, the extinguishing effectiveness of an aerosol is related to the particle size. Smaller particles maximise the surface area for heat absorption, increasing the probability of subsequent decomposition and radical recombination processes.

Large grenades containing up to 2 kg of powder composition have been used by European firefighters where, for example, in burning buildings the smoking grenades are simply hurled through the plate glass windows. Now that really is 'fighting fire with fire'!

Table 1.2 lists the current applications of black powder. In general, as the balance of the ingredients in the composition shifts from the near stoichiometric 75:15:10 mix, the rate of burning decreases but is still fast enough to be of major importance in firework rockets, delay fuses, igniters and pyrotechnic smokes.

CHAPTER 2

The Characteristics of Black Powder

For about 500 years black powder enjoyed dominance as a propellant, explosive and igniter, and as the major firework ingredient its use remains unsurpassed. The prime reason for the longevity of black powder is its ‘quickness’, even at relatively low pressures, and this is brought about by manufacturing techniques (as described earlier) and the chemical reactivity of the constituents.

As with most pyrotechnic reactions, the energetic properties which are demonstrated involve a comprehensive mixture of inorganic, physical and solid-state chemistry and these have been well documented by authors such as Conkling, McLain and Ian von Maltitz.

THE SOLID STATE

It is common practice to restrict the use of the term ‘solid state’ to substances which are of a crystalline nature, a feature which is equally applicable to potassium nitrate, sulfur and charcoal.

Crystalline substances exhibit a defined shape and volume on the atomic or molecular scale where the crystal symmetry is repeated to form a clearly defined geometrical, three-dimensional form, called a crystal lattice.

Potassium nitrate crystals at room temperature form what is known as a rhombic lattice comprising positive and negative ions. This lattice has three axes of unequal length, intersecting at right angles. At 130 °C the KNO_3 crystals are said to undergo a sharp solid–solid (rhombic to trigonal) transition which has the effect of ‘loosening’ the solid structure, making the substance more reactive and easier to ignite.

Held together by electrostatic forces (or ion-ion interactions), as the temperature is raised towards 130 °C, vibrational, translational and rotational motion increases. The oxygen ions in the nitrate cluster are indistinguishable from each other and this is said to make rotation of the nitrate ion easier.

At a temperature of 338 °C, the vibrational and translational motion overcomes the electrostatic forces holding the lattice together and the KNO_3 melts. The relatively low melting points of substances such as potassium nitrate are normally directly related to ease of ignition – a very important feature of gunpowder type products.

Sulfur exists in two crystalline forms, rhombic and monoclinic, the latter comprising three axes of unequal length, two of which intersect at right angles. The bonding within each crystal lattice is covalent and with an electronic structure approaching the configuration of an inert gas atom, the element shows purely nonmetallic chemistry.

Both rhombic and monoclinic sulfur contain eight sulfur atoms per cyclic molecule in a crown (distorted octagon) configuration.

The S_8 rings which originate in the crystalline solid become unstable as the temperature is raised, eventually forming open chains.

Sulfur also exhibits pseudo-plastic behaviour, especially under pressure, with the result that the compaction of gunpowder during manufacture produces considerable plastic flow, forming a conglomerate of interconnecting passageways to the extent that the internal free volume can fall to a few percent. It is this reduced porosity that gives black powder its unique burning properties and makes the material perform almost as a compound rather than as a composite mixture.

The many forms of so-called amorphous (non-crystalline) carbon such as charcoals and lampblack are all actually microcrystalline forms of graphite. The latter has a covalently bonded layer structure comprising a network of joined flat hexagonal C_6 rings where the separation of the layers is reported to be 3.35 Å. This is about equal to the sum of the Van der Waals (intermolecular) radii, indicating that the forces between layers should be relatively slight, as is evidenced by the observed softness and lubricity of the material.

The physical properties of charcoal-type materials are mainly determined by the nature and magnitude of their surface areas. In finely divided forms, vast surfaces are presented with only partially saturated attractive forces, thereby absorbing large amounts of gases and vapours, including appreciable quantities of sulfur dioxide, an important process during the combustion of gunpowder.

While crystal structures can be characterised by the geometric symmetries repeated throughout the lattice, the overall physical properties

of a solid such as KNO_3 are dictated by defects or imperfections within the material. In nature, a crystal may contain many discontinuities in the structure such as cracks and jogs together with structural dislocations running between grain boundaries.

Grinding KNO_3 with a mortar and pestle gives the impression that the crystals are weak and easily broken, as is indeed the case. This weakness is due to crystal defects where the tensile strength of each crystal can be several orders of magnitude less than the theoretical value.

Lattice defects also play a prominent role in the reactivity of pyrotechnic materials, where the displacement or absence of atoms or ions from their normal positions within a lattice can have a pronounced effect on properties, as can the introduction of foreign species or “dopants” within a crystal.

Collectively, the inherent defects outlined above allow mechanisms by which electrons, heat and other substances can penetrate and move through a lattice, thereby enhancing the reactivity of pyrotechnic compositions.

OXIDATION AND REDUCTION

From the viewpoint of inorganic chemistry, the reaction of potassium nitrate with sulfur and charcoal can be described as an oxidation–reduction reaction in which electron transfer between reacting species involves a loss or gain of electrons resulting in an oxidation or reduction process respectively.

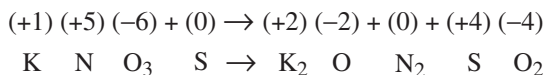
For example, in the reaction:–



consideration can be given to the oxidation numbers of individual species.

Simple ions such as K^+ have an oxidation number of +1, nitrogen has a value of +5 in the nitrate ion, where oxygen is always –2 while elemental sulfur has a value of 0. On the product side, potassium and oxygen retain values of +1 and –2 respectively while nitrogen changes to 0 in the elemental N_2 . Similarly, the oxygen in SO_2 retains a value of –2 while sulfur changes to +4.

Inserting the oxidation numbers in the reaction above gives:



In the above reaction, sulfur is oxidised to SO_2 , losing 4 electrons while nitrogen gains 5 electrons in forming elemental nitrogen.

In balancing the equation,



sulfur loses $5 \times 4 = 20$ electrons while nitrogen gains $4 \times 5 = 20$ electrons, so maintaining the balance.

The following formal rules enable other chemical reactions to be followed in terms of “oxidation numbers”:

1. Hydrogen is normally +1 while oxygen is normally -2, exceptions being peroxides and metal hydrides. This rule should be applied first.
2. Common ions have oxidation numbers according to their charge. Thus Cl^- is -1, Zn^{2+} is +2 and Al^{3+} is +3. As previously mentioned, the oxidation number of an element in its standard state is zero. Rule 2 should be applied after Rule 1.
3. In a polar covalent molecule such as H-Cl , all of the electrons in the bond between the atoms are assigned to the more electronegative atom, thus Cl^- has an oxidation number of -1, leaving the hydrogen atom with an oxidation number of +1. Rule 3 should be applied after Rule 2.
4. In respect of ions, the sum of the oxidation numbers of all the atoms will equal the net charge while in respect of neutral molecules, the sum of the oxidation numbers will be zero. This Rule should be applied last.

Hence, the gunpowder reaction product, potassium carbonate, K_2CO_3 , can be assigned the oxidation numbers $\text{K}_2(+2)$ $\text{C}(+4)$ $\text{O}_3(-6)$ on application of the above rules.

ELECTRONEGATIVITY

Yet another important feature of inorganic oxidisers such as potassium nitrate rests with the nature of the atoms forming the chemical bonds. Many pyrotechnic compositions rely on chlorates, perchlorates or nitrates as high-energy oxidisers whilst high explosives commonly are based on nitrated organic substances. The reason for this lies with the electronegativity of the atoms concerned.

Bonding electrons are not shared equally between unlike atoms, which are bonded together because of the difference in the affinity of different

atoms in a molecule for electrons. The tendency of atoms to pull electrons towards themselves is expressed by a characteristic called the 'electronegativity' as quantified by Pauling.

While fluorine is the most electronegative element (4.0 on Pauling's scale) and therefore the most powerful oxidiser, pyrotechnically important elements also rate highly *e.g.* nitrogen (3.0), chlorine (3.0) and oxygen (3.5) on the scale of electronegativity, which also depends on the position of the element in the Periodic Table.

Hence as we go down the halogen column of the Periodic Table the atoms become less electronegative. This is because of the increasingly effective shielding of the charge on the nucleus by inner electrons. Alkali-metal atoms, on the other hand, have a great tendency to lose their outer electrons and therefore have a low electronegativity, as evinced by sodium (0.9) and potassium (0.8).

It is also possible to predict which bonds will be ionic and which bonds will be covalent. For example two elements of very different electronegativity, like a halogen and an alkali metal, will form an ionic bond because an electron is almost completely transferred to the atom of higher electronegativity; whereas two elements possessing similar electronegativities form covalent bonds.

Carbon occupies an intermediate position in the electronegativity scale (with a value of 2.5) and forms covalent bonds with neighbouring elements in the Periodic Table.

When there is a considerable difference in the electronegativities of two elements, the bond is said to be polar, that is to say there is a high degree of ionic character. This the case with salts such as sodium chloride. However, in the majority of bonds the sharing of the electron pair is not exactly equal and the bond is said to have partial ionic character.

The nitrate ion in potassium nitrate contains the highly electronegative atoms nitrogen and oxygen which are covalently bonded. When such atoms form a bond there is less stability than when bonds involve atoms of differing electronegativities. Intense competition for the electron pair in the N–O bond is thought to be the reason for some of this instability.

In KNO_3 the nitrogen atom also has a large, positive oxidation number (+5 as described previously). This number indicates electron deficiency to the extent that the nitrate is highly reactive as an electron acceptor. The nitrogen atom needs to accept electrons, to relieve bonding stress and the carbon atoms in fuels such as charcoal represent excellent electron donors.

Similar considerations apply to chlorates and perchlorates as oxidisers and to sulfur and organic compounds as fuels. Thus the vigorous and

fiery reactivity of gunpowder is mainly attributable to crystal characteristics and defects, unstable bonds and the transfer of electrons.

PHYSICAL CHEMISTRY

This branch of chemistry is largely mathematical, and can be somewhat daunting but, without it, we would know very little about reaction rates, heats of reaction and indeed, whether a given reaction could be expected to proceed at all. The latter is addressed in the Second Law of Thermodynamics.

The Second Law has been expressed in many ways but perhaps the most useful is in terms of a thermodynamic quantity called the entropy, S .

The thermodynamic arrow of entropy points towards a natural tendency to disorder which tells us that the universe will expand rather than contract, that the bath water will run out of the bath, cooling as it does so, while gunpowder, when ignited, will disappear as smoke and flame. The latter can never reform as the intimate mixture of potassium nitrate, sulfur and charcoal from which it started – there being no “going back” or reversal during such processes.

In other words any spontaneous change, such as combustion, will render a system and its surroundings closer to an ultimate state of equilibrium, from which no further change would be expected to spontaneously occur.

Spontaneity can be expressed mathematically by introducing further thermodynamic quantities, one of which is called the free energy, G . In fact, it is the *change* in free energy that is important in predicting chemical reactions and this change is written as ΔG .

For pyrotechnic reactions, many of which proceed at constant pressure and temperature, the two quantities that define the free energy of a system are the entropy, as discussed above, and the enthalpy, H , which represents the heat content of a system.

The driving force for such reactions is found in the values of entropy, enthalpy and free energy according to the equation:

$$\Delta G = G(\text{products}) - G(\text{reactants}) = \Delta H - T\Delta S :$$

(where T is the absolute temperature).

For a reaction to be spontaneous, the products must be of a lower free energy than the reactants. That is to say, the change in the free energy must have a negative value. In order to satisfy this requirement it can be seen from the above equation that the entropy change, ΔS , should have a positive value, ensuring that the $-T\Delta S$ term is negative.

At room temperature, entropy effects are so small that they have little effect on the direction of a chemical reaction unless the difference in ΔG or ΔH between reactants and products is correspondingly small. But at the high temperature encountered in pyrotechnic reactions such as the combustion of gunpowder, the relative importance of the change in entropy increases until it becomes a dominant factor. Hence, the importance of the temperature term in the free energy equation.

Finally it should be appreciated that pyrotechnic reactions usually follow a sequence of SOLIDS \rightarrow GASES. This is in accordance with a positive value for ΔS being associated with an increase in the disorder of a system. Quantitatively $S_{\text{(solid)}} < S_{\text{(liquid)}} \ll S_{\text{(gas)}}$.

Therefore the gunpowder reaction, which starts from solid components that evolve heat and form gases should be, and is, favoured thermodynamically, and is spontaneous.

INFLUENCE OF PELLET DENSITY ON BURNING TIME

The plastic flow of sulfur is thought to be responsible for the increase in the burning time that is experienced with black powders of various pellet sizes as the pellets (or grains) are compressed to higher bulk densities.

Figure 2.1 shows the result of compressing 3.5 mm and 10.5 mm pellets to densities ranging from 1.6 to 2.0 g cm⁻³. Although the burning process is still not fully understood, the increase of burning time with

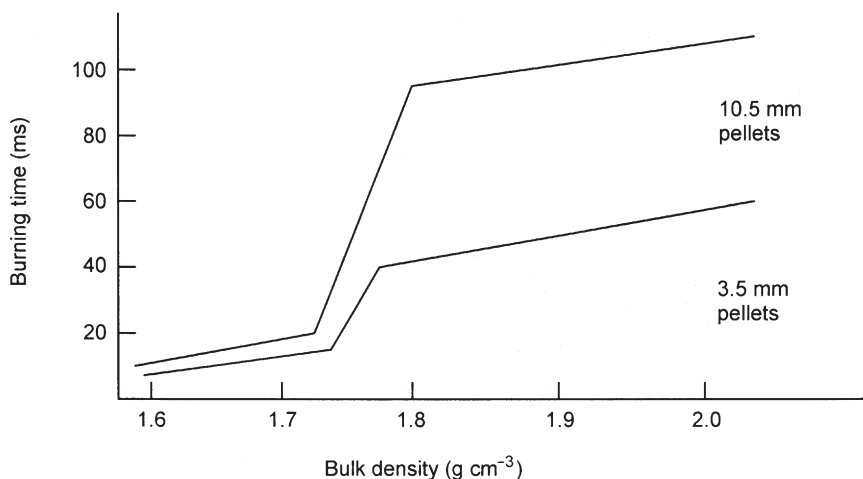


Figure 2.1 Influence of pellet density on black powder burning time.

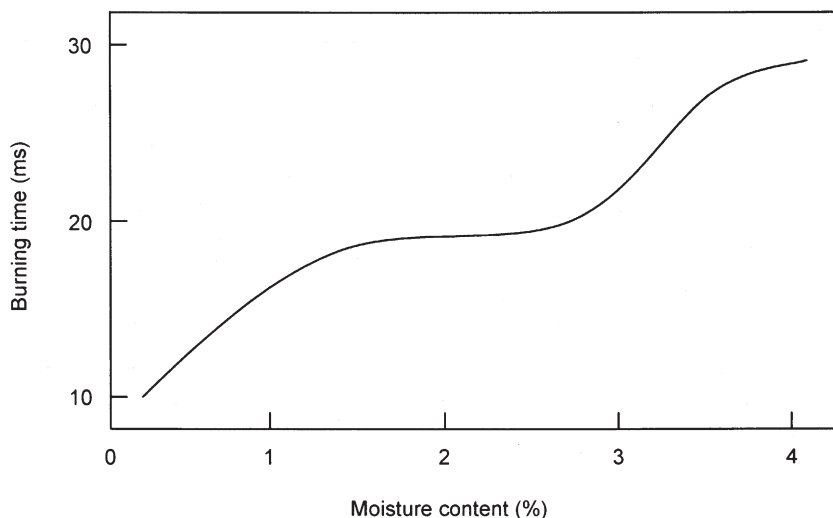


Figure 2.2 Influence of moisture content on black powder burning time.

density is likely to be associated with mechanisms involving the free volume or ‘openness’ of the pellets.

INFLUENCE OF MOISTURE ON BURNING TIME

Increasing amounts of moisture are also known to produce significant increases in the burning time of gunpowder grains. Water will degrade the performance of most pyrotechnics by virtue of unwanted side reactions, and in the case of gunpowder the adverse effect of moisture is also thought to be as a result of occupying the free volume.

Figure 2.2 shows that an increase in moisture level from 1 to 3% is sufficient to reduce the burning rate by approximately half.

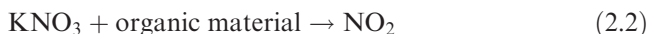
THERMAL DECOMPOSITION

At temperatures below the ignition point, the thermal decomposition of black powder provides an interesting insight into the processes which are thought to control the reaction rate during subsequent burning. In decomposition experiments it has been shown that the overall reaction proceeds in several steps. As the temperature is increased the steps become shorter and the reaction faster. Since these reactions involve gases, the effect of pressure is also important.

The first reaction has been shown to be the formation of hydrogen sulfide (H_2S) from sulfur and volatile organic material originating from the charcoal as shown in reaction (2.1),



while at the same time,



The NO_2 can also be produced by reactions between sulfur and potassium nitrate (KNO_3) with the formation of nitric oxide (NO) and nitrogen dioxide (NO_2) as shown in reactions (2.3) and (2.4):



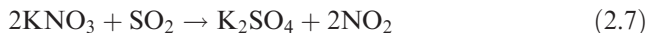
There is then a gas-phase reaction between the main products of these reactions, as in reaction (2.5):



It has been suggested that reaction (2.5), with the regeneration of sulfur, proceeds until all of the H_2S has been used up. The NO_2 then reacts with the free sulfur as in reaction (2.6):

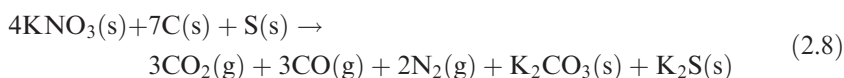


The SO_2 produced in this way then immediately reacts with the KNO_3 as shown in reaction (2.7):



The NO_2 is not liberated at this stage but continues the chain. Reactions (2.5) and (2.6) are endothermic (absorb heat) but reaction (2.7) is strongly exothermic and produces the heat necessary to promote further decomposition and leads to burning.

When burning is established, an overall (but over-simplified) equation can be written as shown in reaction (2.8):



where (s) = solid and (g) = gas phase.

At this stage, the spread of combustion from grain to grain is by a hot spray of molten potassium salts.

The important point to note here is that nearly all of the pre-ignition steps, including two endothermic reactions, take place in the vapour phase. Thus, if ignition is to occur at low pressures, sufficient heat energy must be available for a sufficient time period:

- (1) to volatilise the initial reactants;
- (2) to build up a local concentration of sufficient density to react;
- (3) to supply the heat needed to take the reactions to the point where they become exothermic.

THERMAL IGNITION OF BLACK POWDER

It will be appreciated from the previous paragraphs that the ignition of explosives such as black powder is not an instantaneous process. Classically, as the temperature of the black powder is raised, slow decomposition sets in according to the process:



The rate of decomposition can be followed (for example) by measuring the volume of gas produced as a function of charge temperature as shown in Figure 2.3.

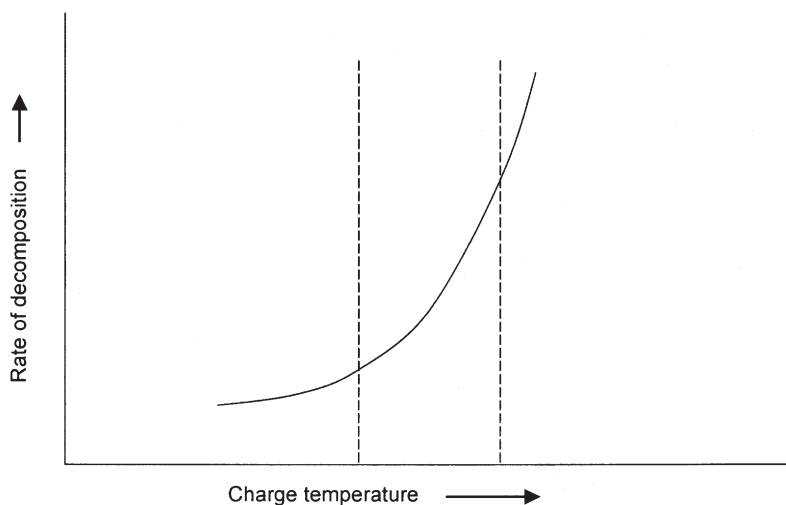


Figure 2.3 The rate of decomposition of black powder as a function of charge temperature.

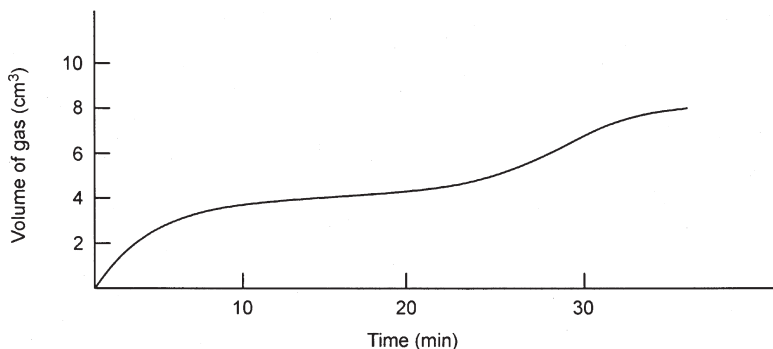


Figure 2.4 Gas evolution from gunpowder measured at atmospheric pressure and 290 °C.

The dashed lines in Figure 2.3 represent the ignition temperature range for black powder which, depending on the conditions of the experiment, typically falls between about 280 and 400 °C.

Alternatively, the decomposition can be followed isothermally (at a controlled temperature), again by measuring the rate of gas production. Figure 2.4 shows a typical result for isothermal decomposition.

The pre-ignition period begins with the application of the ignition stimulus, and ends with the start of a self-sustaining combustion. During this period, the rate of heat transfer to and the rate of heat production in the gunpowder become important in relation to the rate of heat loss from that portion of the material being ignited. As the temperature rises, chemical bonds break and molecular collisions occur while the number of molecules having sufficient energy (E) to react rise exponentially in accordance with the Arrhenius equation, (2.9),

$$k = Ae^{-E/RT} \quad (2.9)$$

where k is the reaction rate constant, A is known as the frequency factor and is a constant related to the material, E is the activation energy in kJ mol^{-1} , R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature.

Since E is the numerator of a negative exponent, the reaction rate increases as E decreases.

The time to ignition can be expressed by equation (2.10) which is similar in form to the Arrhenius equation,

$$t = Be^{E/RT} \quad (2.10)$$

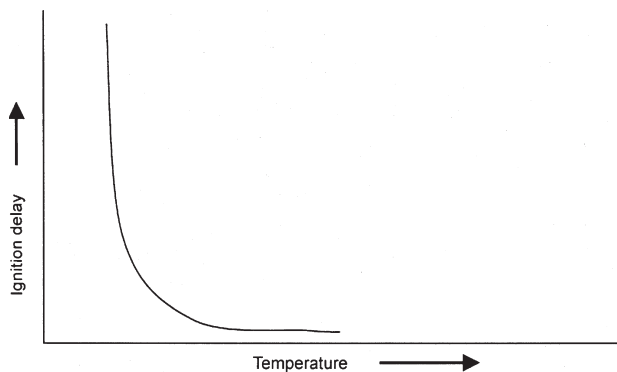


Figure 2.5 Curve showing the variation of ignition delay with temperature.

where t is the time to ignition (*i.e.* ignition delay) at a temperature T in degrees absolute, B is the pre-exponential factor (*i.e.* a constant for the particular material) while E and R are as described for equation (2.9).

Hence, by plotting the ignition delay (t) against temperature (T) a curve is obtained as in Figure 2.5.

Activation energies for black powders (and many other energetic materials) can be determined empirically from the logarithmic form of the Arrhenius equation (2.11):

$$\log t = E/2.303RT + \log B \quad (2.11)$$

By plotting $\log t$ versus $1/T$ a straight line is obtained whose slope is related to the activation energy by $E = [2.303(\text{slope})]R$ as shown in Figure 2.6.

Depending on the sulfur content of the black powder, activation energies ranging between 56 and 130 kJ mol⁻¹ have been obtained, the higher figure being associated with sulfurless fine grain gunpowder (SFG).

Other work has shown that high volatile content charcoals lower the activation energy and reduce the ignition temperature of the black powder, while removal of volatile matter from the charcoal increases both activation energy and ignition temperature.

In summary, the thermal decomposition of black powder can be said to consist essentially of an initial reaction in which sulfur reacts with KNO₃ and/or volatile substances originating from charcoal followed by a main reaction involving charcoal and KNO₃.

High activation energies (greater than 300 kJ mol⁻¹) are associated with material that possesses greater thermal stability and that is less sensitive to an ignition stimulus.

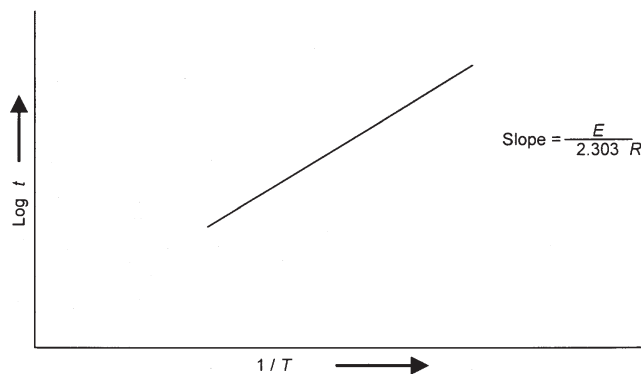


Figure 2.6 Arrhenius plot for black powder.

THERMAL ANALYSIS OF BLACK POWDER

Thermal analytical techniques such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have all been successfully employed in studying the pyrotechnic reactions of energetic materials such as black powder, as well as of binary mixtures of the constituents.

TG is a method associated with mass change in which the mass of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme. On the other hand, DTA is a method associated with temperature change in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substances are subjected to a controlled temperature programme.

Multiple techniques are also possible such as TG–DTA whereby the mass loss of a sample and the DTA curve may be obtained simultaneously.

DSC is a method associated with enthalpy (heat content) change in which the difference in energy inputs into a substance and a reference material are subjected to a controlled temperature programme. By convention, the enthalpy change is regarded as negative when a reaction produces heat.

Analysis by TG

Typical thermogravimetric curves for black powder and its ingredients have been obtained as shown in Figure 2.7, and the main events depicted by the curves can be presented as in Table 2.1.

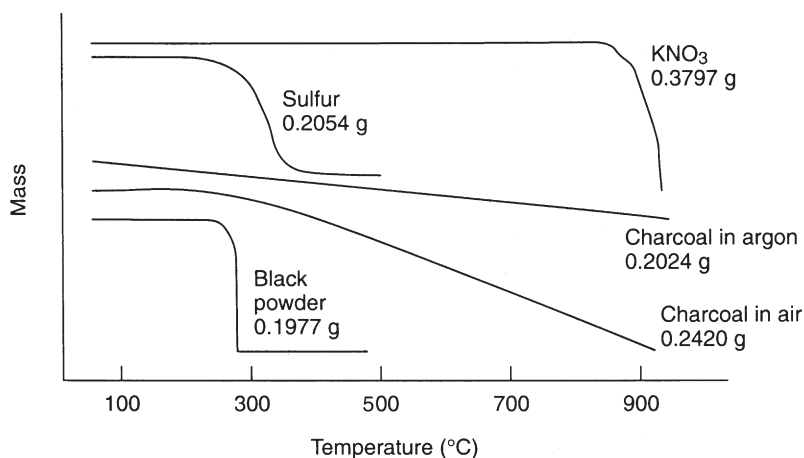


Figure 2.7 Thermogravimetric curves for black powder and its ingredients.

Table 2.1 Main thermal events depicted by the TG curves of Figure 2.7.

Substance	Mass loss		Thermal events
	From (°C)	To (°C)	
KNO ₃	700	950	Thermal decomposition to potassium oxide
Sulfur	225	444	Sulfur vaporisation
Charcoal (heated in argon)	100	900	Loss of volatile constituents
Charcoal (heated in air)	50	950	Loss of moisture and oxyhydrocarbons then complete oxidation
Black powder	250	275	Violent decomposition

The TG curves in Figure 2.7 were obtained by heating the samples in a furnace at a rate of $15^{\circ}\text{C min}^{-1}$ under an atmosphere of air or argon, and plotting the mass loss as a function of furnace temperature.

Analysis by DTA

By contrast, DTA curves for black powder and its ingredients have been obtained as shown in Figure 2.8. The DTA curves are more complex than those obtained by TG and include crystal phase transitions as described in Table 2.2.

Apart from the additional information on heat release and phase changes given by DTA, the apparent discrepancy in the black powder

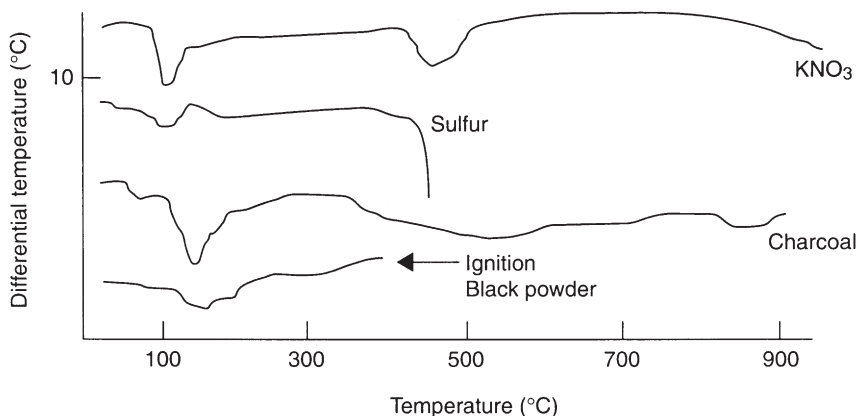


Figure 2.8 DTA curves for black powder and its ingredients from a heating rate of $15^{\circ}\text{C min}^{-1}$.

Table 2.2 Main thermal events depicted by the DTA curves of Figure 2.8.

Substance	Mass loss		Thermal events
	From ($^{\circ}\text{C}$)	To ($^{\circ}\text{C}$)	
Black powder	95	200	Endotherm – overlapping peaks from crystalline transition of KNO_3 , transition and fusion of sulfur and vaporisation of volatile matter from charcoal.
	250	300	Exotherm – pre-ignition followed by violent decomposition.
KNO_3	128	200	Endotherm – rhombic – trigonal crystal transition.
Sulfur	334	360	Endotherm – KNO_3 melting.
	105	110	Endotherm – rhombic–monoclinic crystal transition.
Charcoal	120	125	Endotherm – sulfur melting.
	444		Endotherm – sulfur boiling.
	100	300	Endotherm – loss of volatile constituents.

ignition temperatures as determined by DTA and TG is explained by the fact that in DTA, the curves are plotted as a function of sample temperature, while with TG the curves are plotted as a function of the furnace temperature. If the sample in the TG thermobalance undergoes an exothermic reaction, its temperature will increase at a faster rate than

that of the furnace temperature, while during an endothermic reaction the sample temperature will lag behind that of the furnace.

Analysis by DSC

Differential Scanning Calorimetry (DSC) is a technique in which the difference in energy put into a substance and a reference material is measured as a function of temperature whilst the substance and the reference material are subjected to a controlled temperature programme. Thus, when an exothermic transition occurs, the energy released by the sample is compensated by a decreased energy input to the sample in order to maintain a zero temperature difference. Because this energy input is precisely equivalent in magnitude to the energy released in the transition, direct calorimetric measurement of the transition is obtained from the balancing electrical energy. The DSC curve is recorded with the chart abscissa indicating the transition temperature while the peak area measures the total energy transfer to or from the sample.

In practice, the DSC system consists of two separate 'control loops', one for average temperature control, the second for differential temperature control. In the average temperature loop, a programmer provides an electrical signal which is proportional to the desired temperature of the sample and reference holders. The programme temperature information is relayed to a computer. The programmer signal is compared with the average signal from platinum resistance thermometers permanently embedded in the sample and reference holders. The resultant difference signal is amplified in the average temperature amplifier. If the temperature called for by the programme is greater than the average temperature of the sample and reference holders, more power will be fed to the heaters of both sample holders. If the average temperature is higher than that demanded by the programme, the power to both heaters will be decreased.

In the differential control loop, signals representing the sample and reference temperatures, measured by the platinum thermometers, are fed to a circuit which determines whether the reference or sample temperature is greater. The differential temperature amplifier will then proportion a small increment of power between the reference and sample heaters in such a way as to correct any temperature difference between them. This is done by increasing the power to one while decreasing the power to the other. A signal proportional to the differential power is also transmitted to the computer. The integral of the resulting peak is calculated by the computer and is equivalent to the internal energy change.

A typical DSC response for black powder is shown in Figure 2.9.

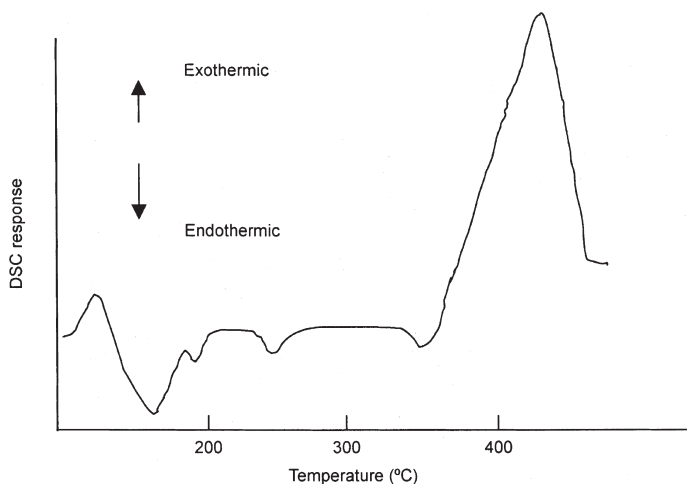


Figure 2.9 DSC curves for black powder from a heating rate of $80^{\circ}\text{C min}^{-1}$ in nitrogen.

As with the DTA curves, the endotherms originate from phase transitions and volatilisation, while the single exotherm represents the violent decomposition of black powder.

Collectively, the thermal analysis techniques can be used to compare different batches of gunpowder and its constituents or to make more fundamental studies of, for example, the stability of the explosive under various physical or chemical conditions.

As well as calculation of the temperatures and heat releases of the relevant exotherms, DSC data can be fitted to a differential equation (2.12) of the form,

$$\frac{df}{dt} = k(1 - f)^n \quad (2.12)$$

where f is the fractional degree of conversion of the sample to products (*i.e.* $f=0$ at the start and 1.0 at the end of the exotherm), t is the time in seconds, the exponent n is a constant and k is the reaction rate constant (in units of s^{-1}). The rate constant varies during the course of the exotherm because of its strong dependence on temperature as shown earlier by the Arrhenius equation (2.9).

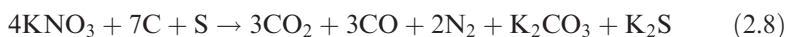
Such kinetic information can be used to estimate the thermal runaway times for the exotherm. This is the time taken for the explosive (under adiabatic conditions and considering a particular exotherm) to react at various initial temperatures.

The analysis of the kinetics of reacting solids is an area fraught with problems. This is because chemical kinetic theory strictly applies only to reactions of gases and liquids, and therefore absolute values of kinetic parameters derived from DSC must be treated with caution. However, it is quite reasonable to use the data in a comparative manner where this is derived from similar systems studied under the same conditions.

STOICHIOMETRY

The thermal analysis of black powders used for different purposes and containing differing proportions of ingredients can give an indication of the system stoichiometry by virtue of the rate and magnitude of measured exothermic events.

For example, the stoichiometry of a typical black powder containing KNO_3 (77%), charcoal (17%) and sulfur (6%) can be represented by the simplified equation (2.8), seen earlier as:



This ignores the water gas reaction (2.13)



and the presence of trace species such as water and minor solid products.

VOLUME OF EVOLVED GASES

From equation (2.8), the gaseous reaction products are seen to be 3CO_2 , 3CO and 2N_2 . Therefore, the reaction produces 8 moles of product gases from 4 moles of KNO_3 (404 g) plus 7 moles of charcoal (84 g) plus 1 mole of sulfur (32 g) which is equivalent to a total of 520 g of black powder.

To calculate the number of moles of gas produced per gram of black powder burned,

$$\frac{8}{520} = 0.015 \text{ mol g}^{-1}$$

and the volume of gas produced at standard temperature and pressure (STP) per gram of black powder burned is given by the Ideal Gas Law, equation (2.14).

$$V = \frac{nRT}{P} \quad (2.14)$$

STP refers to a temperature of 25 °C (298 K) and a pressure of 1 atmosphere (10^5 Nm^{-2}). Therefore,

$$V = \frac{0.015 \times 8.314 \times 298}{10^5} = 3.8 \times 10^{-4} \text{ m}^3 \text{ g}^{-1} \quad (2.15)$$

where R is the universal gas constant in units of $\text{J K}^{-1} \text{ mol}^{-1}$, n is the number of moles, T is the absolute temperature and $1 \text{ J} = 1 \text{ Nm}$.

If the actual temperature of the product gases is 2000 °C, the calculated volume at this temperature and one atmosphere pressure would be considerably greater, as shown by equation (2.16).

$$V_{2000^\circ\text{C}} = \frac{2273}{298} (3.8 \times 10^{-4}) = 2.91 \times 10^{-3} \text{ m}^3 \text{ g}^{-1} \quad (2.16)$$

HEAT OF REACTION

The heat associated with the combustion of an energetic material such as black powder is called the heat of reaction. The heat of explosion is the heat of reaction associated with the rapid decomposition of such a material in an inert atmosphere.

Assuming the reaction of black powder given in equation (2.8) is at constant pressure; if only pressure–volume work is considered, the enthalpy change for the reaction at the temperature concerned is equal to the sum of the enthalpies of the products minus the sum of the enthalpies of the reactants [equation (2.17)],

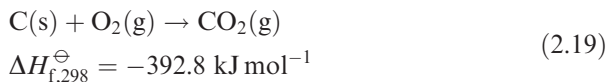
$$H_{(\text{reaction})} = \sum \Delta H_{(\text{products})} - \sum \Delta H_{(\text{reactants})} = Q_p \quad (2.17)$$

where Q_p is the heat of explosion.

If the reaction is a standard state reaction where the starting materials in their standard states react to give products in their standard states, and the standard heats of formation ($\Delta H_{f,T}^\ominus$) of the elements are assumed to be zero at any given temperature, then the standard heat of reaction, $\Delta H_{T(\text{reaction})}^\ominus$, is expressed as in equation (2.18):

$$\Delta H_T^\ominus (\text{reaction}) = \Delta H_{f,T}^\ominus (\text{products}) - \Delta H_{f,T}^\ominus (\text{reactants}) \quad (2.18)$$

For example, the enthalpy of formation of CO_2 from combustion of the black powder constituent, charcoal, is given by reaction (2.19):



Normally, the standard state is the most stable state at one atmosphere pressure and at the given temperature. Most tabular data, as used for the calculation of reaction temperatures, are given at 0 °C or 298 K. The overall calculation for the heat of reaction of black powder at different temperatures is simplified by using tabulated data of the enthalpy function, $H_T^\ominus - H_{298}^\ominus$ for the reaction products, since no enthalpy measurements can be made in the sense of an absolute quantity.

Table 2.3 lists the molar internal enthalpies of black powder reaction products such as CO_2 where c_p values are the molar heat capacities of the products at constant pressure. Using these, it is possible to estimate the heat of reaction at a particular temperature by assuming two temperature values and summing up the internal enthalpies for the reaction products multiplied by their corresponding number of moles as in Table 2.4.

Plotting the sum of the enthalpies at the two reference temperatures yields an estimate for the heat of reaction for the 77:17:6 black powder composition over an extrapolated temperature range (see Figure 2.10). For a reaction temperature of, say, 2500 K, the theoretical heat of reaction is approximately 1410 kJ mol^{-1} .

TEMPERATURE OF REACTION

Further use of tabulated data (such as those in Table 2.3) enables an estimate to be made of the temperature of the reaction of black powder. Using equation (2.18), the standard enthalpy change may be calculated from the standard heats of formation of the reactants and products as in equation (2.20).

$$\Delta H_{298}^\ominus(\text{reaction}) = \Delta H_{f,298}^\ominus(\text{products}) - \Delta H_{f,298}^\ominus(\text{reactants}) \quad (2.18)$$

Thus,

$$\begin{aligned} \Delta H_{298}^\ominus(\text{reaction}) = & \{1[\Delta H_f^\ominus(\text{K}_2\text{CO}_3)] + 2[\Delta H_f^\ominus(\text{N}_2)] \\ & + 3[\Delta H_f^\ominus(\text{CO})] + 3[\Delta H_f^\ominus(\text{CO}_2)] + 1[\Delta H_f^\ominus(\text{K}_2\text{S})]\} \\ & - \{4[\Delta H_f^\ominus(\text{KNO}_3)] + 7[\Delta H_f^\ominus(\text{C})] + 1[\Delta H_f^\ominus(\text{S})]\} \end{aligned} \quad (2.20)$$

Table 2.3 Molar internal enthalpies of reaction products $c_p(T - T_0)$; $T_0 = 25^\circ\text{C} \approx 300\text{ K}$.

Temp. (K)	CO		CO ₂		H ₂ O		H ₂		O ₂		N ₂		NO	
	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹
700	4.99	20.89	7.68	32.16	5.98	25.04	4.75	19.89	5.22	21.85	4.93	20.64	5.11	21.39
900	6.60	27.63	10.33	43.25	8.00	33.49	6.21	26.00	6.91	28.93	6.52	27.29	6.75	28.30
1100	8.24	34.50	13.04	54.59	10.12	42.37	7.71	32.28	8.62	36.09	8.14	34.00	8.43	35.29
1200	9.08	38.01	14.43	60.41	11.22	46.98	8.47	35.46	9.49	39.73	8.97	37.55	9.28	38.86
1300	9.92	41.53	15.84	66.32	12.34	51.67	9.25	38.73	10.36	43.38	9.81	41.07	10.14	42.46
1400	10.78	45.14	17.25	72.23	13.48	56.44	10.04	42.03	11.25	47.10	10.65	44.59	11.01	46.10
1500	11.62	48.66	18.70	78.30	14.45	60.50	11.06	46.31	12.54	52.50	11.50	48.15	11.95	50.03
1600	12.47	52.21	20.07	84.03	15.56	66.15	11.77	49.28	13.30	55.69	12.33	51.63	12.79	53.55
1700	13.32	55.77	21.46	89.86	16.71	69.96	12.50	52.33	14.10	59.04	13.17	55.14	13.64	57.11
1800	14.16	59.29	22.85	95.67	17.87	74.82	13.26	55.52	14.91	62.43	14.00	58.62	14.49	60.67
1900	15.03	62.93	24.28	101.66	19.06	79.80	14.04	58.79	15.76	65.99	14.87	62.26	15.36	64.31
2000	15.81	66.20	25.73	107.73	20.29	84.91	14.84	62.14	16.63	69.63	15.73	65.86	16.23	67.96
2100	16.77	70.22	27.19	113.84	21.51	90.06	15.66	65.57	17.51	73.31	16.60	69.50	17.11	71.64
2200	17.65	73.90	28.66	120.00	22.79	95.42	16.49	69.04	18.41	77.08	17.47	73.15	17.99	75.32
2300	18.54	77.63	30.16	126.28	24.01	100.53	17.33	72.56	19.32	80.89	18.35	76.83	18.88	79.05
2400	19.42	81.31	31.62	132.39	25.28	105.85	18.19	76.16	20.24	84.74	19.23	80.52	19.78	82.82
2500	20.30	85.00	33.11	138.63	26.54	111.12	19.04	79.72	21.16	88.60	20.11	84.20	20.66	86.50
2600	21.19	88.72	34.61	144.91	27.83	116.52	19.91	83.36	22.11	92.60	20.99	87.90	21.56	90.27
2700	22.09	92.49	36.12	151.23	29.12	121.93	20.78	87.01	23.06	96.55	21.88	91.61	22.46	94.04
2800	22.98	96.22	37.63	157.56	30.42	127.37	21.67	90.73	24.01	100.53	22.77	96.34	23.36	97.81

2900	23.88	99.99	39.15	163.92	31.73	132.85	22.55	94.42	27.97	104.55	23.67	99.11	24.27	101.62
3000	24.78	103.75	40.68	170.33	33.04	138.84	23.48	98.31	25.94	108.61	24.56	102.83	25.17	105.39
3100	25.68	107.52	42.21	176.73	34.36	143.87	24.34	101.91	26.91	112.67	25.46	106.60	26.08	109.20
3200	26.57	111.25	43.73	183.10	35.67	149.35	25.21	105.64	27.88	116.73	26.35	110.33	26.98	112.97
3300	27.47	115.02	45.26	189.50	37.00	154.92	16.14	109.45	28.87	120.88	27.24	114.05	27.89	116.78
3400	28.37	118.79	46.80	195.95	38.33	160.49	27.05	113.26	29.85	124.98	28.15	117.86	28.81	120.63
3500	29.28	122.60	48.34	202.40	39.66	166.06	27.96	117.70	30.84	129.13	29.05	121.63	29.72	124.44
3600	30.18	126.36	49.88	208.85	40.99	171.63	28.88	120.92	31.83	133.27	29.95	125.40	30.63	128.25
3700	31.09	130.17	51.43	215.34	42.33	177.24	29.79	124.73	32.83	137.46	30.85	129.17	31.55	132.10
3800	32.00	133.98	52.97	221.79	43.67	182.85	30.71	128.58	33.83	141.65	31.76	132.98	32.47	135.95
3900	32.89	137.71	54.51	228.23	45.01	188.46	31.69	132.69	34.82	145.79	32.65	136.71	33.37	139.72
4000	33.80	141.52	56.06	234.72	46.35	194.07	32.55	136.29	35.82	149.98	33.56	140.52	34.29	143.57
4100	34.71	145.33	57.61	241.21	47.70	199.72	33.48	140.18	36.83	154.21	34.46	144.28	35.21	147.42
4200	35.62	149.14	59.17	247.74	49.05	205.37	34.41	144.07	37.83	158.39	35.37	148.09	36.13	151.28
4300	36.53	152.95	60.72	254.23	50.40	211.02	35.34	147.97	38.85	162.66	36.28	151.90	37.05	155.13
4400	37.44	156.76	62.28	260.77	51.76	216.72	36.27	151.86	39.85	166.85	37.19	155.71	37.97	158.98
4500	38.35	160.57	63.84	267.30	53.11	222.37	37.20	155.76	40.78	170.75	38.10	159.52	38.89	162.83
4600	39.26	164.38	65.40	273.83	54.47	228.07	38.13	159.65	41.88	175.35	39.00	163.29	39.81	166.68
4700	40.17	168.19	66.96	280.36	55.84	233.80	39.07	163.59	42.89	179.58	39.91	167.10	40.73	170.54
4800	41.08	172.00	68.51	286.85	57.18	239.41	40.00	167.48	43.90	183.61	40.81	170.87	41.64	174.35
4900	41.99	175.81	70.07	293.38	58.54	245.11	40.93	171.37	44.92	188.08	41.72	174.68	42.57	178.24
5000	42.90	179.62	71.64	299.96	59.90	250.80	41.87	175.31	45.94	192.35	42.63	178.49	43.49	182.09

Table 2.4 Calculation of the sum of the enthalpies of the reaction products from gunpowder [reaction (2.8)] at two reference temperatures (2000 and 3000 K).

Species	'n'	$H_{3000}^{\ominus} - H_{298}^{\ominus}$ (kJ mol ⁻¹)	kJ mol ⁻¹ × 'n'	$H_{2000}^{\ominus} - H_{298}^{\ominus}$ (kJ mol ⁻¹)	kJ mol ⁻¹ × 'n'
K ₂ CO ₃	1	480 ^a	480	344.38	344.38
N ₂	2	102.83	205.66	65.86	131.72
CO	3	103.75	311.25	66.20	198.60
CO ₂	3	170.33	510.99	107.73	323.19
K ₂ S	1	160 ^a	160	140 ^a	140
			Σ = 1667.90		
					Σ = 1137.89

^aEstimated.

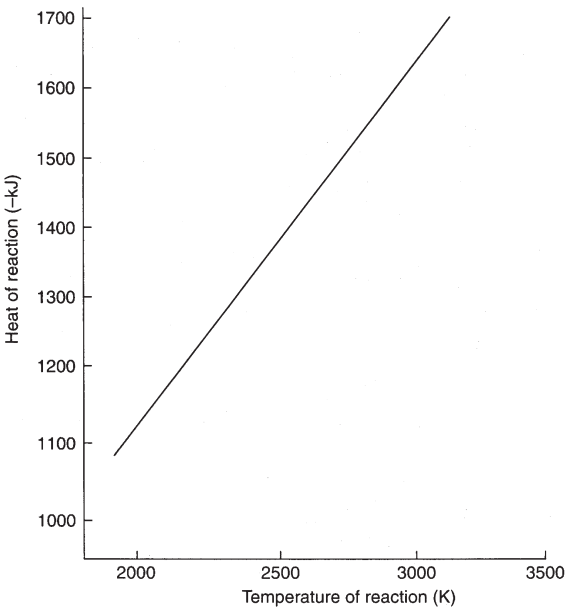


Figure 2.10 Estimate of the heat of reaction for the 77:17:6 black powder composition from the sum of the product enthalpies at two reference temperatures.

Therefore,

$$\begin{aligned} \Delta H_{298}^{\ominus}(\text{reaction}) &= \{[1 \times (-1151.0)] + [2 \times (0)] + [3 \times (-110.6)] \\ &\quad + [3 \times (-393.8)] + [1 \times (-1000)]\} - \{[4 \times (-494.0)] \\ &\quad + [7 \times (0)] + [1 \times (0)]\} \\ &= (-3664.2) - (-1976.0) = -1688.2 \text{ kJ mol}^{-1} \end{aligned}$$

using estimated enthalpy data for K₂S.

The adiabatic flame temperature may now be read from the graph shown in Figure 2.10. In this example, $-1688 \text{ kJ mol}^{-1}$ corresponds to a theoretical flame temperature of about 3070 K.

SULFURLESS GUNPOWDER

Although the unique burning properties of gunpowder have ensured that the material continues to be used into the 21st century, there are occasions when a slower burning powder is required or when the presence of sulfur is unacceptable on the grounds of compatibility.

In the nineteenth century the size of rifled guns increased to the extent that dangerously high breech pressures were encountered when gunpowder was employed to propel increasingly heavy shells. One way of overcoming this was to use a slower burning powder. Sulfurless powders gave lower breech pressures which operated over longer burning times and these were used until the development of cordite.

Early versions of slow burning, sulfurless powders were brown in colour and known as “Cocoa powder”, the colour originating from an incompletely carbonised charcoal with a carbon level of about 50%.

The stoichiometric equation for the burning of sulfurless gunpowder has been given as in reaction (2.21)



The above reaction corresponds to a composition containing saltpetre (87.1%) and charcoal (12.9%).

A modern use of sulfurless gunpowder has been in the fusing of military weapons where delay elements are interposed between the igniter and the main charge. This popularity arose because of the possibility of corrosion when using conventional gunpowders, the sulfur in the powder being slightly acidic due to trace quantities (around 0.01%) of sulfuric acid.

In firework manufacture the use of gunpowder for priming pressed compositions containing chlorates can also be questioned on the grounds of chemical incompatibility. Sulfuric acid is known to react with chlorates to form chloric acid, HClO_3 , which would be avoided by the use of sulfurless gunpowder.

However, at the present time it appears that there is not a significant problem with the employment of sulfur gunpowder for the priming of chlorate compositions, and so the main use of sulfurless powders again rests with the military, particularly where igniter and priming compositions are in contact with magnesium.

In manufacture, sulfurless gunpowders are available with a potassium nitrate content of 70–80% and a charcoal level of 20–30%.

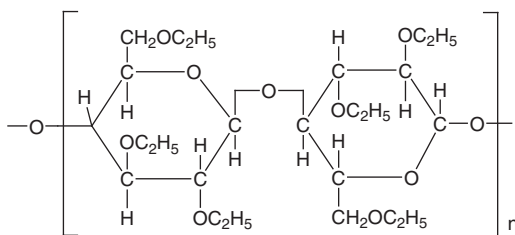
MOISTURE RESISTANT GUNPOWDER

Despite the desirable qualities of gunpowder, which include long-term stability when dry, ease of ignition, ease of loading and relative insensitivity to rough handling when filled into items such as fireworks, it suffers the disadvantage of a variable moisture content which dictates the need for careful quality control.

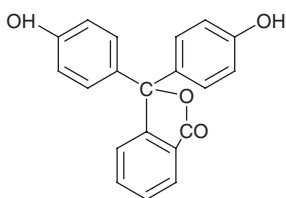
In the United Kingdom, standard quality testing before using gunpowder includes a determination of the volatile matter (which is mainly moisture) by oven drying under controlled conditions. As a general guide, the moisture level determined in this way would be expected to fall between 0.5 and 1.4% for an acceptable powder.

In North America the problem of moisture absorption has been addressed by developing a moisture resistant gunpowder substitute based on potassium nitrate but augmented with potassium perchlorate. The latter is said to absorb less moisture than the nitrate at a given humidity. In addition, the gunpowder substitute contains a hydrophobic binder, called ethyl cellulose, (2.22) (celluloses have a history of use in pyrotechnics) together with an organic fuel, known as phenolphthalein, (2.23) which is said to enhance the burn rate.

The burn rate of the gunpowder substitute is claimed to be comparable to gunpowder at 1720 psi while the flame temperatures are also in good agreement at 2064 K and 1949 K respectively.



Ethyl cellulose
(2.22)



Phenolphthalein
(2.23)

Whilst it is apparent that the gunpowder substitute has been developed for use in munitions, it remains to be seen whether the material can be used to the same extent in fireworks. Obvious applications would be as replacements for quickmatch and piped match, both of which are notoriously prone to dampness during wet or humid conditions.

CHAPTER 3

Rockets

PROPELLANT

The initial development of the firework rocket and the military rocket probably occurred during the same period in history. Both used black powder as the rocket propellant.

In sending a rocket into the sky we are calling into action several laws of physics and chemistry, and the same laws apply whether the application is a small firework rocket weighing a few ounces or a solid propellant ‘booster’ for the space shuttle containing around 300 tons of propellant. These fundamental processes may be conveniently divided into internal ballistics and external ballistics.

Internal Ballistics

When black powder is used to propel rockets it is classed as a composite propellant (where the fuel and oxidiser are intimately mixed) and forms part of a rocket motor in which the powder is compressed to form a monolithic single grain inside a combustion chamber as shown in Figure 3.1. As well as gunpowder, the composite propellant mix will contain a binder which is used to improve the cohesion of the ingredients. Binders form a distinct phase and tend to reduce the sensitivity of the propellant to shock and impact. When based on organic materials, as is normally the case, they will serve as part of the fuel component also.

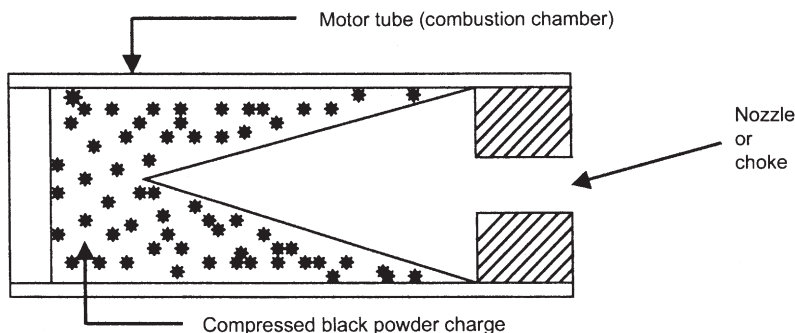


Figure 3.1 The essential components of a firework rocket motor.

The importance of compressing the gunpowder grain is to control the rate of burning by ensuring that the surface of the grain is not porous to the hot combustion gases. Such penetration would result in a progressive increase in the rate of combustion and loss of ballistic control. Interestingly, the burning rate laws that were discovered for the burning of gunpowder in the 19th century are equally applicable to more modern solid propellants such as cordite.

Piobert's law of 1839 states that 'burning takes place by parallel layers where the surface of the grain regresses, layer by layer, normal to the surface at every point'. Thus the combustion gases flow in the opposite direction to the rate of combustion progress (or surface regression).

Piobert's law applies even when the gunpowder grains are less than 1 millimetre in diameter such as in the powder charges used in early firearms. In a musket, for example, breech pressures of up to 10,000 psi may be experienced, with corresponding burn times of less than two milliseconds. On the other hand, the gunpowder grain which is pressed to form a firework rocket motor can be several centimetres in diameter and is designed to operate at pressures that rarely exceed 500 psi. In this case the burn time will be measured in seconds rather than milliseconds and this brings us on to Vieille's law.

Vieille's law of 1893 is mathematical, but if a book on fireworks was permitted to contain just one equation, this would be it [equation (3.1)]:

$$R_B = bp'' \quad (3.1)$$

The above relationship basically shows that the rate of burning (R_B) normal to the burning surface is dependent on the ambient pressure (p). Although an over-simplification, it is universally accepted that the higher the pressure, the greater the heat transfer onto the surface of the grain and hence, the higher the rate of burning.

The constants ' b ' and ' n ' are dependent upon the chemical composition of the grains and their initial temperature. The burning rate equation (3.1) is based on the various empirical measurements and differs with the type of propellant. For one type of gunpowder the equation might be expressed as follows:

$$R_B = 1.6p^{0.24} \quad (3.2)$$

In this example, R_B is the linear rate of burning in mm s^{-1} and p is the rocket motor chamber pressure in pounds per square inch (psi).

Substituting a pressure of, say, 300 psi into equation (3.2) gives a rate of burning of 6.3 mm s^{-1} , whereas a pressure of 1000 psi ($6.9 \times 10^6 \text{ mN m}^{-2}$) results in a rate of 8.4 mm s^{-1} . These values may be plotted on log-log graph paper to give a straight line as in Figure 3.2, whose

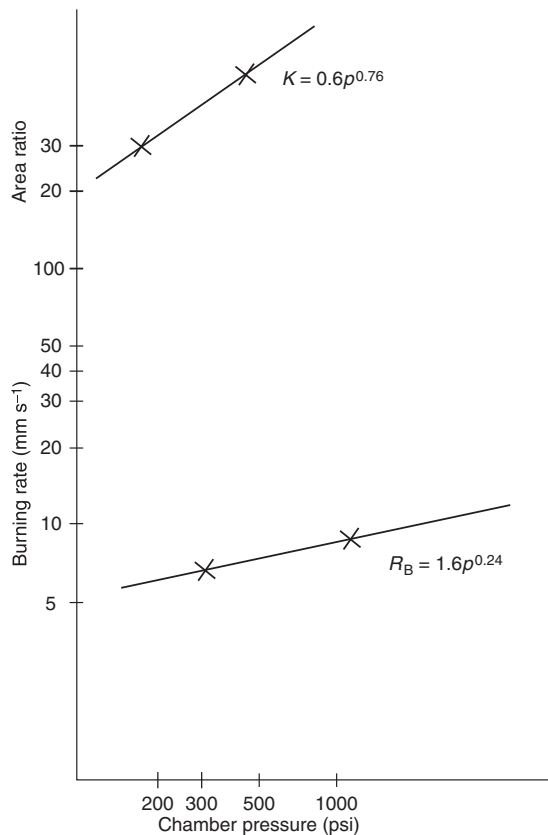


Figure 3.2 Burning rate and area ratio data from black powder propellant.

slope is equal to the pressure exponent, n , whose value is 0.24, from equation (3.3):

$$n = \frac{\log_{10} R_B - \log_{10} R'_B}{\log_{10} p - \log_{10} p'} \quad (3.3)$$

where R'_B is the lower rate of burning (6.3 mm s^{-1}) and p' is the lower chamber pressure (300 psi).

When designing a gunpowder charge for a firework rocket we can use Vieille's law to determine the burning speed of the charge at a particular pressure, and a similar law to calculate the pressure operating within the rocket body or 'motor'. But in order to estimate the operating pressure we need to know two further things: the area of the burning propellant surface and the cross-sectional area of the nozzle (or choke) through which the powder gases pass. You will notice on firing a rocket that there is an initial rapid acceleration, after which the flame dies down and the rocket 'coasts'. The sudden acceleration is because the area of propellant is increased near the nozzle. In fact, the gunpowder charge is pressed with a spike so that there is a deep 'cone' at the ignition end, this serving to increase the surface area of the propellant to perhaps 100 times that of the area of the nozzle. As propellant is consumed, its area increases and the gas flow or 'thrust' increases.

The ratio of propellant area (A_p) to nozzle area (A_N) is known as the propellant area ratio, K , *i.e.*

$$K = \frac{A_p}{A_N} \quad (3.4)$$

In fact, an area ratio equation such as (3.4) can be compared with the burning rate equation (3.2) by taking note of the fact that ' n ' [or 0.24 in equation (3.2)] becomes ' $1 - n$ ' (or 0.76) in the area ratio equation. Therefore, equation (3.4) may be written,

$$K = Cp^{1-n} \quad (3.5)$$

where C is a further constant dependent upon the propellant.

For example, if the initial propellant surface area is 100 cm^2 and the nozzle area is 1 cm^2 , the area ratio is expressed by equation (3.6):

$$K = \frac{100}{1} = 100 \quad (3.6)$$

Table 3.1 Pressure–time data for firework rocket motor.

<i>Inward burning increment (cm)</i>	A_P (cm^2)	A_N (cm^2)	K	P (psi)	R_B ($mm\ s^{-1}$)	<i>Incremental burn time (s)</i>	<i>Overall burn time (s)</i>
0.0	25	1	25	150	5.3	0.38	0.38
0.2	30	1	30	170	5.5	0.36	0.74
0.4	40	1	40	220	5.8	0.34	1.25
0.6	50	1	50	300	6.3	0.32	1.57
0.8	60	1	60	350	6.5	0.31	1.88
1.0	10	1	10	50	4.1	0.49	2.37

Burning rate equation $R_B = 1.6p^{0.24}$. Area ratio equation $K = 0.6p^{0.76}$.

The constant, C , can be found by empirical measurements in much the same way as the burning rate constants are determined, to give a value of 0.94 in the area ratio equation (3.7):

$$K = 0.6p^{0.76} \tag{3.7}$$

The complete pressure–time profile for the firework rocket motor as depicted in Figure 3.1 can be obtained if we assume that the propellant surface increases in area during burning inwardly in parallel layers (according to Piobert’s law).

Typical results from applying the above concepts are presented in Table 3.1 where the chamber pressures and burn times relate to burning in increments to give an overall burn time in seconds.

The data in Table 3.1 may then be plotted as in Figure 3.3 to give the pressure–time profile for the firework rocket motor.

THRUST AND SPECIFIC IMPULSE

Finally, the thrust (F) of a rocket motor is also known to be related to the rate of burning and is obtained *via* the mass flow rate using the relationship given in equation (3.8):

$$F(\text{th}) = \bar{R}.I_{\text{sp}}.D.\bar{A}_p \tag{3.8}$$

In this equation $F(\text{th})$ is the theoretical thrust, \bar{R} is the average rate of burning, I_{sp} is a performance parameter related to the propellant called the specific impulse, D is the propellant density and \bar{A}_p is the average area of the burning surface.

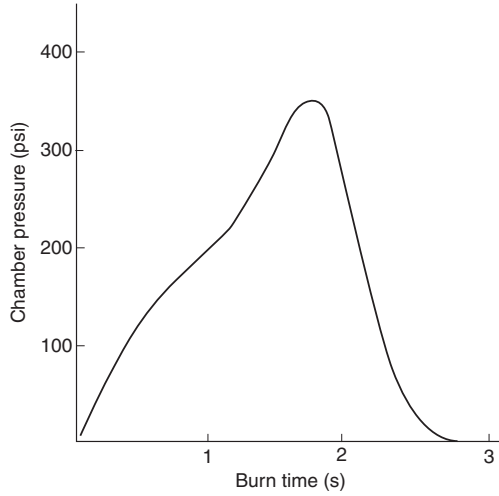


Figure 3.3 Pressure–time profile of a rocket motor.

The performance of rocket propellants is commonly studied by means of the specific impulse which can be expressed as the thrust delivered per unit weight of propellant consumed as shown by equation (3.9).

$$I_{\text{sp}} = \frac{1}{W} \int_{t_1}^{t_2} F(\text{th}) \, dt \quad (3.9)$$

In the above equation W is the weight of propellant and t_1 and t_2 are the times between which the thrust is measured.

The specific impulse, under fixed pressure conditions, is invariant for any propellant system and is the basic chemical comparison parameter used in evaluation.

For the rocket motor described above, a typical theoretical thrust can be obtained from the following parameters:

$$\bar{R} = 20 \, \text{mm s}^{-1} \equiv 0.020 \, \text{m s}^{-1}$$

$$I_{\text{sp}} = 600 \, \text{N s kg}^{-1}$$

$$D = 1800 \, \text{kg m}^{-3}$$

$$\bar{A}_p = 30 \, \text{cm}^2 \equiv 0.0030 \, \text{m}^2$$

Substituting the above values into equation (3.8) gives a theoretical thrust of 64.8 Newtons (N). One Newton is equivalent to 0.22 lb force and so the thrust from the rocket motor is about 14.3 lbs. For a

firework rocket weighing 1 lb a thrust to weight ratio of 14.3 is perfectly reasonable and such a design would be cheap and not highly stressed.

External Ballistics

In the propulsion of a solid propellant rocket relatively small masses of materials are ejected through the nozzle at a very high velocity while the relatively higher mass of the rocket is propelled forwards at a correspondingly lower velocity.

The product of mass and velocity is called 'momentum' and the law of conservation of momentum tells us that the total momentum of an isolated system (such as a rocket) is constant. For example, if two bodies collide, then their total momentum before impact is equal to their total momentum after impact.

In the case of a rocket, the chemical reaction between the fuels and oxidisers in the propellant forces product gases through the nozzle at a certain momentum, while the momentum of the rocket increases in the opposite direction.

Newton's third law of action and reaction is somewhat less fundamental than the conservation law and states that action and reaction are equal and opposite. Hence, if a body A exerts a force (action) on a body B, then B will exert an equal and opposite force (reaction) on A. Applied to a rocket, the downward force on the product gases from the nozzle is equal to the upward force on the rocket.

The primary function of the nozzle is to convert the gunpowder heat energy into thrust with the minimum conversion loss.

In summary, the rocket accelerates because the propellant burning surface increases in area, giving increased thrust while the rocket mass diminishes, as propellant is consumed, giving increased forward velocity.

Rocket Trajectory

The position of an object in flight, such as a rocket, as a function of time is routinely determined using ballistics equations and tables which are commonplace but rather complex.

In a simplified form, the firework rocket trajectory can be discussed in terms of basic equations of motion, simplified even further by the fact that the rocket rises in the air for a few seconds after which the flight is prematurely terminated when the pyrotechnic effects are released.

Distance Travelled with Uniform Acceleration

If a rocket moves in a straight line with uniform acceleration ' a ' and the velocity increases from a value ' u ' to a value ' v ' in a time, ' t ', then from the definition of acceleration:

$$a = \frac{v - u}{t}$$

from which

$$v = u + at \quad (3.10)$$

Now if a rocket with a velocity u accelerates with a uniform acceleration a , for a time t and attains a velocity v , the distance s travelled by the rocket in the time t is given by

$$\begin{aligned} s &= \text{average velocity} \times t \\ &= \frac{1}{2}(u + v) \times t \\ \text{but } v &= u + at \\ \therefore s &= \frac{1}{2}(u + u + at)t \\ \therefore s &= ut + \frac{1}{2}at^2 \end{aligned} \quad (3.11)$$

From which it can be seen that a rocket with an initial velocity of 25 m s^{-1} and a uniform acceleration of 10 m s^{-2} with a flight time of 3 seconds will cover a distance of 120 m in vertical flight *i.e.*

$$s = 25 \times 3 + \frac{1}{2} \times 10 \times 3^2 = 120 \text{ m}$$

Motion Under Gravity

The theoretical distance of 120 m can never be realised in practice as the distance travelled according to equation (3.11) will only apply theoretically. Hence the gravitational acceleration ($g = 9.8 \text{ m s}^{-2}$) must be taken into account as shown by equation (3.12)

$$s = ut + \frac{1}{2}at^2 - \frac{1}{2}gt^2 \quad (3.12)$$

So that the distance travelled under gravity becomes

$$s = 25 \times 3 + \frac{1}{2} \times 10 \times 3^2 - \frac{1}{2} \times 9.8 \times 3^2 \quad \text{or} \quad s = 75.9 \text{ m}$$

The Trajectory in the Atmosphere

In addition to gravity, atmospheric forces act on the ascending rocket, which unlike gravity are surface forces. The surrounding atmosphere flows along the surface of the rocket when in flight. A pressure force is exerted perpendicular to each surface element due to the adhesion of air molecules on the surface, while frictional forces arise in a tangential direction, in accordance with the internal friction of the air.

Air resistance (or drag) is quantified by a dimensionless drag coefficient which is related to the external configuration of the rocket. Other factors that influence drag being the air density, the diameter of the rocket and the square of the rocket velocity.

Allowing for a drag correction of 0.9 in the modest velocity and acceleration of the small firework rocket as described above results in a reduction in the distance travelled from 75.9 m to 63.4 m.

For firework rockets the most important factors include the weight of the rocket, the weight of the propellant, the specific impulse of the propellant and the shape and size of the rocket.

In summary, the rocket motor acts as a gas generator whose force is sufficient to overcome the combined effects of gravity and the drag which act in a direction opposite to the flight path. Stability in flight is crudely provided by the stick or tail that ensures the centre of gravity is forward of the centre of pressure. At the centre of pressure the combined effects of cross-wind force (perpendicular to the direction of motion) and the drag force act to restore the tail-stabilised rocket to alignment with the motion of the centre of gravity. Look at a firework rocket carefully and you will see it 'shuttlecock' into the wind, by virtue of the tail (Figure 3.4).

ROCKET DESIGN AND MANUFACTURE

In the United Kingdom, rockets currently available range in size from very small fireworks weighing upto 20 g (which are available to the general public) to professional display types, (as shown in Figure 3.5) which weigh in excess of 150 g.

The latter show multi-effects including coloured floral bursting patterns, crackle, glitter, rain and stars, while maroon-type rockets are commonly used to signal the start or finish of a display.

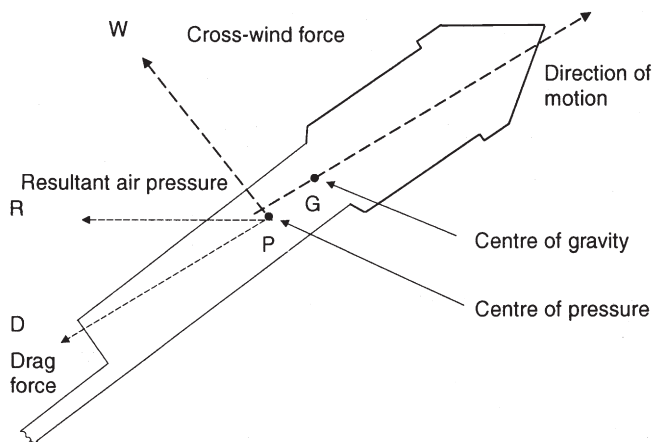


Figure 3.4 Forces acting on a firework rocket.



Figure 3.5 Firework girls plus rockets. Pains Mitcham *ca.* 1926.
(Courtesy of Pains Fireworks Ltd.)

A range of professional display rockets is also illustrated in Figure 3.6.

A typical formula for a silver star would contain meal gunpowder (72% by weight) antimony sulfide (16%), aluminium powder (5%) and dextrin (7%) while golden twinkler stars can be made from a mixture

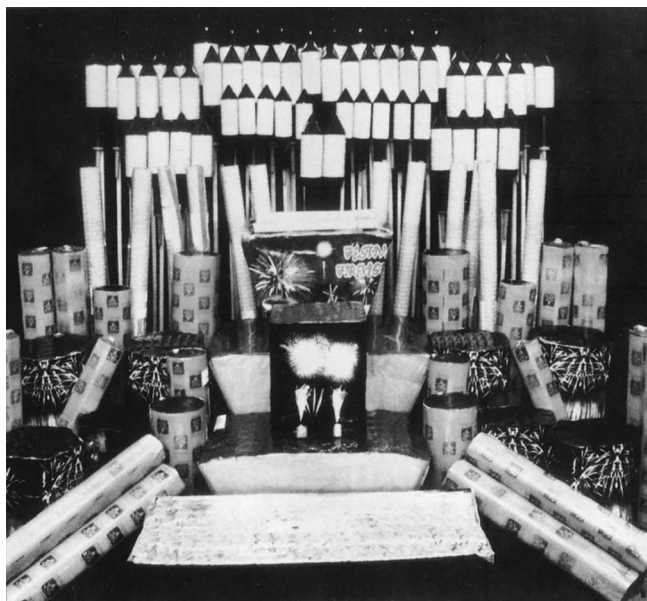


Figure 3.6 Professional rocket pack *ca.* 1990.
(Courtesy of Pains Fireworks Ltd.)

containing meal gunpowder (58%), aluminium powder (4.5%), antimony sulfide (24.5%) sodium oxalate (6%) and dextrin (7%).

For the more adventurous, parachute rockets are available in 22 and 25 mm calibre, or even ‘festoons’ or bag rockets with sticks up to three metres in length. The latter are definitely fired individually!

In manufacture, fuel-rich gunpowder is pressed in increments into the rocket case (or motor) using a long tapering spigot, which, upon withdrawal, leaves a charge with a central hole or conduit tapering outwards towards the nozzle (or choke). This provides a surface area of propellant necessary for the rapid generation of thrust on ignition as described previously. The case is either constricted or a clay nozzle is pressed at the end of the motor, which is then closed off with a length of safety fuse through the nozzle and an outer wrapping of protective paper applied.

When a thunderflash effect is required, a square of touch-paper is placed on the rear propellant surface inside the case at the opposite end to the choke, and a ‘hairpin’ of safety fuse is placed inside the case in contact with the square of touch-paper. Some flash composition, based on potassium perchlorate, barium nitrate and aluminium, is then poured around the safety fuse and the head of the case is closed off with a pressing of clay or by simply being taped over. The all-important stick is

then glued to the outside of the case using the wrappings of the paper label for support.

With larger payloads, such as those containing stars, a plastic cone is normally employed and is designed to be integral with the flight tube. The rocket motor can be pre-pressed into a cardboard motor tube and the whole thing inserted as a cartridge grain before being choked and fused in the normal way.

Inside the plastic cone at the head of the rocket might be a payload of small green stars, each about the size of a pea, based on a composition containing barium nitrate (36%), potassium chlorate (48%), shellac (13%) and dextrin (3%).

A recognised method of making stars is by tumbling the suitably dampened composition in a large barrel until the current sized spheres are formed. Figure 3.7 shows equipment being used for tumbling stars for Wells rockets *ca.* 1968.

A length of match or a pressing of delay fuse connects the rocket motor with the payload so that when the motor burns-out the fuse is lit and communicates with an ejection charge of gunpowder which ignites and ejects the stars.

A schematic diagram of a 35 mm bouquet rocket is presented in Figure 3.8.

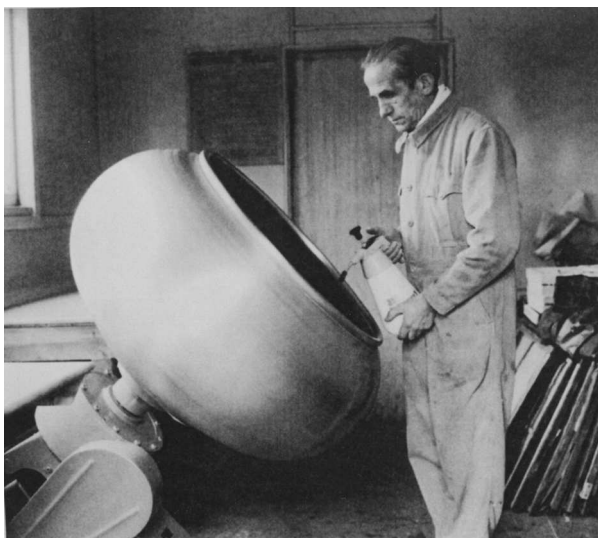


Figure 3.7 Tumbling stars for Wells rockets *ca.* 1968.
(Courtesy of Pains Fireworks Ltd.)

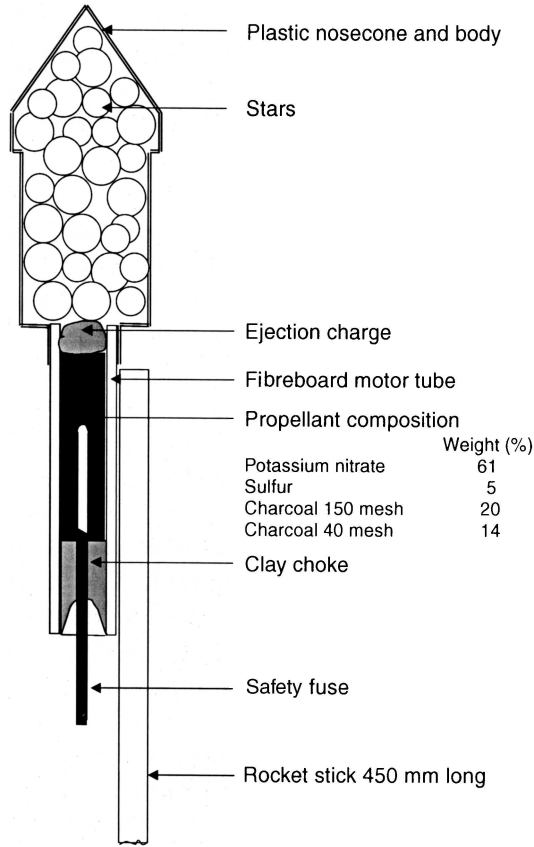


Figure 3.8 Bouquet rocket.

Parachute rockets work on much the same principle, except that the ejection charge pushes out a tube of flare composition, or any other composition, which is connected to the parachute which itself is folded beneath the end-cap at the top of the rocket.

FURTHER DEVELOPMENTS

Obviously, solid rocket propellant compositions have advanced considerably since the days of gunpowder, and it might be mentioned, in passing, that even as late as the Second World War, the Allies held the deluded belief that the large rockets being developed by the Germans were based on solid propellant. However, if one calculates the amount of solid propellant required to lift a payload consisting of one ton of high

explosive plus all of the hardware associated with the rocket, one arrives at an impossibly high all-up weight. It was therefore (incorrectly) argued that the V2 must either have a trivial payload or that the range must be insufficient for the weapon to reach London.

The firework mentality also decreed that even if the range was achievable, in order for an unguided rocket to follow a rainbow trajectory across the English Channel and fall, under gravity, onto London, the launch angle would have to be impossibly precise – about half a degree from the vertical, in fact.

Both arguments were flawed, of course, and Allied Intelligence later showed that the 14 ton V2 rocket bomb was in fact powered with liquid propellant, was guided using gyroscopes, and did indeed carry one ton of explosive. And on the 3rd September 1944 the first V2 fell on London. Some ‘firework’!

Perhaps the most extreme gunpowder rockets are the Japanese “Ascending Dragon” or RYUSEI Skyrockets which are launched in Japan on 10th October in celebration of Health–Sports Day.

The largest RYUSEI rocket is said to be 18m in length and weighs around 40 kg (sic). Built in three sections; the head or payload section holds sequential fireworks and smoke dragons attached externally, while the combustion chamber is made from split pine logs, gouged out and then re-assembled to make a cylinder.

Up to 5 kg of gunpowder mixture comprising saltpetre (10) charcoal (2) and sulfur (1) is packed into the pine cylinder where a blasting hole (nozzle) is bored at the bottom of the cylinder.

Dried bamboo is used to produce the stabiliser or tail and this completes a very simple but undeniably large firework rocket.

Parachutes deploy at the 300 m, or so, maximum altitude, the timing of the effects being set by fuses.

The Japanese RYUSEI rockets represent a cultural tradition. However, the technology involved in achieving the timing of the effects is said to remain the secret of each RYUSEI group, as is much of the construction.

Although gunpowder remains the propellant of choice for the production of firework rockets, there has been development on military compositions since the beginning of the 19th century, notably in Europe.

Of these, the most successful appeared in 1887 when Alfred Nobel patented a nitrocellulose propellant plasticised with nitroglycerine. Known as a double-base propellant, it is virtually smokeless, with a very high specific impulse as compared to gunpowder. Single-base propellants were developed in 1865 and 1890 by Schultz and Vieille respectively and these took the form of gelatinised nitrocellulose for use in firearms and mortars.

In the 20th century, two World Wars saw the introduction of improved solid propellants for military weapons, including rockets. Extruded double-base propellant gave good combustion at low chamber pressures but high values of the pressure exponent, n , led to large variations in thrust and chamber pressure when the ambient temperature varied. In order to overcome this disadvantage composite propellants were developed but, unlike gunpowder, more powerful oxidisers were employed, such as ammonium perchlorate.

At the same time binders were introduced which gave mechanical integrity to the grains as well as acting as fuels. The list of fuel/binders used in solid propellant rockets is extensive and has ranged from asphalt/oil mixtures to polybutadiene rubbers.

A propellant suitable for a small firework motor in modern times has been claimed to be epoxy resin in conjunction with potassium perchlorate as oxidiser.

The wet mixing of the prepolymer components with the powdered oxidiser was said to result in a safer process and gave an extrudable material which could be loaded and cured at moderate temperatures.

A typical propellant composition in relation to the above was given as potassium perchlorate (72%), copper(II) oxide, burn rate enhancer (1.4%), potassium benzoate, fuel (10.9%), charcoal, fuel (5.4%) and epoxy resin (9.6%).

There is nothing to prevent the firework manufacturers from using military-type propellants, of course, and this is exactly what the Russians are said to do when making rockets to reach astonishing heights in firework displays above the tall buildings in Moscow.

Military propellants are based on relatively powerful oxidisers and fuels of high calorific value in order to develop an improved thrust or impulse. Thus the most commonly-used oxidisers are potassium perchlorate, ammonium perchlorate or more esoteric compounds such as hydrazinium nitroformate. Metallic fuels include aluminium, magnesium and beryllium, while binders are mainly hydrocarbons such as polybutadiene, polyisobutylene, polyurethane or poly(vinyl chloride) (PVC) as presented in Table 3.2.

Table 3.3 shows some properties of the most common inorganic oxidisers and their relative efficiencies based on their reaction with carbon.

It will be seen that the variation in density brings about significant differences depending on whether the oxygen content is compared on a mass or volume basis.

But the oxygen content is only a partial guide to the potential of an oxidising agent in a propellant. The percentage of oxygen actually

Table 3.2 Examples of ingredients used for composite propellants.

<i>Oxidiser</i>	<i>Formula</i>
Ammonium perchlorate	NH_4ClO_4
Ammonium nitrate	NH_4NO_3
Potassium perchlorate	KClO_4
Nitronium perchlorate	NO_2ClO_4
<i>Binder</i>	
Polysulfide	$(\text{C}_2\text{H}_4\text{S}_4)_n$
Poly(vinyl chloride)	$(\text{C}_2\text{H}_3\text{Cl})_n$
Polyurethane $[\text{O} \cdot (\text{CH}_2)_4 \text{OOCNH} \cdot (\text{CH}_2)_6 \text{NHCOO} \cdot (\text{CH}_2)_4 \text{O}]$	$(\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_6)_n$
<i>Curing or bonding agents</i>	
Toluene-2,4-diisocyanate	$\text{C}_9\text{H}_6\text{N}_2\text{O}_2$
Triethanolamine $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$	$\text{C}_6\text{H}_{15}\text{NO}_3$
<i>Metal fuel</i>	
Aluminium	Al
Magnesium	Mg
Beryllium	Be

Table 3.3 Some properties of oxidising agents used in composite propellants.

<i>Oxidiser</i>	<i>Density</i> g/cm^3	<i>Oxygen</i> <i>Content g/g</i>	<i>Oxygen Content</i> g/cm^3	<i>% Available</i> <i>Oxygen</i>
Ammonium nitrate	1.73	0.60	1.01	33
Ammonium perchlorate	1.95	0.55	1.07	50
Potassium nitrate	3.1	0.48	1.00	50
potassium perchlorate	2.52	0.46	1.16	100
<i>Reaction with Carbon</i>			<i>Volume of Gas</i> <i>Liberated at</i> <i>STP cm³/g</i>	<i>Heat of</i> <i>Reaction cal/g</i>
$\text{NH}_4\text{NO}_3 + \text{C} \rightarrow \text{N}_2 + \text{CO} + 2\text{H}_2\text{O}$			975	587
$\text{NH}_4\text{ClO}_4 + 2\text{C} \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{Cl}_2 + 2\text{H}_2\text{O} + 2\text{CO}$			789	634
$\text{KNO}_3 + 2\text{C} \rightarrow \frac{1}{2} \text{K}_2\text{CO}_3 + \frac{1}{2} \text{N}_2 + 1\frac{1}{2} \text{CO}$			358	472
$\text{KClO}_4 + 4\text{C} \rightarrow \text{KCl} + 4\text{CO}$			479	525

available for combustion of the fuel/binder is also important, meaning that these two essential ingredients must be compounded in the correct ratio where, in theory, there should be just sufficient fuel to completely reduce the oxidising agent.

In regard to the ammonium salts, the relatively small proportions of available oxygen in these salts is due to the fact that they act on their own fuels to some extent, and can therefore be classed as propellants in their own right.

The reaction of the oxidisers in Table 3.3 with carbon is included because the simple equations lead to a useful insight as to the volumes of gases which will be produced by combustion with the optimum quantity of a fuel.

With the advent of computers, the many product species arising from the combustion of a fuel and oxidiser can be predicted very precisely by entering details of the propellant ingredients into an appropriate program. At the same time thermodynamic data can be obtained, making due allowance for the complication that the combustion processes take place at very high temperatures.

In any event, it is clear from Table 3.3 that potassium nitrate is inferior to potassium perchlorate and the ammonium salts in terms of the volume of gas liberated at STP, the heat of reaction with carbon and the minimalisation of smoke (*i.e.* solid products).

If smokelessness is required, then a double-base propellant can be used. Most of the military propellants enjoy about three times the specific impulse of gunpowder and are deliberately formulated to be fuel-rich so that the exhaust tends to contain carbon monoxide in preference to carbon dioxide, which is a heavier gas. Lighter gases are preferred because they can be accelerated to higher velocities through the nozzle and this factor contributes to a higher value of specific impulse. On the other hand, solid propellants based on gunpowder produce carbon dioxide as well as large quantities of smoke, neither of which are conducive to high values of thrust or impulse.

The superiority of double-base propellant as compared to gunpowder is clearly reflected in the properties of the two products. For example the heat of reaction is about 900 as opposed to 700 calories g^{-1} , while the volume of gas produced is around 950 in comparison to 370 $\text{cm}^3 \text{ atm g}$ at STP. The flame temperatures are listed as 3200 K and 2700 K respectively, while the specific impulse is about 1800 for smokeless propellant and 600 N s kg^{-1} for gunpowder.

But who wants to see a supersonic rocket full of smokeless propellant disappear into the heavens like a flash of light when one can witness the leisurely ascent of a firework rocket as it climbs leaving a graceful trail of sparks?

CHAPTER 4

Mines and Shells

CALIBRES

Without doubt, mines and shells are the most important of the display fireworks in the operator's arsenal: shells give the well known spectacular aerial effects, while mines operate from ground level often as a supplement to the shells.

Although the most common calibres of the mortar tubes associated with these fireworks are 50, 75 and 100 mm, the size of shells seems to know no limit – the record at the moment stands at a calibre in excess of 1 metre or 1000 mm. Obviously, where such astonishingly large devices are concerned, the mortar tubes are no longer made from simple overlapping spirals of Kraft paper but preferably of stainless steel!

Figure 4.1 illustrates a range of shells and mortar tubes from 50 to 125 mm calibre, although these are no longer available to the general public.

CONSTRUCTION OF SHELLS

The shell itself is a clever arrangement of stars built inside a spherical or cylindrical cavity, at the centre of which is a bursting charge of gunpowder or similarly forceful powder. A further quantity of gunpowder, held in a paper pouch, is located outside the base of the shell, and this acts as the lifting charge when ignited by a length of piped match that projects out of the pouch to run from the bottom of the mortar tube, where the shell lies, to the top of the tube where it can be lit using a fuse



Figure 4.1 50, 75, 100 and 125 mm shells plus mortars, *ca.* 1990 (but no longer available to the general public).
(Courtesy of Pains Fireworks Ltd.)

extension. When the match is lit, the gunpowder in the pouch is caused to explode, thereby driving the shell out of the mortar tube and up into the sky. Figure 4.2 shows the construction of a typical 75 mm shell.

A length of delay fuse connects to the inside of the shell and this fuse is lit from the primary explosion. After a delay of several seconds, and ideally when the shell has reached maximum height, the connecting fuse delivers its flame to the gunpowder bursting charge, which promptly explodes, igniting the ball of stars and driving them outwards, with approximately equal force, in the form of a rapidly-expanding ball, a flash or any other desired effect.

The shell case can be made from paper or plastic. For a given calibre, the cylindrical shell holds more stars and is the more straightforward to produce, especially when multiple breaks are required. The much revered ten-break shell (yes, it does burst ten times in the sky!) comprises separate compartments, each connected with a delay fuse to give sequential exploding effects during the flight of the shell. Of course,

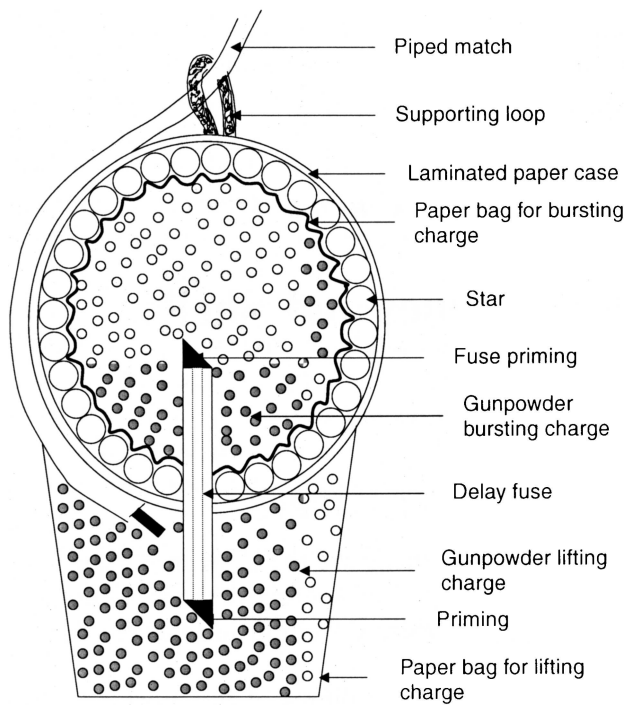


Figure 4.2 Schematic representation of a 75 mm chrysanthemum shell.

multiple bursts can be achieved by using stars that explode during burning – a sort of star within a star – but that is not to detract from the skill and ingenuity and time involved in the making of complex fireworks such as star shells.

Early methods of construction of shells involved the fabrication of hollow spheres using paper strips pasted together in moulds. However, it was difficult to obtain an even burst in this way because, depending on where the joins were located in the shell case, the bursting shell was prone to form non-symmetrical fragments.

Modern methods of shell construction ensure an even distribution of stars on bursting by paying particular attention to the bursting charge in relation to the strength of the shell case. For example, a weak outer case can be adequately burst by a relatively small gunpowder charge. On the other hand, a strongly-made case must be burst by a charge that expands more slowly. Plastic has replaced paper in the manufacture of many round shells which, besides being waterproof, offers the advantage of unit construction whereby the lifting charge may also be contained inside the plastic case.

The most spectacular effects are achieved using cylinder shells in which cylindrical ‘parcels’ are filled with stars, whistles or hummers contained within separate compartments. The difficulty in producing cylinder shells arises from the many operations during manufacture, which include forming the cylinder from paper and cardboard discs, loading the stars, adding lifting charges and fuses, and closing the ends of the cylinder before wrapping the entire unit with string (spiking) to provide an even burst before adding outer layers of Kraft paper to cover the string.

In the fabrication of a multi-break shell such as a three-colour ‘traffic light’ effect, the cylindrical outer case contains three separate compartments in which stars giving red, amber and green effects can be separately loaded.

But the net effect of producing a shell with extra compartments is to make the firework longer and heavier, which in turn dictates an increased gunpowder lifting charge. The stresses on launch are therefore considerably increased, meaning that extra care and expertise is required if the construction and functioning of these large fireworks is to be entirely successful.

In comparison to a spherical shell, a cylinder shell can look decidedly complex to build, as the diagram of a 100 mm three-break firework shows (Figure 4.3).

The method of construction is virtually the same for multi-break shells of all sizes of which a 100 mm, three-colour shell is a typical example.

In essence, three colour compartments (or ‘breaks’) are filled separately, and tied with string (‘spiked’) before stacking one upon the other. The bottom and second breaks are then spiked together after which the first (*i.e.* top) break is spiked on top of the other two.

Pressed gunpowder delay fuses are initially prepared, the top fuse being charged with 25 mm of powder (for a longer burn time) while the remaining two fuses contain about 18 mm of powder each.

The bottom colour compartment is next prepared by rolling 150 mm strips of Kraft paper to make the cylinder, finishing with a solid bottom disc with the paper folded over it.

A paper support tube of about 25 mm diameter is then placed centrally inside the compartment while green stars are filled around it and carefully consolidated. The gunpowder bursting charge is next filled inside the support tube after which the support can be withdrawn. Extra powder can be sprinkled among the stars if preferred before the compartment is levelled and closed with an 18 mm delay fuse and disc. The overhanging Kraft paper is folded over the top of the disc thereby holding it in place and a second disc added before spiking vertically to hold the completed compartment together.

The next step is to build the middle compartment (holding the amber stars). This is accomplished, and fused, in much the same way as that

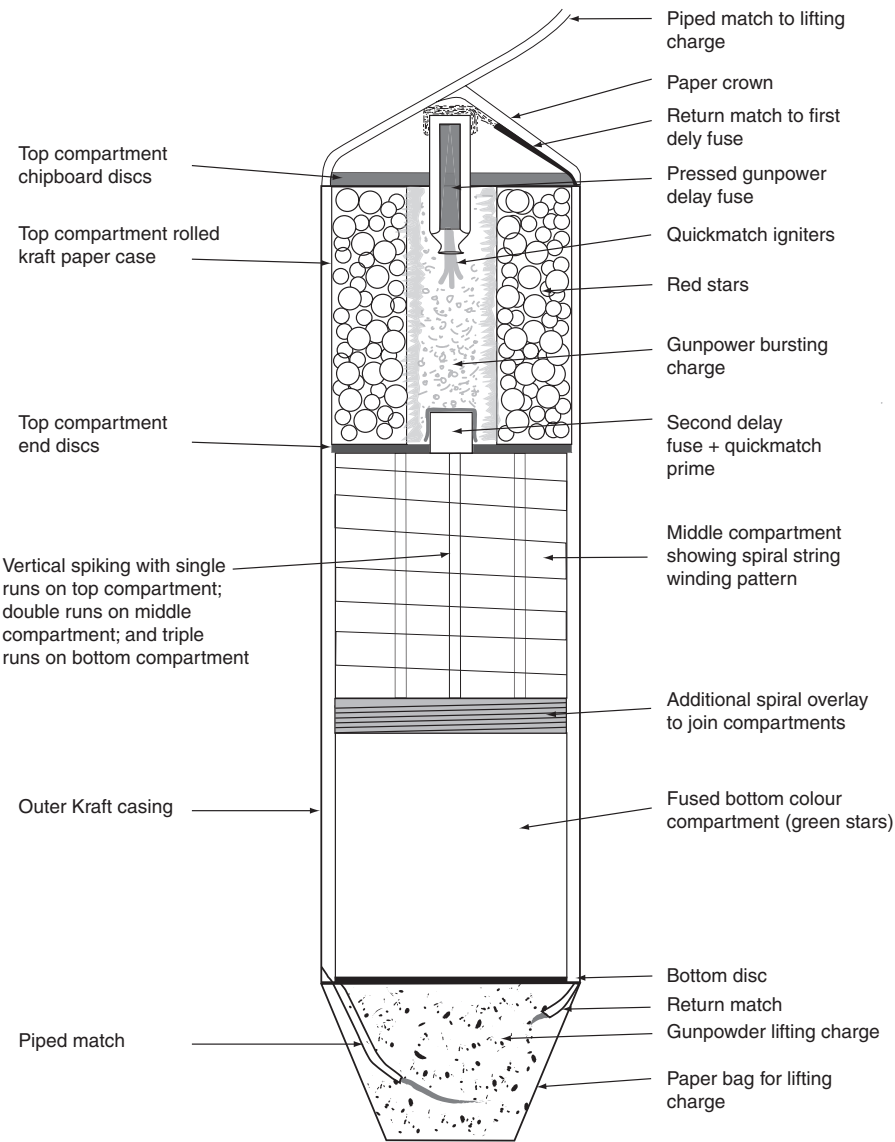


Figure 4.3 Schematic representation of a 100 mm three-break colour shell.

described above except that this compartment contains amber stars and is closed off with a punched disc in order to accommodate the delay fuse primed with quickmatch that projects from the lower compartment. Vertical strings are then laid over the bottom and middle compartments, thereby spiking them together.

After this the first break (*i.e.* top compartment) is prepared, this time being filled with red stars. It is closed using the 25 mm delay fuse and punched discs, before applying more vertical string to spike the stack of three breaks together. Great care is needed at this stage because overlap of the vertical strings, especially on the bottom break (which has received three times as many runs as the top break) will cause enlargement of the diameter at the bottom, making accurate rolling of the outer sheet of Kraft paper extremely difficult.

Finally, the string is laid as a spiral from top to bottom, in a single turn before spiking upwards according to the pattern shown in Figure 4.2, then extra Kraft paper is pasted over the strings to complete the outer case of the shell, and the gunpowder lifting charge is loaded, together with quickmatch fuse. The lift charge consists of about one part by weight of powder for every fifteen parts of shell mass.

FUNCTIONING OF SHELLS

When a three-break shell, such as that described above, functions, it comes apart in the opposite order to which it is assembled, as discussed below.

Initially the main piped match fuse is lit and a fraction of a second later the flame from this fuse reaches the gunpowder lift charge in the bag at the base of the shell.

The gunpowder explodes in a further fraction of a second, the explosion blowing the shell out of the mortar tube in the manner of a shot from a cannon. At the same time a return section of piped match is lit by the explosion, transferring flame back to the top compartment where it reaches the quickmatch placed across the head of the 25 mm pressed delay fuse.

During this time the shell is tumbling in approximately vertical flight, the fuse in the first delay burning through and igniting the gunpowder bursting charge in the top compartment. This second explosion results in ejection (and ignition) of the red stars and is timed to occur near the apogee of the shell's flight.

Almost simultaneously the second fuse is lit by the top break explosion, the burning of this fuse being timed to ignite the gunpowder in the middle compartment just as the red stars are burning out.

In this way the amber stars are ignited and ejected while the third, and final, delay fuse is also burning.

The amber stars then burn out, to be replaced by ejected green stars from the lower compartment, while the remains of the shell are still at a safe height with respect to the spectators on the ground.

Figure 4.4 shows shell stars bursting above fans of Roman candles.



Figure 4.4 Shells and Roman candles.
(Courtesy of Pains Fireworks Ltd.)

Internal Ballistics

Having outlined the form and function of two typical star shells we can now attempt to quantify some of the ballistic effects that give rise to the performance of these spectacular fireworks.

In using gunpowder as a lifting charge for a shell, the propellant is being required to deliver its gas over a much shorter time interval than that employed in a rocket. In consequence, the geometrical form of the propellant is quite different, as is the propellant composition. The internal ballistics calculations call for the introduction of gun-type parameters that would be less appropriate in studying rocket motor ballistics. These include the propellant co-volume (the volume occupied by the combustion products), the geometrical form coefficient (the shape and size of the propellant grains) and the vivacity (quickness) of the propellant, together with the cross-sectional area of the mortar tube and the mass of the shell.

Table 4.1 Some gunpowder properties used in ballistics calculations.

Composition (%)	KNO ₃ 74.3, charcoal 15.3, sulfur 9.4, moisture 1.0
Grain size (mm)	1.0–1.2
Force, $f = nRT$, (kg m kg ⁻¹)	3837
Vivacity, A (s ⁻¹)	4.17
Heat of explosion, Q (kJ)	1550
Explosion temperature, T (K)	2050
Evolved gas volume per kg at STP, V (dm ³)	404
Burning rate equation	$R_B = 2.5p^{0.5}$

Table 4.1 gives examples of the properties of a typical lifting charge propellant. Note that the composition is no longer fuel-rich, but is balanced for ‘quickness’. The explosive force, f , is defined as the working performance per kg, theoretically calculated from the general equation of state for gases: $f = PV = nRT$ where P is the pressure, V is the volume, n is the number of moles of the explosion gases per kg, R is the ideal gas constant and T is the absolute temperature of the explosion.

Pressure in the Mortar Tube. The maximum pressure generated in the mortar tube has been shown to be related to the ballistic parameters presented in equation (4.1),

$$P_m = \frac{Af}{AG(1/\Delta) - \eta} (D_m) \quad (4.1)$$

where P_m is the maximum pressure generated (kg dm⁻²), A is the vivacity or quickness of the propellant (s⁻¹), Δ is the loading density of the propellant (kg dm⁻³), f is the explosive force of the propellant (kg m kg⁻¹), G is the grain shape function, η is the propellant co-volume (dm³) and D_m is the pressure function for maximum pressure (kg dm⁻²).

Substituting typical values into equation (4.1) enables an estimate of the maximum mortar tube pressure to be made [equation (4.2)],

$$P_m = \frac{4.17 \times 3837}{4.17 \times 0.051} \times \frac{1}{(1/0.104) - 0.55} (0.212) \quad (4.2)$$

from which $P_m = 1750$ kg dm⁻², or 17.5 kg cm⁻², or about 250 psi.

Burning Time of the Propellant. At a maximum generated pressure of 250 psi, the burning time of the propellant can be estimated from the

linear burning rate, equation (4.3):

$$R_B = 2.5p^{0.5} \quad (4.3)$$

Thus,

$$R_B = 2.5 \times 250^{0.5} \quad (4.4)$$

and therefore

$$R_B = 39.5 \text{ mm s}^{-1}.$$

If the propellant grain size averages 1.1 mm, then the average radius (or web size) = 0.55 mm. At a rate of burning of 39.5 mm s^{-1} , the average burning time, T_B , will be given by equation (4.5):

$$T_B = \frac{\text{web size}}{R_B} = \frac{0.55}{39.5} = 0.014 \text{ s or } 14 \text{ ms} \quad (4.5)$$

Therefore, the pressure–time curve for the combustion of the gunpowder lifting charge will be approximately as illustrated in Figure 4.5.

When ignited, the lifting charge causes the gas pressure behind the shell to rise and the rate of rise increases rapidly as the burning of the charge progresses. The maximum rate of rise of pressure is about $30\,000 \text{ psi s}^{-1}$. About 14 ms after initiation of the charge, the pressure reaches its maximum value when the rate of increase of pressure due to the burning of the charge is equal to the rate of pressure reduction due to the movement of the shell and ‘leakage’ of gases past the shell providing an increasing volume into which the gases can expand. After this, the pressure gradually decreases as the shell travels towards the muzzle of the mortar tube and then falls to zero after the shell leaves the tube.

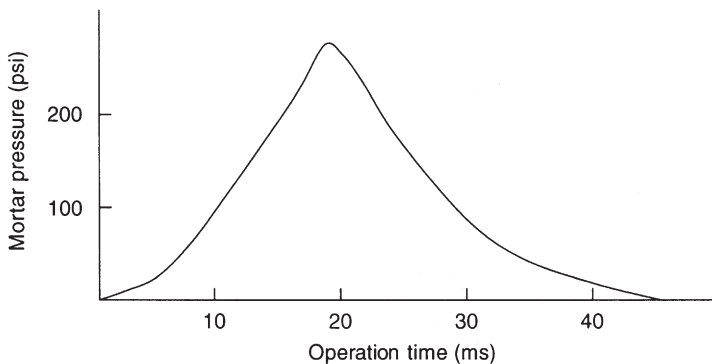


Figure 4.5 Approximate pressure–time curve for combustion of lifting charge within a mortar tube.

Muzzle Velocity of the Shell. A further equation based on gun ballistics has been proposed that allows an estimation to be made of the muzzle velocity of a shell [equation (4.6)],

$$V = \frac{1}{AG} \times \frac{\sigma}{\mu} (W) \quad (4.6)$$

where V is the estimated muzzle velocity (dm s^{-1}), σ is the cross-sectional area of the mortar tube (dm^2), μ is the assumed mass of the shell (kg), W is the velocity function ($\text{kg}^{-1} \text{s}^{-2}$) and A and G have the definitions as listed for equation (4.1).

Substituting appropriate values into equation (4.6) gives the muzzle velocity of the shell as in equation (4.7):

$$V = \frac{1}{0.213} \times \frac{1.81}{0.0132} \times 1.97 = 1270 \text{ dm s}^{-1} \quad (4.7)$$

or

$$V = 127 \text{ m s}^{-1}$$

External Ballistics

The simplest external ballistics calculation is that in which a shell is fired vertically. This type of calculation has also been extended to include the case where a ‘dud’ shell falls back to earth.

Equations (4.8)–(4.15) show how the altitude attained and time of flight can be estimated from basic parameters and Newtonian Laws of Motion.

Altitude Attained. First, the surface area (S) of the shell cross-section is calculated using equation (4.8),

$$S = \pi d_B^2 / 4 \quad (4.8)$$

where d_B is the diameter of the shell (m). Hence,

$$S = 3.142(0.136)^2 / 4 = 0.0145 \text{ m}^2.$$

Secondly, the ballistic parameter, a , is determined from equation (4.9),

$$a = \sqrt{p_B / KS} \quad (4.9)$$

where p_B is the mass of the shell (kg) and K is the coefficient of air resistance ($\text{kg s}^2 \text{m}^{-4}$). The latter is proportional to the mass of air which the projectile must displace per unit of time.

Substituting values into equation (4.9) enables the ballistic parameter to be calculated:

$$a = \sqrt{1.252/0.031 \times 0.0145} = 52.8 \text{ m s}^{-1} \quad (4.10)$$

Thirdly, the altitude parameter, x , is calculated using equation (4.11),

$$x = V_1/a \quad (4.11)$$

where V_1 is the muzzle velocity of the shell from equation (4.7) and a is the ballistic coefficient from equation (4.10). Therefore,

$$x = 127/52.8 = 2.40 \quad (4.12)$$

We must now turn to ballistics tables such as Table 4.2 to determine the ratio of altitude:muzzle velocity squared.

From Table 4.2 it can be seen that a value of x of 2.40 corresponds to a H/V_1^2 ratio of 0.0169. Knowing the muzzle velocity of the shell (127 m s^{-1}) enables an estimate of the maximum altitude to be made as in equation (4.13):

$$H = 0.0169 \times V_1^2 = 0.0169 \times 127^2 = 273 \text{ m} \quad (4.13)$$

Time of Flight. The time of flight (T) of the shell is determined from equation (4.14),

$$T = \left(\frac{a}{g}\right) \arctan \frac{H}{V_1^2} \quad (4.14)$$

Table 4.2 The ratio of altitude: muzzle velocity squared for the altitude parameter, x .

x	$H/V_1^2(\text{m}^{-1} \text{ s}^2)$	x	$H/V_1^2(\text{m}^{-1} \text{ s}^2)$
0.20	0.0500	2.20	0.0186
0.40	0.0473	2.40	0.0169
0.60	0.0438	2.60	0.0155
0.80	0.0394	2.80	0.0142
1.00	0.0354	3.00	0.0131
1.20	0.0316	3.20	0.0121
1.40	0.0283	3.40	0.0112
1.60	0.0253	3.60	0.0104
1.80	0.0228	3.80	0.0097

where g is the acceleration due to gravity (kg m s^{-2}) and a , H and V_1 are as defined previously. Hence:

$$T = \left(\frac{52.8}{9.80} \right) \arctan 0.0169 \quad (4.15)$$

or

$$T = 5.39 \times 0.97 = 5.2 \text{ s}$$

Descent of a 'Dud' Shell. Approximate estimates for the rate of descent if a shell fails to explode can be found by extending the data obtained in the previous section, *i.e.*:

$$H = 273 \text{ m} \quad \text{and} \quad a = 52.8 \text{ m s}^{-1}$$

Three equations (4.16)–(4.18) govern the rate of descent,

$$-H = \frac{2.303}{2g} |a|^2 \log(1 - z^2) \quad (4.16)$$

$$-V_2 = az \quad (4.17)$$

$$T_2 = \frac{2.303}{2g} |a| \log \left(\frac{1 - z}{1 + z} \right), \quad -1 < z < 0 \quad (4.18)$$

where H is the fall height (m), z is a ballistic parameter, V_2 is the falling velocity at the ground (m s^{-1}) and T_2 is the fall time (s).

Therefore, from equation (4.16),

$$\log(1 - z^2) = \frac{-2gH}{2.303a^2} = \frac{-2 \times 9.80 \times 273}{2.303 \times 52.8^2} = -0.833$$

$$(1 - z^2) = 0.147, \text{ i.e. } z = -0.924$$

and from equation (4.17),

$$-V_2 = az = 52.8 \times (-0.924) = -48.8 \text{ m s}^{-1}$$

Finally, the fall time is estimated by applying equation (4.18),

$$T_2 = \frac{2.303}{2 \times 9.80} (52.8) \log \frac{1 + 0.924}{1 - 0.924} = 8.7 \text{ s} \quad (4.19)$$

which tells us that if a 150 mm shell fails to explode, we have rather less than ten seconds in which to get out of the way!

Mortar Tubes

For display shells of 200 mm and above, reinforced fibreglass mortar tubes are invariably used. Welded steel tubes have long been considered to be amongst the safest because, in the event of a pressure-burst, the tube will split in the vicinity of the weld, thus creating a predictable danger zone. With seamless tubes the fragmentation is completely random and creates a shrapnel hazard for the fireworks operator.

Recent work in the USA has demonstrated that a high degree of safety can be achieved by using a tube within a tube, the concentric gap being filled with high-impact, expanded foam. Placing these tubes in a staggered formation in a metallic firing crate shows the assembly to be surprisingly resistant to damage, even when shells are deliberately exploded inside the tubes. The staggered arrangement prevents the explosion from communicating its effects with neighbouring tubes and shells.

Table 4.3 gives some estimates of the results to be expected from firing shells from 50, 75, 100 and 150 mm mortars.

In practice, a 120 mm shell can attain an altitude in excess of 200 metres in approximately five seconds and burst to give a spectacular effect stretching for perhaps 80 metres across the sky.

Large calibre shells, bursting at increasing altitudes, are illustrated in Figures 4.6, 4.7 and 4.8.

Table 4.3 Estimates of shell performance.

	<i>Shell size (mm)</i>			
	<i>50</i>	<i>75</i>	<i>100</i>	<i>150</i>
<i>Mortar fibreboard</i>				
Inside diameter (mm)	52	76	104	155
Length (mm)	350	420	600	1050
L : D ratio	6.73	5.33	5.76	6.77
Wall thickness (mm)	5	10	10	15
<i>Shell</i>				
Diameter (mm)	46	70	94	142
Weight (kg)	0.065	0.210	0.390	0.950
<i>Lift charge (black powder)</i>				
Weight (kg)	0.004	0.013	0.025	0.075
Weight ratio (powder : shell)	0.061	0.062	0.064	0.079
<i>Muzzle velocity ($m s^{-1}$)</i>	93	105	125	130
<i>Maximum altitude (m)</i>	90	110	130	275
<i>Rise time (s)</i>	3.7	4.0	4.1	5.4



Figure 4.6 Red chrysanthemum and silver wave shells.
(Courtesy of Pains Fireworks Ltd.)

Energy Transfer Efficiency

The gunpowder lifting charge beneath a shell provides a source of chemical energy, a proportion of which, depending on the efficiency of the mortar, is converted into kinetic energy in the shell.

However, in practice, the energy of the hot combustion products of the gunpowder is never fully utilised in providing forward motion to the shell. Losses occur unavoidably in several ways – as radiation; as residual energy of motion of the partially expanded gases; as leakage of gas around the shell and as wave motion (noise) in the surrounding atmosphere.

Modern guns are more than 30% efficient, relying on smokeless propellants (where the gas volume at STP is around $1000 \text{ cm}^3 \text{ g}^{-1}$, and heat of explosion is at least 3000 J g^{-1}). On the other hand, gunpowder will only produce about $400 \text{ cm}^3 \text{ g}^{-1}$ gas at STP, while the corresponding heat of explosion is approximately 1550 J g^{-1} .

Hence the efficiency, E , of black powder, in comparison to smokeless powder, as a gun propellant can be estimated on the basis of the above



Figure 4.7 Sunset Swing at Kew Gardens. Crackling palm shells.
(Courtesy of Pains Fireworks Ltd.)

data as:

$$E = \frac{400}{1000} \times \frac{1550}{3000} = 0.206 \quad \text{i.e. about 20\%}$$

The above estimate at least partly explains why early 12-bore gun cartridges, containing 82 grains (5.3 g) of black powder, could alternatively be loaded with 26 grains (1.7 g) of double-base powder to give similar ballistic performance.

In the case of a 75 mm star shell, fired by a 13 g lifting charge to give a muzzle velocity of 105 ms^{-1} , as listed in Table 4.3, the kinetic energy (KE) of the shell is given by equation (4.20).

$$\text{KE} = \frac{1}{2} m V^2 \quad (4.20)$$



Figure 4.8 Bouquet shells with star burst effects.
(Courtesy of Pains Fireworks Ltd.)

Therefore, the kinetic energy of the shell at the muzzle will be:

$$\frac{1}{2} \times (0.210 - 0.013) \times 105^2 = 1086 \text{ Joules or } 1.086 \text{ kJ} \quad (4.21)$$

where the mass of the shell at the muzzle allows for the loss of the 0.013 kg lift charge.

The muzzle energy can be compared with the overall explosion energy from the gunpowder lifting charge, which is typically about 1550 kJ kg^{-1} , and hence the available energy from the 0.013 kg lifting charge is $1550 \times 0.013 = 20.15 \text{ kJ}$. The energy transfer efficiency in firing the shell is therefore:

$$\frac{1.086}{20.15} \times 100 \cong 5.4\%$$

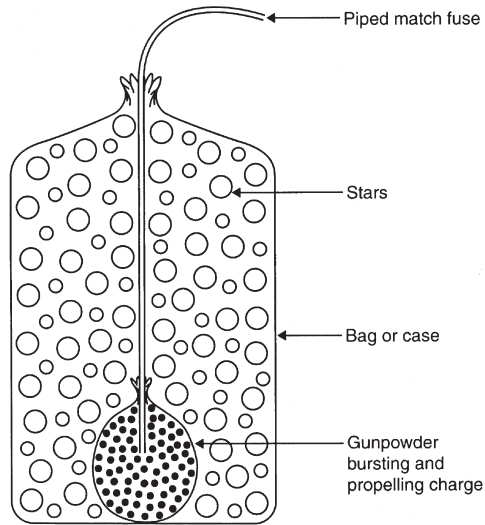


Figure 4.9 Schematic representation of a 75 mm mortar mine.



Figure 4.10 Shells and mines light up the night sky above the River Thames in London to celebrate the Spice Girls–Virgin Records contract. (Courtesy of Pains Fireworks Ltd.)

An efficiency of 5.4% might seem surprisingly low, but it should be considered within the context of the limitations presented above.

MINES

Mines, are essentially shells that burst at ground level, the mortar tubes being used to give the projectiles height and direction. They are available in the common shell calibres such as 75 mm (Figure 4.9) and can therefore be fired from a common set of mortar tubes. Indeed, if a shell does, for any reason, explode prematurely in its mortar tube the effect is known as ‘mining’.

Obviously, with no lifting charge and fewer compartments, the mine is a little simpler in construction than the shell, but the range of effects is equally varied and interesting and includes comets, stars, whistlers, hummers, fountains and serpents.

The modest height achieved with the above effects is especially effective when used in conjunction with salvos of shells (Figure 4.10) or as an alternative to shells in display venues where the height is restricted for any reason (Figure 4.11).



Figure 4.11 Mine launched serpents bore their way into the night sky.
(Courtesy of Pains Fireworks Ltd.)

CHAPTER 5

Fountains

COMPOSITIONS

Fountains are popular fireworks and range from small devices of only approximately 15 mm in diameter up to professional fireworks of 125 mm or more. They may be fired singly or in groups to provide, as the name suggests, a bright fountain of sparks. If a string of fountains is hung from a rope and fired in the inverted position, as is common practice in the UK, the plumes produce a waterfall effect which can last for several minutes. Similarly large devices can be angled on lofting poles up to eight feet tall or even mounted on revolving blocks to give an interesting spatial distribution of sparks. With the larger fireworks the blue touch-paper is replaced with a fuse or match that terminates in a depression pressed into the surface of the composition. While waterfall effects can be achieved with fountains, other waterfall units have thin cases which are designed to burn away as propellant is consumed.

Although the compositions used in fountains are usually based on black powder propellant, the sparks that are responsible for the fountain effect originate from other substances within the composition. These substances are known as ‘emitters’ and it is the physical and chemical properties of the emitters that determine the characteristics of the fountain. Various additives are also used to promote the visual effects or to cheapen the composition.

Broadly speaking, the components of the propellant react to produce hot combustion gases which heat up the particles of the emitter and eject them from the body of the firework. On contact with the air, the hot emitter particles ignite to produce the well known fountain effect as

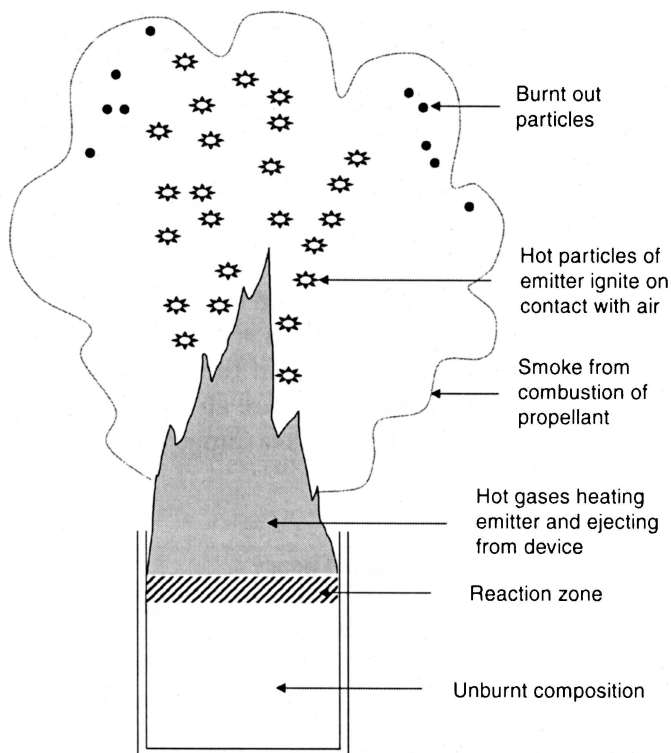


Figure 5.1 Diagrammatic representation of fountain combustion.

illustrated in Figure 5.1. Typical emitters which have been used in such fireworks include carbon, titanium, aluminium, iron or a magnesium/aluminium alloy. Antimony trisulfide (Sb_2S_3) is also commonly used to enhance the ‘glittering’ effect in a series of chemical reactions with the gunpowder and aluminium.

The following compositions reflect the use of some of the materials introduced above and the diverse nature of the effects which can be produced.

1. <u>Based on carbon</u>	Weight (%)
Gunpowder	84
Charcoal (150 mesh)	16

Gives a forceful emission of fire and sparks especially when used in a tube with a choke or nozzle.

2. <u>Based on iron</u>	Weight (%)
Potassium nitrate	54
Sulfur	9

Charcoal 400–100 mesh	13
Iron 60 mesh	24

Used in cones for gold sparks.

3. <u>Based on aluminium</u>	Weight (%)
Potassium chlorate	52.2
Potassium nitrate	8.7
Red gum	4.3
Aluminium # 810	17.4
Aluminium flitters # 812	17.4

Produces a cascade or waterfall effect.

4. <u>Based on titanium</u>	Weight (%)
Gunpowder	38
Potassium nitrate	28
Sulfur 40–80 mesh	27
Titanium 20–40 mesh	7

Can be used in a tube without a choke or nozzle, to give bright silver sparks.

But in order to gain a deeper understanding of how fountains work it is necessary to grasp the nettle of atomic theory and also of the electron.

Atomic Theory

Imagine an atom as a bubble magnified to an immense size (about the size of a small town). If you had the magical and perceptive powers of Alice in Wonderland you might penetrate the outer cover of the empty bubble and wander through its atmosphere which, on closer inspection, would be seen to be ‘not quite empty’.

Fuzzy little clouds of electrons would make blurred impressions on your imagination and you would feel powerful forces emanating from them. As you got closer to the centre of the bubble the forces would continue, until at the centre you would discover the nucleus – a quivering concentration of matter and energy about the size of a grape. On this scale the pips would represent the sub-atomic particles (including protons and neutrons) held together by enormous energy while the clouds of electrons would be at a distance of about 2 miles from the nucleus!

Now the protons carry positive charges, while the neutrons are electrically neutral. But nature has arranged things so that the negative

charges of the electrons are exactly balanced by the positive charges of the protons, thus keeping the atom ‘whole’.

The rest of the atom is sparsely populated but also vibrant and dynamic. The ghostly electrons are arranged in vague clouds and have no clearly defined position. Heisenberg’s Uncertainty Principle (1927) tells us that we can’t pin-point their positions. Instead, we have to talk in terms of the ‘probability’ of there being electrons of a certain energy in certain positions (or orbits) around the nucleus at certain times.

The most significant feature from a firework maker’s point of view is that the outermost electrons (furthest from the nucleus) possess higher energies than their innermost cousins and are also reactive. In fact, they are so reactive that they can be made to rearrange their positions in the hierarchy of the atom.

Quantum Theory

Profound and astonishing discoveries from the early parts of the 20th century also tell us that the classical laws of physics break down under two extreme conditions:

- (1) when things are viewed on the scale of the universe; and
- (2) when things are viewed on an atomic scale.

So far as atoms are concerned, the quantum theory (as it is called) dictates that the electrons are arranged in groups (starting with pairs) around the nucleus in discrete energy levels, or shells. As the distance from the nucleus increases, the number of electrons in each shell generally increases, as does the energy.

But there is a limit to the number of electrons in each shell; for example, the first shell can hold up to two electrons, the second has eight, and so on.

Also, the amount of energy ascribed to each shell is fixed in an orderly fashion. The electrons in the first shell may have an amount of energy, x , but no more and no less. Similarly, for succeeding shells, the energy increases by a series of fixed amounts. There is no ‘shedding’ or gaining of energy in arbitrary or indiscriminate amounts.

When an atom becomes excited (for example, under the influence of heat) an electron might ‘jump’ to a higher energy level or shell within the atom, but only to a precise energy level or ‘step’. Similarly, when an atom ‘relaxes’, the electron has a natural tendency to occupy the lowest available shell. In doing so it ‘steps down’ to the lower energy level, shedding a ‘quantum’ of energy as it does so.

The emission of radiation due to redistribution of electrons among the permitted molecular energy levels follows the same pattern as with atomic emissions.

But for any absorption or emission process, the total energy must be conserved. This leads to the relation given by equation (5.1),

$$E^I - E^{II} = \Delta E = h\nu \quad (5.1)$$

where E^I is the energy of the higher energy state, E^{II} is the energy of the lower energy state, and ν is the frequency of radiation that is related to the energy difference, ΔE , by a constant, h , known as Planck's constant.

Thus, a molecule may exist in many states of different energy. The internal energy in a certain state may be considered to be made up of contributions from rotational energy, E_{rot} , vibrational energy, E_{vib} and electronic energy, E_{el} as described by equation (5.2):

$$E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} \quad (5.2)$$

Electronic, vibrational and rotational changes all contribute to the emission (or absorption) of a single photon but, as will be seen from Figure 5.2, electronic energy levels are widely separated. For

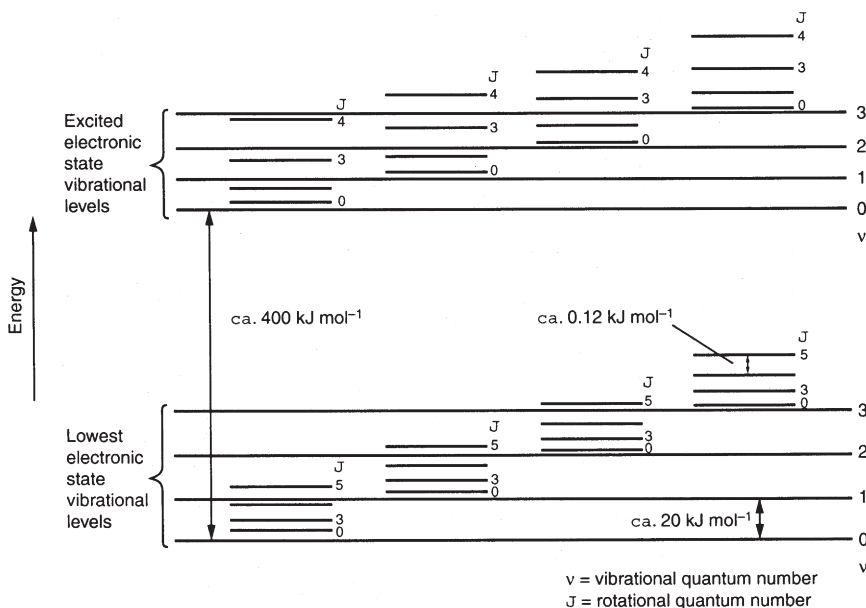


Figure 5.2 Energy levels of a diatomic molecule (e.g. TiO). Two electronic states are shown, together with some vibrational and rotational levels.

a diatomic molecule such as TiO , the electronic energy levels are separated by about 400 kJ mol^{-1} , while the vibrational and rotational energy levels are separated by about 20 kJ mol^{-1} and 0.12 kJ mol^{-1} respectively.

In summary, the titanium fountain effect arises because of the combustion of the metal particles, and appears in the form of radiation which comprises:

- (1) Atomic line emissions from Ti in the UV and visible regions of the electromagnetic spectrum (see Figure 8.6).
- (2) Band emissions from excited oxide molecules in the UV, visible and IR regions.
- (3) Continuum black body radiation.

Atomic line emissions are produced by the excitation of atoms as discussed previously. The emission of the light occurs at positions in the spectrum corresponding to definite wavelengths or frequencies.

Band emissions, on the other hand, are characteristic of excited molecules and a molecule, like an atom, can exist in a number of electronic energy levels. The change from one particular level to another results from the absorption or emission of a definite (*i.e.* quantised) amount of energy. But, because of simultaneous changes which occur in the rotational or vibrational energy of the molecule, a series of closely spaced lines appear in the spectrum in the form of a band.

In contrast to line and band emissions, the emissivity of a hot body can be a function of temperature only. Hence, after absorbing incident radiation, the hot body re-emits a spectrum dependent on its surface temperature, which is known as black body radiation.

The spectral distribution of the radiation occurs over a range of wavelengths in the form of a continuum (or energy curve) with no discrete lines or bands.

Titanium Fountains

Having introduced the theory of emission, we can proceed to the events which occur in a typical titanium fountain (Figure 5.3). This 150 g firework will burn for about 25 seconds giving a fountain effect extending some 3 to 4 metres.

On ignition of the firework a reaction zone moves down the pressed composition and the components of the gunpowder react producing heat and hot gases. The latter entrain the titanium particles and eject them from the firework tube. During this process the metal particles are

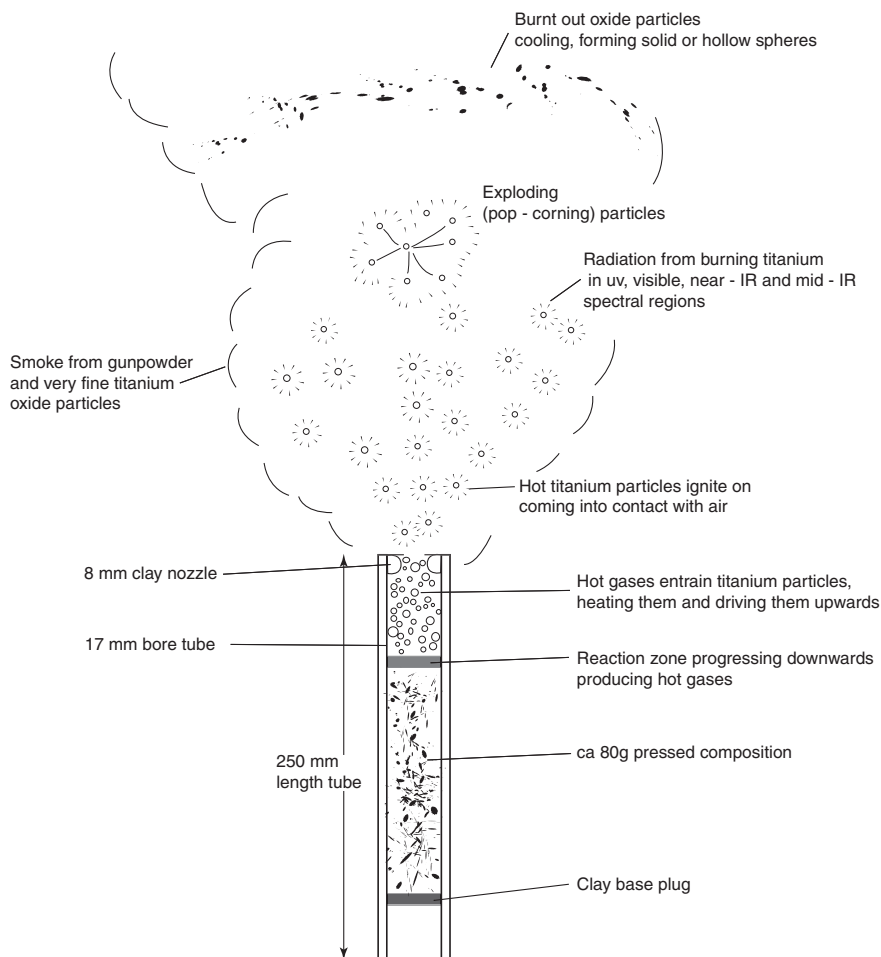


Figure 5.3 Diagrammatic representation of a 4 oz titanium fountain.

heated to their ignition temperature whereby they ignite on coming into contact with the air. Ideally, the composition will be finely balanced so that no titanium burns prematurely inside the tube and no titanium fails to ignite when outside it.

The metal particles melt and burn as near spherical droplets as they are ejected at typical speeds of about 0.3 to 3 ms^{-1} . After the titanium is consumed, rapidly cooling spheres and hollow spheres of oxide remain which either fall to the ground or drift away with the smoke, depending on their size.

Sometimes exploding or ‘pop-corning’ droplets also appear which give rise to vivid star-shaped spark trails.

THE COLOUR OF SPARKS

As well as emitting at characteristic frequencies due to specific energy transitions, an emitting species such as a hot metal oxide will also possess a component due to black body radiation as introduced above, which occurs at all frequencies and is a function of temperature only.

Therefore, the emissivity or radiance of a hot oxide particle will comprise contributions from both black body radiation and molecular energy transitions as illustrated in Figure 5.4.

Although it is known that the colour of black body radiation is only dependent upon temperature, sparks have colours that are also dependent upon the type of emitting material. However, the form of the radiance curves does not relate exactly with known molecular energy transitions. This suggests that the mechanism of emission in excess of black body radiation is not yet fully established. It is possible that some emission bands only become active when the metal oxide particle is molten, or that the energy is dissipated simply *via* collisions with other molecules rather than the emission of photons.

Thus, although the colour of sparks is dependent upon flame temperature and may be similar to that of black body radiation, the overall colour effect can include contributions from atomic line emissions, from metals (seen in the UV and visible regions of the electromagnetic spectrum), from band emissions from excited oxide molecules (seen in the UV, visible and IR regions) and from continuum hot body radiation and other luminescence effects. So far as black body radiation is concerned, the colour is known to change from red (500 °C; glowing cooker

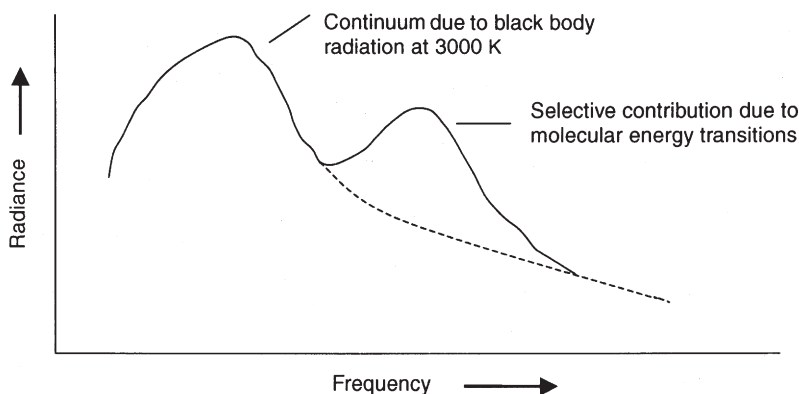


Figure 5.4 Schematic representation of firework fountain radiance based on titanium emitter.

element) to reddish orange (510–1150 °C), to orange (1150–2250 °C) and finally to white (above 2250 °C). In comparison, the adiabatic flame temperatures for various elements are as listed in Table 5.1.

Table 5.2 lists some of the common active materials present in fountains. It shows that ‘pure’ metals such as aluminium or titanium have boiling points that are high enough to enable the particles to survive passage through the flame of the fountain (which is typically around 2700 °C). On the other hand, magnesium has a relatively low boiling point (about 1120 °C) with the result that the metal is volatilised in the flame and good sparks are not produced.

Table 5.1 Adiabatic flame temperatures for various elements.

<i>Material</i>	<i>Adiabatic flame temperature (°C)</i>
Be	4000
B	2600
Mg	3200
Al	3500
Si	2300
Ti	2900
V	3100
Mn	3100
Fe	2200
Zr	4200
Mo	2600
W	2700

Table 5.2 Some active materials present in fountains.

<i>Material</i>	<i>Iron</i>	<i>Aluminium</i>	<i>Titanium</i>	<i>Potassium sulfide</i>
Origin	Metal or chemical reaction	Metal	Metal	Chemical reaction
Composition	Fe (+C)	Al	Ti	K ₂ S ~ K ₂ S ₇
Melting point (°C)	1536	662	1660	143–840 (approx.)
Boiling point (°C)	2872	2493	3318	
Oxide melting point (°C)	1377 (FeO)	2042 (Al ₂ O ₃)	1870 (TiO ₂)	
Oxide boiling point (°C)	3417 (FeO)	3527 (Al ₂ O ₃)	3827 (TiO ₂)	
Oxygen required for burning (g g ⁻¹)	0.289 (FeO)	0.890 (Al ₂ O ₃)	0.667 (TiO ₂)	
Heat of combustion (kJ g ⁻¹)	4.9 (FeO)	31.0 (Al ₂ O ₃)	19.7 (TiO ₂)	

However, on the grounds of cost, availability, reactivity and safety, the list of metal powders used by the firework maker reduces to Al, Ti, Fe and Mg/Al alloy (magnalium).

Depending on the firework composition, the sparks due to an aluminium-based emitter can range from silver to gold, whereas titanium gives silver to white sparks and iron powder gives a gold effect. For orange-red sparks, potassium sulfide is preferred, the emitter being formed from chemical reactions in a gunpowder type of composition as previously detailed in Table 1.2.

THE BRIGHTNESS OF SPARKS

A further factor that contributes to the overall appearance of a firework fountain is the brightness of the sparks. As with colour, the brightness is dependent upon the temperature and characteristics of the material used. The brightness of black body radiation varies with temperature as shown in Figure 5.5.

This figure shows that the brightness at 1000°C is assigned the arbitrary value of unity while the scale is normalised to it. Thus the brightness at 2000°C is 5000 times greater than the brightness at 1000°C . Conversely, the brightness at 600°C is only $1/10\,000$ th the brightness at 1000°C .

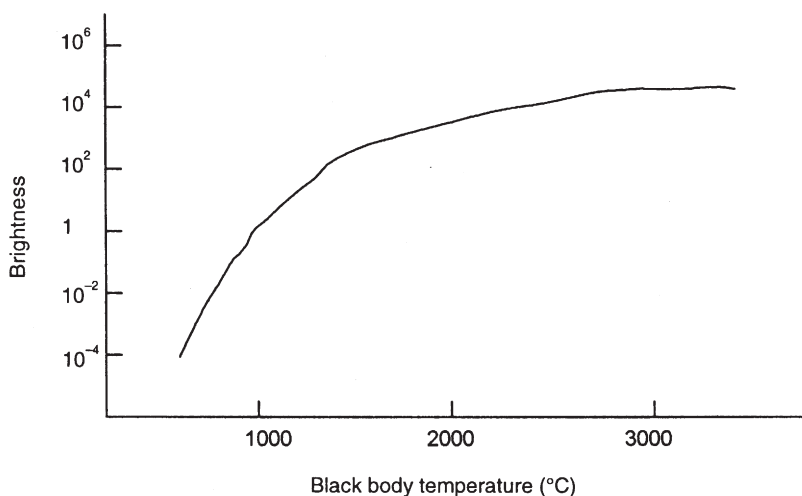


Figure 5.5 The brightness of black body radiation as a function of temperature.

PARTICLE COMBUSTION

The primary consideration in the burning of a metal particle in air is the limitation of the temperature attained by the boiling of the resultant oxide.

Two schemes for particle combustion have been proposed which differ mainly in the consideration of the condensed oxide formed by the combustion reaction.

In the first scheme the metal boiling point is less than the oxide boiling point and the model consists of a vaporising droplet of metal surrounded by a detached reaction zone where condensed oxides appear as fine droplets. The reaction rate is said to be controlled by the vapour phase diffusion of metal and atmospheric oxygen into the reaction zone as in Figure 5.6.

For vapour phase combustion, the burning rate of spherical droplets can be expressed as in equation (5.3):

$$W = Kr^n \quad (5.3)$$

where W is the burning rate, K is a constant involving the latent heat of vaporisation, r is the droplet radius and n is a constant (approximately 1).

In the second scheme, the metal boiling point is greater than that of the oxide and the model suggests that reaction occurs at the metal droplet surface when the vaporised droplet is said to be surrounded by a bubble of molten metal oxide, as in Figure 5.7.

For example, titanium is a non-volatile metal with a melting point of about 1660°C and boiling point approaching 3320°C . The oxide TiO_2 has melting and boiling points of 1870 and 3827°C , respectively. In the

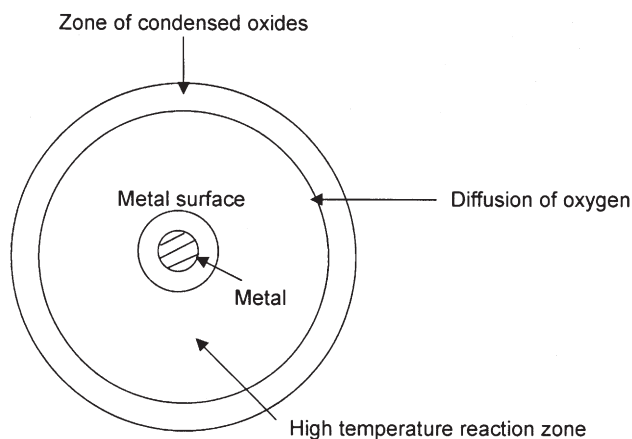


Figure 5.6 Combustion mechanism for vapour phase diffusion flame.

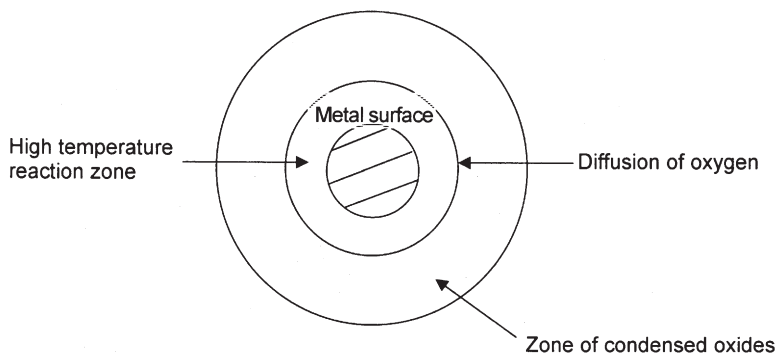


Figure 5.7 Combustion mechanism for surface burning.

fountain, large ‘flitters’ build up a brittle oxide layer on the surface before any melting occurs. Oxidation continues with heat feedback to the metal until the ‘flitter’ melts, shattering the oxide shell and fragmenting into small droplets which burn by diffusion at around 3000 °C.

The kinetics that control the small droplet reaction are characterised by the dissolution of titanium oxide which, in turn, exposes further, unoxidised metal. Interestingly, this process appears to be independent of the type of oxidant, whether it be potassium perchlorate, potassium nitrate or atmospheric oxygen.

Titanium is therefore an important ingredient in fountain compositions. It is characterised as a non-volatile metal with non-volatile oxides. The particles are easily ignited, even in the form of large ‘flitters’, and once ignited they grow progressively brighter and finally explode in a spectacular star formation.

The fragmentation of sparks has been observed in several metals (including magnesium, aluminium and titanium), and where such fragmentation occurs violently it is termed ‘popcorning’ as previously mentioned regarding titanium fountains. In order to account for this phenomenon, several mechanisms have been suggested.

The first mechanism proposes that metal volatilisation causes rupture of molten droplets (as with magnesium), whereas the second considers the production of a volatile oxide such as CO inside materials such as steels that contain an excess of 0.1% carbon. The third mechanism involves the formation of oxy-nitride compounds which decompose at high temperatures, liberating nitrogen (as with titanium).

The easy ignitability and uninhibited combustion of titanium and largely due to its ability to dissolve sizeable amounts of oxygen as a solid solution without the formation of a second phase. Data have also been published on the size dependence of the burning time of titanium

particles in an 'oxygen-rich' medium according to equation (5.4),

$$\log T = 1.59 \log D - 1.30 \quad (5.4)$$

where T is the burning time (ms) and D is the particle diameter (μm).

Thus for a life of three seconds for a burning particle travelling through air, a particle size in the region of $1000 \mu\text{m}$ (or 16 BSS mesh) is required. In this respect titanium would be the metal of choice because of its ignitability. On the other hand, aluminium might well prove hard to ignite in such large particle sizes.

The chemical composition as given for the 38 mm fountain shown in Figure 5.8 relies on the gunpowder ingredients potassium nitrate, sulfur and charcoal to provide heat and gas while antimony trisulfide and fine aluminium act as emitters. Barium nitrate is effective in producing intermittent burning and enhances the flickering effect when used in conjunction with Sb_2S_3 . The organic substance dextrin is used as a binding ingredient which helps to consolidate the pressed composition.

Charcoal is used in excess because the decomposition of the extra charcoal is endothermic, the overall effect being to lower the exothermicity of the fountain composition and so reduce the burning rate. However, the main advantage in using extra charcoal is that a reducing atmosphere is produced within the fountain such that the possible reaction of the emitter prior to ejection is greatly reduced.

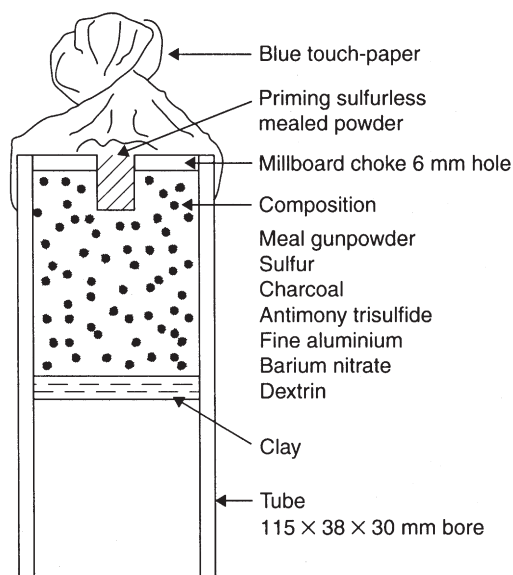


Figure 5.8 38 mm fountain.

More exotic effects call for more exotic materials, and considerable effort has gone into formulating compositions that are both spectacular in effect and safe to produce and handle. Thus a 30 mm fountain might contain mealed (or fine) gunpowder, potassium nitrate, sulfur, charcoal, antimony trisulfide, barium nitrate, fine aluminium and flitter aluminium with a dextrin binder. This composition is certainly a good deal more complicated than that used for sparklers but is relatively safe to produce and gives a good burst of white sparks.

The charcoal, or rather the coated charcoal, contributes to the fountain effect as does the gunpowder and aluminium by processes such as those described above. The flitter aluminium has a rather coarser particle structure than does the fine aluminium so that sparks from the former are longer lived and can survive a greater drop-height. Antimony trisulfide is commonly used to enhance the 'glittering' effect in a series of chemical reactions with the gunpowder and aluminium.

Thus, in summary, the composition can be divided into propellant, emitter and additives. The propellant is invariably gunpowder, whilst the emitter might be carbon, steel, iron, aluminium, magnesium/aluminium alloy or even titanium. Additives are often used to promote the visual effects and to cheapen the composition.

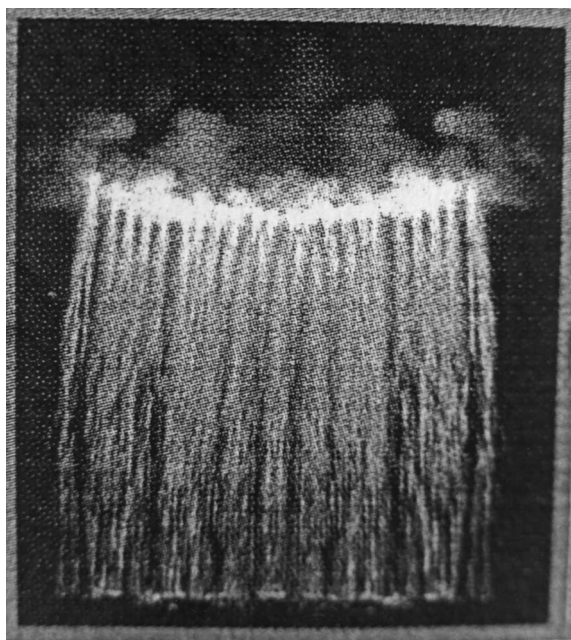


Figure 5.9 7 metre wide silver waterfall effect.
(Courtesy of Pains Fireworks Ltd.)

Some fountain compositions tend to be oxidant-rich due to the presence of excess potassium nitrate or sometimes various oxalates. The reason for this is to reduce the burning rate and/or to enhance the visual effects. Certainly if gunpowder is considered to be a mixture of fuels (charcoal and sulfur) and oxidant (potassium nitrate) then the maximum rate of burning should coincide with a slightly under-oxidised system. The burning rate is therefore reduced by adding excess nitrate to the system.

Varying the ratios of the components must be done with a degree of caution however. With titanium compositions in particular there is a definite limit to the gunpowder/titanium balance beyond which the composition can explode during pressing; the titanium ‘flitters’ act as tiny razor blades which can friction ignite the gunpowder.

Fountains are particularly suited to festive occasions such as weddings, where silver and gold can be produced alternately from the same fireworks to give graceful arches and fans, or they may be used to supplement other effects such as personalised messages with hearts and flowers. Alternatively, the larger fountains can make successful contributions to daylight pyrotechnics displays (Figure 5.9).

CHAPTER 6

Sparklers

There are two main types of sparkler: wire sparklers that are sold in many shops for most of the year and tubed sparklers that resemble pencils in shape and size.

WIRE SPARKLERS

The wire sparkler might look the simpler of the two types but it can in fact be the more difficult to make. First, a good quality wire must be used that will not corrode during the subsequent dipping operations or in storage.

If iron or steel is used as the spark source it too must be protected from corrosion by coating with a low-viscosity oil such as paraffin. A typical gold sparkler composition contains iron filings, aluminium powder, barium nitrate and dextrin or gum arabic as a binder. The mixture must be of the correct consistency for repeated dipping, and the final drying operation, in currents of warm air, must also be carefully controlled. Just to make things more interesting, the sparklers are not made one at a time, but in huge bundles that are dipped together and then dried. In order to make ignition easier, a priming mix can afterwards be painted onto the tip of the sparkler.

As well as acting as a support for the pyrotechnic composition, the steel wire serves as a heat conductor, promoting the smooth propagation of the pyrotechnic reaction along the sparkler.

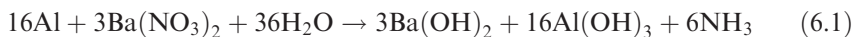
The following composition illustrates the use of steel filings for wire sparklers (the salient features of spark production having been discussed during the considerations in the preceding chapter).

COMPOSITION	FORMULA	WEIGHT (%)
Barium nitrate	$\text{Ba}(\text{NO}_3)_2$	50
Steel filings	Fe	30
Aluminium powder	Al	8
Boric acid	H_3BO_3	2
Charcoal	C	1
Dextrin	$(\text{C}_6\text{H}_{10}\text{O}_5)_n \text{H}_2\text{O}$	9

Barium nitrate is used as an oxidiser in reaction with the aluminium which acts as an energetic fuel, raising the combustion temperature; the main reaction products being Al_2O_3 , BaO and N_2 , where the oxides produce a coherent ash that does not melt or fall from the wire. The high melting point of barium nitrate (ca. 595 °C) results in a high ignition temperature for the composition, such that the firework can be none too easy to light with a match!

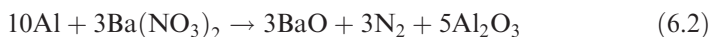
Charcoal is used as a fuel and burning rate stabiliser while dextrin (starch gum) forms a viscous dispersion in water such that it can be added to the pyrotechnic ingredients to form a slurry that will adhere to the wires when dipped. It is normally necessary to dip the wires several times in order to build up a satisfactory coating before drying in a current of warm air.

A common problem in the production of gold sparklers is the tendency for the $\text{Ba}(\text{NO}_3)_2$ and Al to react in the wet slurry according to reaction (6.1):



This decomposition evolves heat which further accelerates the reaction which is detectable by the smell of ammonia. The reaction rate is increased at high pH and can be effectively controlled by maintenance of a suitable pH using a weak acid such as boric acid. Stronger acids would attack the Al powder and Fe filings in the composition.

On ignition, barium nitrate and aluminium react exothermically as in reaction (6.2):



The above reaction produces heat and a slight gas pressure which ejects the glowing iron filings to form gold sparks which then cool quickly.

Barium nitrate is superior to either sodium or potassium nitrate with regard to physical stability, while the heat concentration is also higher because barium oxide has better refractory properties than does either potassium or sodium oxide.

A potential disadvantage in large fireworks is the high equivalent weight of barium, but for small fireworks such as sparklers the mass of the composition is not an issue.

TUBED SPARKLERS

For the tubed sparkler the main composition is filled loosely and hence there is no need for a binder. A gold sparkler might be based on potassium nitrate, sulfur, charcoal, steel grit and mealed powder (fine gunpowder) as in Figure 6.1. Again, large batches are made – a typical filling box contains 100 rolled paper tubes packed in square formation for the powder to be charged in. Obviously, each tube must first be

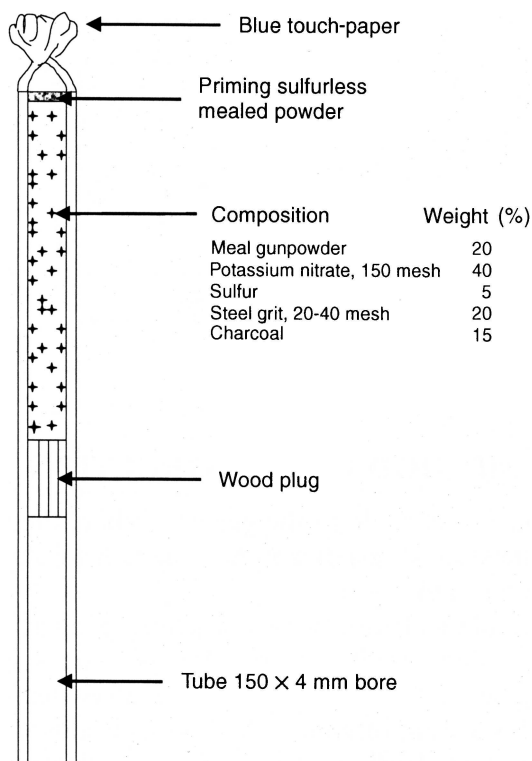


Figure 6.1 Schematic representation of a tubed sparkler.

plugged in order to prevent the powder charge from falling straight through, and this is achieved by using wooden plugs which are inserted to about halfway down the tubes. During filling, the bundles of tubes are shaken and more powder is charged in until each is filled. A priming mix based on grain gunpowder, sulfurless mealed powder and gum arabic is then painted across the mouth of each tube which, when dry, can be finished with a wrapping of blue touch-paper and a label applied.

The ignition process is basically the same for any tubed firework, but when the sparks start to fly, the chemistry becomes very different. Sparks are self-luminous but they need atmospheric oxygen to sustain the high temperature oxidising reaction with the steel particles or other emitters that are present, as described in the previous chapter.

In operation, the mealed gunpowder provides the gas and heat necessary for the combustion of the other fuels and oxidisers that are present. The potassium sulfide that is formed produces orange-red sparks, whereas the steel particles contribute with gold ones. Pine needle-shaped sparks may also be seen when a spark suddenly breaks up into smaller particles. This phenomenon is said to be the result of residual carbon particles exploding in a glowing, active material.

CHAPTER 7

Bangers

METHOD OF CONSTRUCTION

Although no longer available to the general public, the modest banger has changed little since Roger Bacon first made his exciting discoveries more than 700 years ago.

One of the simplest of fireworks, the penny banger, is produced in large quantities using very small cardboard tubes where the first operation is to press a clay plug into the bottom of each tube. This is followed by applying a label.

A bundle of such tubes is then inverted such that an explosive charge consisting of fine grain gunpowder and mealed gunpowder can be loaded in. After this a length of Bickford-type safety fuse is glued into the top of each loaded tube. Finally a mealed powder primer and blue touch-paper are applied to the fuse end.

When the touch-paper is lit, the potassium nitrate, with which it is impregnated, causes the paper to smoulder until it reaches the mealed powder priming. This priming rapidly ignites, which in turn ignites the first grains in the delay fuse which then burn progressively, from grain-to-grain.

The 40 mm or so of delay fuse burns noisily for several seconds and when the end of the fuse is reached, smoke, flame and hot particles are showered onto the main gunpowder filling which promptly explodes. The explosion creates a pressure pulse which operates over a few thousandths of a second but which is enough to shatter the tube and clay plug and enter the air as a blast wave.

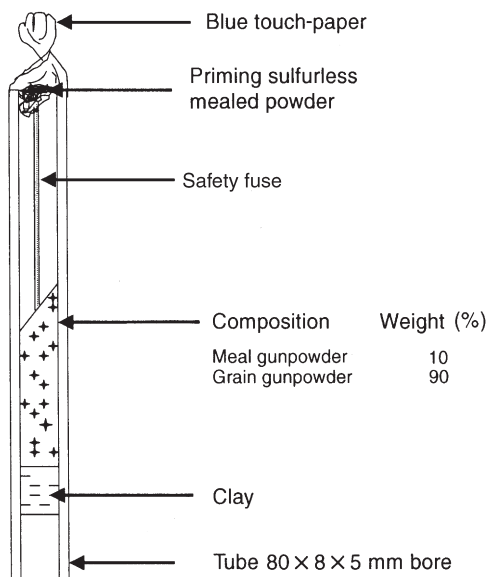


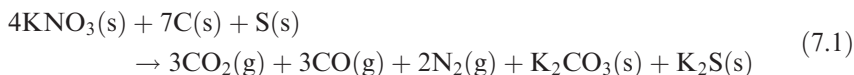
Figure 7.1 Schematic representation of a 'penny' banger.

It is possible to estimate the pressure that would be reached if the banger as depicted in Figure 7.1 did not explode but remained intact as a 'closed vessel'.

Volume of Evolved Gases

At standard temperature and pressure (STP) one mole of an ideal gas occupies a volume of 22.4 dm^3 . Therefore, if the number of moles of gaseous products originating from the gunpowder charge is calculated, an estimate can be made of the 'closed vessel' pressure.

First, a simplified reaction for the gunpowder decomposition can be written as in reaction (7.1):



From the above reaction the molar quantities associated with the combustion of a 2 g charge of gunpowder can be listed as in Table 7.1.

The gaseous products of reaction are CO_2 (0.012 moles), CO (0.012 moles) and N_2 (0.008 moles). The total number of moles is therefore 0.032 which corresponds to an 'ideal' STP gas volume of $22.4 \times 0.032 \text{ dm}^3$ or 0.717 dm^3 .

Table 7.1 Molar quantities associated with the combustion of a 2 g charge of gunpowder.

	<i>Molecular mass (M)</i>	<i>Number of moles (n)</i>	<i>Mass (M × n)</i>	<i>Moles per kg</i>	<i>Moles per 2 g charge</i>
<i>Reactants</i>					
KNO ₃	101.11	4	404.44	7.68	0.015
Carbon	12.01	7	84.07	13.45	0.027
Sulfur	32.06	1	32.06	1.92	0.004
			520.57 g		
<i>Products</i>					
CO ₂	44.01	3	132.03	5.76	0.012
CO	28.01	3	84.03	5.76	0.012
N ₂	28.02	2	56.04	3.84	0.008
K ₂ CO ₃	138.21	1	138.21	1.92	0.004
K ₂ S	110.26	1	110.26	1.92	0.004
			520.57 g		

Theoretical Maximum Gas Pressure

The equation of state (7.2) can now be applied in estimating the maximum pressure in the firework body, assuming the internal volume to be 4 cm³.

$$P = \frac{nRT}{V} \quad (7.2)$$

Here, P is the maximum pressure (atm), n is the number of moles of gas, R is the universal gas constant (0.08205 dm³ atm deg⁻¹ mol⁻¹), T is the estimated flame temperature (K) and V is the volume (dm³). Therefore,

$$\begin{aligned}
 P &= \frac{0.032 \times 0.08205 \times 2500}{0.004} \\
 &= 1640 \text{ atm, or } 23\,800 \text{ psi}
 \end{aligned}$$

Of course, the construction of the firework dictates that such outrageously high pressures can never be reached and in the normal course of events the firework body ruptures at a pressure of about 20 atm (300 psi).

Airblast and Sound

On bursting, the banger releases some 5 kJ of energy to the outside world.

In fireworks that emit flashes and bangs, the sound is produced by the rapid release of large quantities of gas, in accordance with the principles presented above. The compositions that are used can take the form of relatively slow burning gunpowders (enclosed in a strong container as depicted in Figure 7.1) or fast burning powders based on potassium perchlorate and powdered metal fuels such as aluminium or magnesium; some of which are so fast burning that they are capable of detonation.

All of the sonic disturbances in question take the form of progressive (forward moving) waves in air, in the manner of sine curves whose characteristics are governed by the laws of physics. The wave motion commences at the source of the energy release, *i.e.* the exploding firework, and is caused by the sequential disturbance (*i.e.* vibration) of the individual particles in the air.

The energy passes through the air by means of rapidly alternating interchanges between kinetic energy (motion) and potential energy (pressure). And since the energy is continually lost as heat, the wave motion (or noise) eventually dies out.

In the extreme case of a detonation in air from, for example, an aluminium based composition, the shock wave caused in the air by the explosion is termed 'airblast.' Blast and sound waves in air are longitudinal; meaning that the vibration of the air particles and the movement of the wave are in the same direction.

Immediately after detonation, the detonation shock wave travels away from the source of the explosion faster than the expanding gaseous products. However, this high velocity wave rapidly decays into a blast wave, which is caused by the impulse which the expanding gases impart to the surrounding atmosphere. The blast wave is of lower velocity ($< 1000 \text{ m s}^{-1}$) but longer profile and travels a great distance in comparison to the short lived detonation wave.

Finally the velocity of the blast wave falls from supersonic to sonic (ca. 330 m s^{-1}) and its characteristics begin to resemble those of an ordinary sound wave.

With very large detonations (not yet within the scope of fireworks)! the residual high pressure may be experienced by the human body as "airblast," while the higher of the superposed frequencies ($> 20 \text{ Hz}$) are audible as noise, where the human auditory response commonly falls between about 20 and 20,000 Hz.

As a general rule, fireworks do not involve detonation conditions and so their effects are restricted to blast and sound waves. Pressures in the shock front of blast waves are much lower than detonation pressures and blast pressures are normally quoted as overpressures.

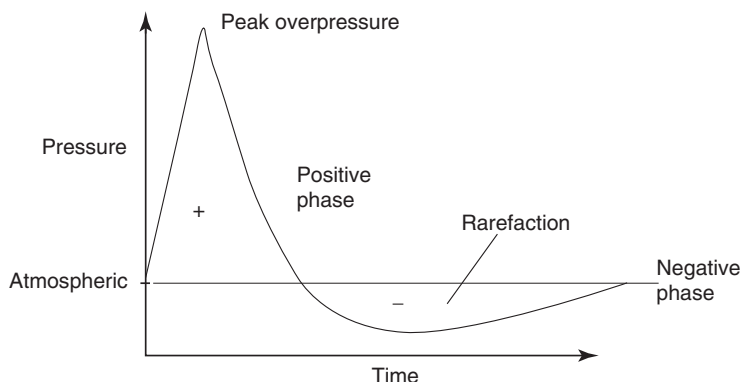


Figure 7.2 Profile of a blast wave.

Figure 7.2 shows the profile of a blast wave. It will be seen that the compression phase appears as a steep pressure pulse which rapidly decays. The negative phase (or rarefaction) which follows is the result of the elasticity of the air and this phase is of a longer duration.

A cycle of compression and rarefaction is repeated at decreasing amplitudes until the oscillation is damped out; but for firework purposes only a single cycle need be considered.

The most important parameters of a blast wave are the impulse and the peak overpressure. The former involves both the overpressure and the time during which it exists at a specified distance, while the time depends, in turn, on the profile and wave velocity.

In considering the loudness of fireworks we need to quantify the intensity of the sound, and this is proportional to the square of the wave amplitude of vibration. In fact, noise is perceived as a ratio of intensities, meaning that increase in loudness is registered by taking the logarithm of the ratio of intensities, ' I ' (or overpressures, ' P ') where $I \propto P^2$. That is to say the power carried by a sound wave is proportional to the square of the pressure. Relative intensities are expressed in 'bels' (after Graham Bell). But, in practice, the bel is too large a unit, and the 'decibel' (dB) is usually adopted. This is defined as one-tenth of a bel, such that the number of decibels

$$\text{dB} = 2 \times 10 \log_{10} \left(\frac{P_2}{P_1} \right)$$

where P_2 is the measured overpressure in the wave front and P_1 is the reference pressure (normally taken as $20 \mu\text{Pa}$ or $20 \times 10^{-11} \text{ bar}$).

Hence at a measured overpressure of $P_2 = 0.02$ bar, on a flat decibel scale, the noise level equates to

$$20 \log_{10} \left(\frac{0.02}{20 \times 10^{-11}} \right) \text{ dB or } 160 \text{ dB}$$

As a rough guide, the most vulnerable windows can be broken by 0.1 bar (about 1.5 psi), and so the output by fireworks such as penny bangers is always designed to be less than this.

When we pay two pence instead of one penny for our bangers we expect a bigger bang for our money. One way of achieving this is to include an extra fuel in with the powder mix in order to produce more heat. Commonly, aluminium is used and a typical composition might be based on potassium nitrate, sulfur and pyrotechnic fine aluminium. If the composition is also packed into a larger tube to give, say, double the weight of explosive then the louder bang will be quite noticeable.

In fact, most of the reactions involving the oxidation of aluminium are highly exothermic. The optimum amount of aluminium added to the composition will vary depending upon the amount of available oxygen, but the extra heat generated will more than compensate for the non-gaseous solid aluminium oxide which is formed.

Bangers have ceased to be available to the general public in the UK since 1997, on safety grounds. More recently, the CEN (European Standardisation of Fireworks) has set maximum sound level requirements of 120 dB at distances of 1, 8 and 15 m for Category 1, 2 and 3 (nitrate or perchlorate based) flash bangers respectively.

CHAPTER 8

Roman Candles

METHOD OF CONSTRUCTION

The fireworks that operators refer to as ‘candles’ or ‘Romans’ originated in Rome at the time of the Renaissance in the 14th century. Every person in the audience is familiar with these fireworks that eject a succession of stars, mini-shells and hummers into the sky, the projectiles reaching greater heights with every shot while the fireworks send great columns of sparks skywards between those shots.

As with rockets, Roman candles may be fired individually or in fans or bouquets to give a multiple effect (Figure 8.1 and 8.2).

Although candles appear to be among the most simplistic of fireworks they can be quite tricky to produce. The characteristically long paper tubes have very thick walls in order to withstand the high temperatures and internal pressures that operate during firing. A 35 cm long tube, as depicted in Figure 8.3, has typically a bore of 15 mm and walls 6 mm thick. It contains up to seven stars that are cylindrical in shape and varied in composition to give, for example, alternate red, green and snowflake effects.

Cylindrical stars are commonly ‘pumped’ using hand-operated pumps that are forced into the tray of composition. The pump comprises a line of brass or copper tubes, each fitted with a spring-loaded plunger to eject the compressed composition in the form of a star that is of the same diameter as the tube.

A red star might be based on potassium perchlorate, strontium carbonate and charcoal together with various binders and solvents to facilitate the pumping of solid stars. The composition for a green star

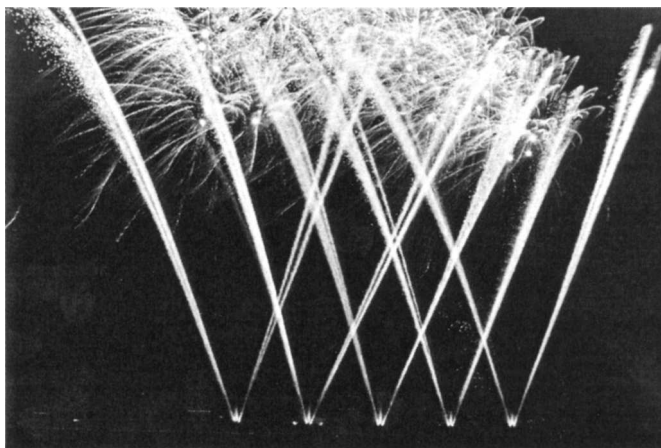


Figure 8.1 Perfectly synchronized bouquets of Roman candles.
(Courtesy of Pains Fireworks Ltd.)



Figure 8.2 Roman candle effects.
(Courtesy of Pains Fireworks Ltd.)

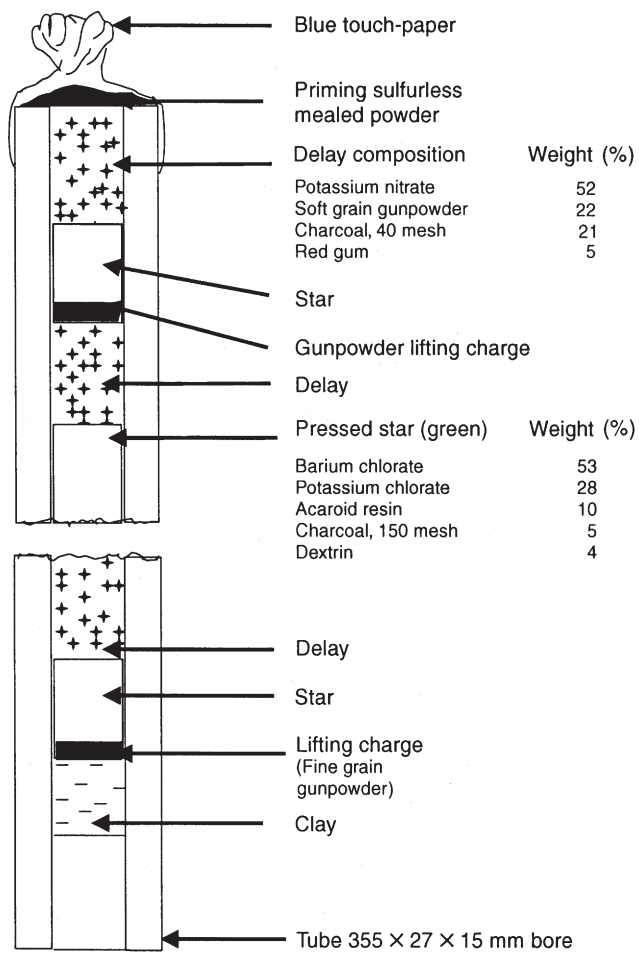


Figure 8.3 Representation of a 27 mm Roman candle.

could contain barium chlorate, potassium chlorate and charcoal together with binders, while the snowflake star is commonly made from potassium nitrate, barium nitrate, sulfur, charcoal, aluminium and binders. It is important that the stars are neither too loose nor too tight in the bore of the tube because a loose fit will allow too much gas to escape during ejection and the stars will fail to gain height. Conversely, a very tight fit can result in misfires or explosion within the tube.

In filling, each tube is set on a supporting stud and a quantity of clay is pressed at the bottom using a drift to form a solid plug. A predetermined amount of fine grain gunpowder is then placed into the tube followed by a star. Further gunpowder is then poured into the gap around the side of



Figure 8.4 Pains Fireworks, Mitcham, *ca.* 1925.
(Courtesy of Pains Fireworks Ltd.)

the star. Delay composition (based on potassium nitrate, sulfur and charcoal) is loaded in and lightly tamped. The process is then repeated, using increasing quantities of lifting charge, followed by a star and delay composition until the tube is full. The filled firework is retained in the upright position for priming, followed by the application of blue touch-paper and a label.

The larger Roman candles are fitted with plastic end-caps in the obvious interest of waterproofing, and the fuses are extended to include a piped match and a delay fuse. Display fireworks are often arranged as fans on a wooden framework (Figure 8.4) or wrapped as bundles with an interconnecting fuse.

As with most modern fireworks, the manufacturing process is as automated as possible, with waterproof materials being used in the construction where appropriate.

EMISSION OF RADIATION BY STARS

Burning stars, such as those originating from Roman candles or shells (Figure 8.5), emit radiation in the ultra-violet, the visible, near-infrared and mid-infrared regions of the electromagnetic spectrum, as displayed in Figure 8.6.



Figure 8.5 Roman candle stars.
(Courtesy of Pains Fireworks Ltd.)

In the near-UV, visible and near-IR regions of the spectrum, emission is due to electronic transitions in excited atoms and molecules, while in the near- and mid-IR it is due to vibrational transitions within molecules.

As outlined in Chapter 5, radiant emission from atoms and molecules occurs when an electron in a higher energy orbital around the nucleus of an atom (or nuclei in the case of molecules), drops into a lower energy orbital, usually closer to the nucleus. The difference in energy between the two states of the electron appears as energy according to the Planck relationship (1900) given by equation (8.1),

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad (8.1)$$

where ΔE is the difference in energy, h is Planck's constant, ν is the frequency of the radiation, λ is the wavelength of the radiation and c is

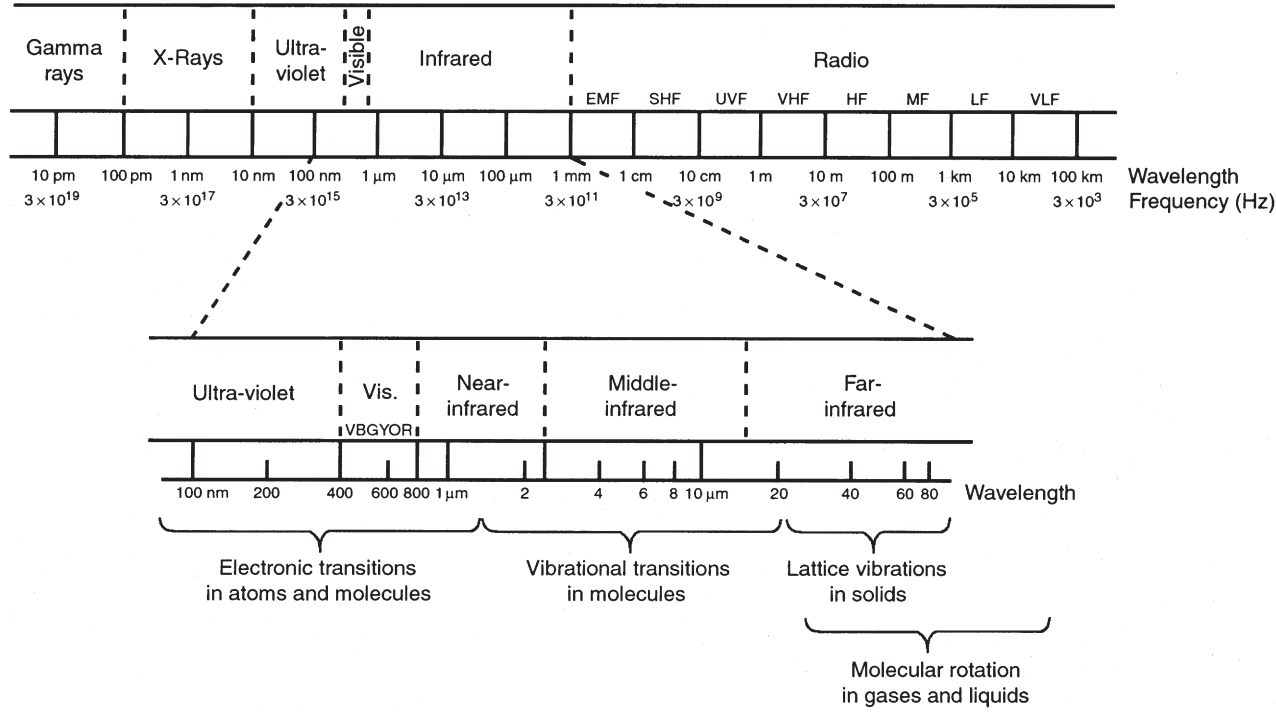


Figure 8.6 The electromagnetic spectrum.

the velocity of light. The reverse process occurs when the atom or molecule absorbs radiation.

In general, excited atoms emit spectral lines, *i.e.* the radiation lies in very narrow wavelength ranges of width 10^{-3} to 10^{-1} nm. In practice, atomic resonance lines from species, such as strontium in a red star, contribute little to the visual effect since the emission falls in the short wavelength part of the spectrum (this line may be observed in a Bunsen burner flame at 461 nm).

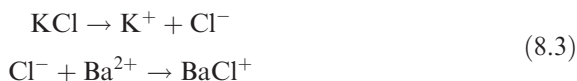
On the other hand, for molecules, the electronic transitions result in bands 10–50 nm in width due to the changes in vibrational energy levels which also occur. A third type of radiation emitted by stars in the near-UV–visible–near-IR region is a continuum emission originating from hot particles (*e.g.* hot Al_2O_3 particles) but this is considered to be grey body radiation and does not contribute to the colour of the star.

CHEMISTRY OF THE GREEN STAR

Under the influence of heat, oxidisers such as potassium perchlorate decompose into the chloride and oxygen as in reaction (8.2):



At higher temperatures ($>2500^\circ\text{C}$) the KCl ionises and the chlorine that is liberated reacts with fragments from barium compounds to form light-emitting species such as BaCl in accordance with reaction (8.3):



The main species responsible for the green colour of barium flames is BaCl, while contributions are also made from BaO and BaOH as shown in Table 8.1.

Although the use of barium chlorate, $\text{Ba}(\text{ClO}_3)_2$, provides an oxidising species directly combined with a flame colouring species, barium chlorate greatly sensitises the firework composition towards shock and friction and its use has been substantially phased out. When barium nitrate is used instead, a chlorine source such as potassium perchlorate or PVC [poly(vinyl chloride)] must be added. Hence, a green star composition might contain barium nitrate, potassium perchlorate, aluminium powder and organic binders.

Table 8.1 Main emission bands/lines for a green star.^a

<i>Species</i>	<i>Wavelength (nm)</i>	<i>Description</i>
Ba	553.6	Atomic resonance line
Ba ⁺	455.4	Resonance line of first ionised state of Ba
BaOH	487, 512, 740, 828, 867	Species responsible for green colour in Ba flames
BaO	535–678 549, 564, 604, 649	Much weaker than BaOH lines
BaCl	507–532 514, 524	Present when composition contains chlorine, and is main species responsible for green colour

^aThe wavelengths in bold type indicate the strong emission lines of a green star.

Table 8.2 Ionisation of elements in flames.

<i>Element</i>	<i>Ionisation energy (kJ mol⁻¹)</i>	<i>% Ionisation at</i>	
		<i>2200 K</i>	<i>2800 K</i>
Li	519.6	<0.01	16.1
Na	494.9	0.3	26.4
K	418.0	2.5	82.1
Rb	402.5	13.5	89.6
Cs	374.9	28.3	96.4
Mg	736.4	0	<0.1
Ca	588.9	<0.1	0.2
Sr	548.4	<0.1	17.2
Ba	502.0	1.0	42.8
Cu	744.5		

When potassium perchlorate is included in the composition, potassium ions are formed as seen in reactions (8.2) and (8.3). However, potassium emits in the near-IR region of the electromagnetic spectrum and so has little effect on the colour. On the other hand, the ionised form of Ba is undesirable since it emits in the blue region, and potassium salts are often added to Ba stars to suppress ionisation.

Ionisation in Flames

Ionisation of elements in flames is very temperature-dependent, as shown in Table 8.2.

Adding an element of lower ionisation energy can therefore suppress the ionisation of the desired emitting species so that, say, for Ba stars, potassium salts may be added to bring about the change described by

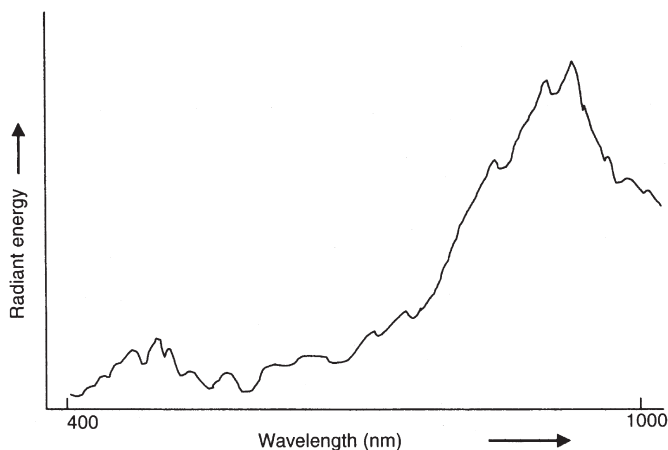


Figure 8.7 Radiant spectrum of a green star.

reaction (8.4):



Reference to Table 8.1 shows that in the absence of chlorine-containing species the visible emission is dominated by BaOH, in spite of the fact that the equilibrium concentration of BaOH is many orders of magnitude smaller than that of BaO. The reason for this is that the hydroxide is formed directly in an excited state in a process known as chemiluminescence, as shown by reaction (8.5):



Here, $[\text{BaOH}]^*$ is the excited molecule that releases energy ($E = h\nu$) at frequency ν which corresponds to the green region of the visible spectrum.

Collectively, the molecular and atomic emissions displayed in Table 8.1 give a radiant spectrum as shown in Figure 8.7.

CHEMISTRY OF THE RED STAR

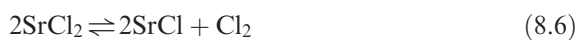
The chemistry that governs barium salts, as used in green stars, is somewhat analogous to that of the strontium salts employed in red stars since both elements are found in the same group of the periodic table. While the use of compounds such as strontium chloride, strontium chlorate or strontium perchlorate might be considered to be appropriate

primary ingredients in a red star composition, the salts are ruled out on the grounds of hygroscopicity or mechanical shock sensitivity. Therefore, alternatives such as strontium nitrate are used; the compound serves as both an oxidiser and as a colour source.

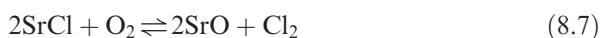
Strontium carbonate may be included to enrich the colour, but this substance is not an oxidiser and the 'balance' must be redressed by adding a further oxidiser such as potassium perchlorate together with a balance of fuels such as aluminium powder and organic binders.

During combustion, strontium nitrate and strontium carbonate decompose to give strontium oxide whose spectrum is seen as a pinkish flame due to the positions of the emission bands and to the difficulty in obtaining a high concentration of strontium oxide vapour in the flame. This difficulty is due to the high sublimation temperature of the oxide which is in excess of 2500 °C.

Strontium chloride has a melting point of 870 °C and exerts a considerable vapour pressure above this temperature. The boiling point of SrCl₂ is 1250 °C and at temperatures above this it dissociates forming strontium monochloride and chlorine according to reaction (8.6):



At still higher temperatures reaction (8.7) predominates:



An excess of chlorine, introduced into reaction (8.7) causes a shift to the left and an improvement in the flame saturation of strontium monochloride. Table 8.3 shows the main emission bands/lines for a red star.

Figure 8.8 shows the radiant spectrum of a typical red star.

Table 8.3 Main emission bands/lines for a red star.^a

<i>Species</i>	<i>Wavelength (nm)</i>	<i>Description</i>
Sr	460.7	Atomic resonance line
SrOH	506, 722, 620, 626, 646, 659, 668, 682, 707	Main species responsible for red colour in Sr flames
SrCl	618, 636, 661, 624, 636, 648, 662, 675, 676	Present when composition contains chlorine
SrO	350–92 750–872	Very weak emissions

^aStrong bands are indicated in bold type.

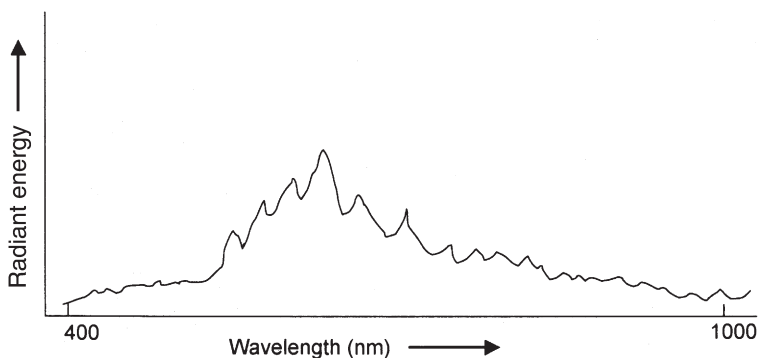


Figure 8.8 Radiant spectrum of a red star.

In practice, both red and green star compositions are formulated to have a negative oxygen balance (*i.e.* there is an oxygen deficiency) since the presence of a reducing atmosphere in the flame inhibits the oxidation of MCl to MO (where M is Sr or Ba), thus enhancing the colour purity of the flame.

CHEMISTRY OF THE BLUE STAR

The difficulty in producing a good blue flame stems from several important considerations. Firstly, impurities in the chemicals present in the firework tend to produce yellow flames, which detract from the blue; secondly, coloured flames follow similar physico-chemical phenomena but operate in different regions of the spectrum. Consequently the copper salts (that are normally utilised for the production of blue stars) decompose thermally to produce a variety of emissions that radiate from about 325 to 660 nm (*i.e.* from green, blue and violet to orange-red) simultaneously polluting the 'pure' blue flame which appears in the 400 to 455 nm region.

As if all this were not enough, the functioning of the human eye is such that blue flames are perceived as white at long distance meaning that anybody involved in the development of a blue flame, *e.g.* as used in the signalling for a pilot to come offshore and guide a ship in to harbour, will be faced with fairly challenging work!

Some of the best blue flames are obtained from compositions based on potassium perchlorate, cuprous chloride, hexachloroethane, polyisobutylene, pyrotechnic copper powder and cellulose dust.

In terms of chemistry, the potassium perchlorate is the oxidiser that oxidises the organic fuels (polyisobutylene, *etc.*) in exothermic reactions as discussed previously.

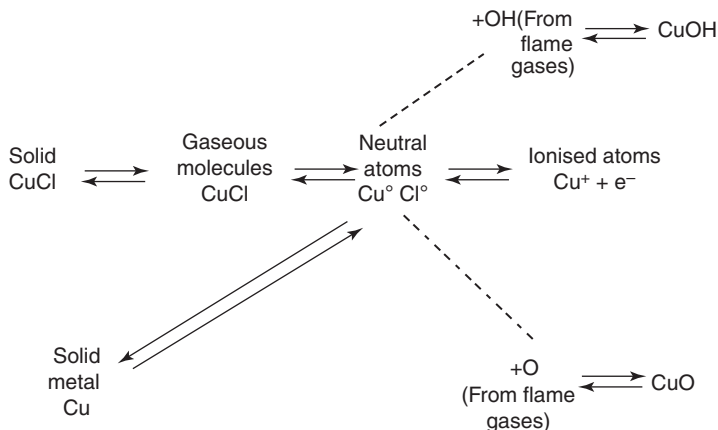


Figure 8.9 Chemistry of cuprous chloride and copper powder as emitters.

The main species responsible for the blue flame from such a composition is cuprous chloride, CuCl ; hence the use of this salt together with the chlorine producer (hexachloroethane) and a source of extra copper (pyrotechnic copper powder). The cellulose dust acts as a moderator to control the burning rate of the pressed composition.

Figure 8.9 outlines the sequence of events occurring in a burning blue star based on cuprous chloride and copper.

Because of the low dissociation energies of copper compounds the flame tends to contain free copper atoms. These emit weakly in the green region of the spectrum, but on the addition of a halogen (such as chlorine) the colour of the flame changes from green to blue. This change is mainly due to band spectra (of several wavelengths) from gaseous CuCl molecules (a molecule is a combination of atoms but the processes of excitation are essentially similar).

Initially the solid CuCl is vaporised. If the resulting gaseous CuCl molecules remain undissociated they will emit the required band spectrum in the blue region.

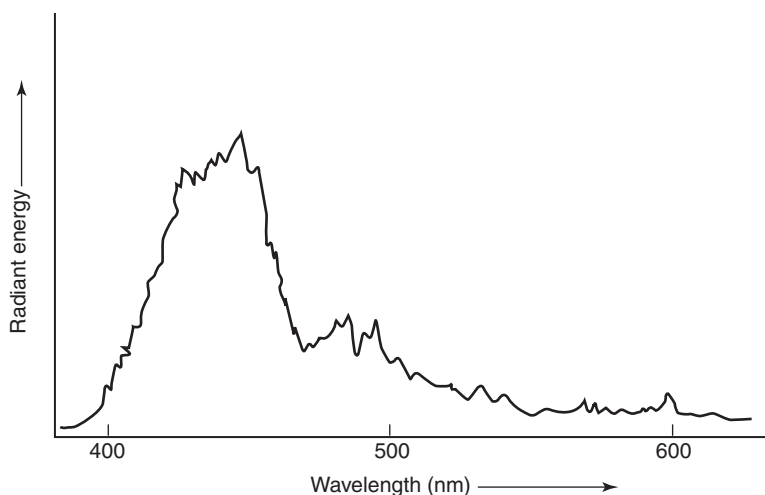
Increasing the temperature causes dissociation of the CuCl molecules into neutral atoms which, in turn, emit an atomic spectrum composed of atomic (arc) lines. In this state, one of two things can occur. The atoms can combine with hydroxide radicals (charge carrying radical symbol $\cdot\text{OH}$ species commonly found in flames) or oxygen atoms to form CuOH or CuO . These gaseous molecules emit a band spectrum and behave like CuCl .

Alternatively, the atoms can be heated further until ionisation occurs (loss of electrons), these ionised atoms emit ultra-violet light and hence a

Table 8.4 Main emission bands/lines for a blue star.^a

<i>Species</i>	<i>Wavelength (nm)</i>	<i>Description</i>
Cu	325–522	Atomic spectrum. Green
CuOH	535–555	Band spectrum. Green-yellow
CuCl	435–526	Band spectrum. Present when composition contains chlorine. Main species responsible for blue colour in Cu flames.
CuO	580–655	Band spectrum. Orange-red

^aThe wavelengths in bold type indicate the strong emission lines of a blue star.

**Figure 8.10** Radiant spectrum of a blue star.

colourless ionic spectrum. Finally, a reversion to the ground-state takes place due to impacts with other species and by the spontaneous emission of light.

Table 8.4 lists the main emission bands and lines for the blue star described above while Figure 8.10 shows the associated radiant spectrum where the band spectrum in the 435–526 nm region (due to CuCl) is particularly prominent.

Figure 8.10 illustrates the radiant spectrum for an ‘improved’ blue star.

SUMMARY

In summary, a correctly formulated coloured star composition is one which, when burning, produces combustion species which emit radiation in the wavelength of the desired colour.

Chlorine containing compounds such as hexachloroethane are often added to star compositions because metal–chloride species such as CuCl are relatively stable in the flames and because the emission wavelengths shift in such a way as to produce better colours.

Potassium salts including chlorate and perchlorate are useful oxidising agents which can also suppress ionisation as discussed previously.

The strong strontium (red), barium (green) and copper (green) colours in a flame have also been attributed to a process known as ‘chemiluminescence’ whereby excited SrOH , BaOH and CuOH molecules are formed directly in the excited state in the flame and are not dependant on ground-state concentrations.

CHAPTER 9

Gerbs and Wheels

GERBS

A gerb (pronounced 'jerb') is a small firework that is built as something of a cross between a fountain and a rocket. Gerbs can therefore be used as 'drivers' for rotating devices or as display pieces with ornamental plumes, or both.

Like the fountain, the gerb, as shown in Figure 9.1, relies on gunpowder to produce thrust, the pressure being increased within the paper case by using a restricting choke or nozzle made of clay. Simple gerb compositions contain mealed powder, potassium nitrate, sulfur and charcoal – this gives a gold effect.

Method of Construction

In production, gerbs are pressed to varying degrees depending on the thrust required, and have a depression within the choke to produce a rapid pressure rise on ignition. Antimony trisulfide can be used in place of charcoal when a more compact, whitish flame is required.

A vertical rotating device like a windmill might have four sails with driving gerbs at the end of each sail, the central pivot being located at the point where the sails cross. Each gerb is connected *via* a circuit of piped match, which when lit provides more or less simultaneous ignition. For added effect, lances (small flares) can be used to highlight the outline of the sails and these are also simultaneously ignited by inter-connecting piped match. Obviously there is a fair amount of smoke and flame as

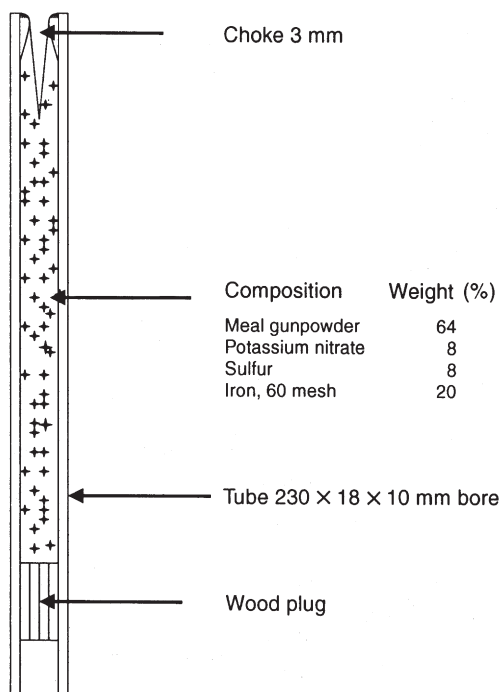


Figure 9.1 Schematic representation of a 20 mm gerb.

well as debris generated from the larger devices such as windmills, and the golden rule is to light the fuse (which enters the match) at arms length and then stand well clear.

The effects from gerbs can be enhanced by introducing further ingredients such as steel filings, antimony trisulfide or aluminium to the composition. Small, pressed stars (which are solid pellets containing pyrotechnic composition and binders) can be utilised to add colour to the jet of fire, or a small gunpowder charge might be included on top of the clay in the base of the paper tube to make the gerb finish with a loud report.

'Drivers' are basically gerbs in which the composition has been adjusted to give an increased speed of burning, thereby increasing the thrust. Again, they are used to provide impulse for rotating devices such as wheels and are again connected by lengths of piped match.

The saxon is yet another small firework displaying gerb technology; in this case showing even greater ingenuity in the method of construction and the effects produced. To make this firework, a long tube is filled with gerb-type composition, but plugged at both ends and in the middle using clay. The central, inert portion is then drilled through from the outside

to create a pivot hole through which a nail can pass, thus enabling the saxon to revolve like a propeller.

Now if a second hole is drilled in the side of the tube, just beneath one of the end plugs and at right angles to the pivot hole, gas will be released from this second hole on ignition, causing the saxon to rotate.

The other end of the firework is drilled similarly, but making sure that the third hole is on the opposite side of the tube to the second so that the thrust is from the opposite side, as required for circular motion.

In order to achieve simultaneous ignition both holes are connected using match, but the operation time of the firework may be doubled by arranging for one half of the saxon to be ignited first, and then before burning ceases in the first half, a connecting match provides ignition in the second half.

Alternatively, both outlet holes can be bored on the same side of the tube so that as one half burns out, the second portion can be ignited but the saxon will reverse direction, throwing out a spectacular array of sparks.

When used in combination with gerbs, saxons can contribute to spectacular set-pieces such as lattice poles and mosaics, with the gerbs providing overlapping crosses of fire while the saxons fill in the gaps with vivid circles of flame and sparks.

WHEELS

The name Catherine occurs fairly regularly throughout history, most of these ladies being associated with royalty. However, in the third or fourth century there was apparently a virgin martyr of Catholic origin in Alexandria. Legend represents her as being condemned to torture on a toothed wheel; hence the evolution of the firework known as 'St Catherine's Wheel'.

Method of Construction

In the manufacture of Catherine wheels (pin wheels), paper pipe of the length required to make a spiral is closed at one end by twisting or folding it over. Depending on the desired effects, gunpowder with added charcoal and steel is used as a filling to give a glittering shower of sparks of various intensities, while aluminium or titanium can be added to boost the effects. In order to colour the flame, oxidising salts of appropriate metals can be incorporated, but the proportion of gunpowder or mealed powder is usually kept high because, in the absence of any other thrust-producers, the wheel will fail to turn.

After filling, the ends of the tubes are closed and moisture is applied in order to soften the said tubes which are then passed between rollers and partially flattened. Each tube is wound into the well known spiral configuration around a wooden or cardboard disc before placing it in a frame so that the firework can be glued without uncoiling and then being allowed to dry.

A blue touch-paper is applied to the end of the spiral and the central disc drilled to accept a nail or a pin. It is important that anything used to pin the wheel to a post is a good fit in the pivot hole because a tight fit will inhibit rotation, whereas a loose fit will allow the wheel to tip forwards and perhaps catch on the post.

Always a popular firework, Catherine wheels with diameters of up to 50 cm are readily available. Other wheels are more complicated in construction and combine the effects of gerbs, saxons, fountains, lances and rockets in ways that are always attractive to the eye, as well as being dramatic (Figure 9.2).

Giant wheels of fire driven by gerbs are effected by binding the fire-works to the rim of rotating wooden frames. Alternatively, drivers can be sited at the ends of a pair of wooden arms, pivoting from a central

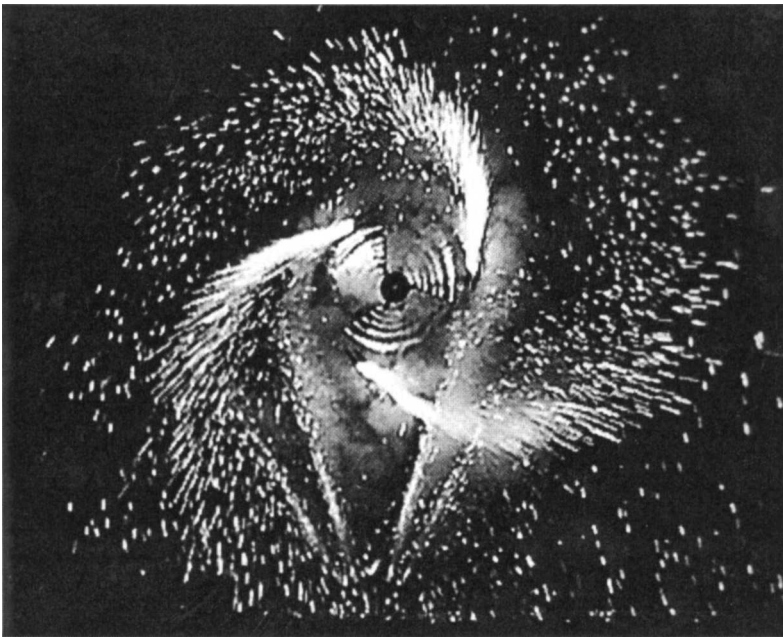


Figure 9.2 Catherine wheel in action.
(Courtesy of Pains Fireworks Ltd.)

block. For added effect, a smaller, contra-rotating pair of arms can be suspended from the same pivot point to provide an inner circle of fire.

Perhaps one of the most ambitious devices is the rocket wheel, which consists of two wheels, each up to one metre in diameter. These are arranged to spin horizontally, rather than vertically, on a specially designed spindle that holds the wheels one above the other, about one metre apart and at a suitable height above the ground.

The rims of the wheels are fitted with eyelets to accept rockets whose sticks are supported by the lower wheel. These are matched to fire at intervals as the wheels revolve, while a battery of Roman candles fires from the centre of the top wheel. Both wheels are fitted with gerbs and drivers to effect rotation, the complete device being appropriately matched such that the overall effect includes two revolving circles of fire, each throwing out glittering arrays of sparks, while candle stars emanate from the centre and rockets fly off vertically.

By contrast, a crown wheel is one of the simplest fireworks to set up. It resembles a flying saucer and rests, without ceremony, on a nail fixed in the top of a post. Although it spins at about the same speed as a Catherine wheel and uses a similar pyrotechnic composition, the crown wheel is not fixed in any way.

Upon ignition, the firework spins like a Catherine wheel, but in the horizontal plane. This effect is pleasing enough, but the audience is even more impressed when the wheel suddenly takes off like a flying saucer, throwing out a shower of sparks as it goes. The firework has further tricks to play, however, for depending upon the construction, it can dip and rise in the sky once or even twice more before finally burning out.

THE MALTESE WHEEL

While an inexpensive pin-wheel can readily be created by securing a pair of gerbs in diametrically opposed positions, onto the rim of a small cardboard disc, adding connecting fuses as described previously, the Maltese Wheel (as shown in Figure 9.3), represents the other end of the scale, both in terms of size and ingenuity.

This wheel has a diameter exceeding 30 ft and stands some 40 ft high when assembled for display on its platform.

A cleverly arranged system of lances (flame wands whose form and function are detailed in the following chapter) provides a pattern of fire depicting the classical Maltese Cross (Figure 9.4) whilst further portfires create a diamond pattern on pivoting of the segments within the Cross (Figure 9.5).

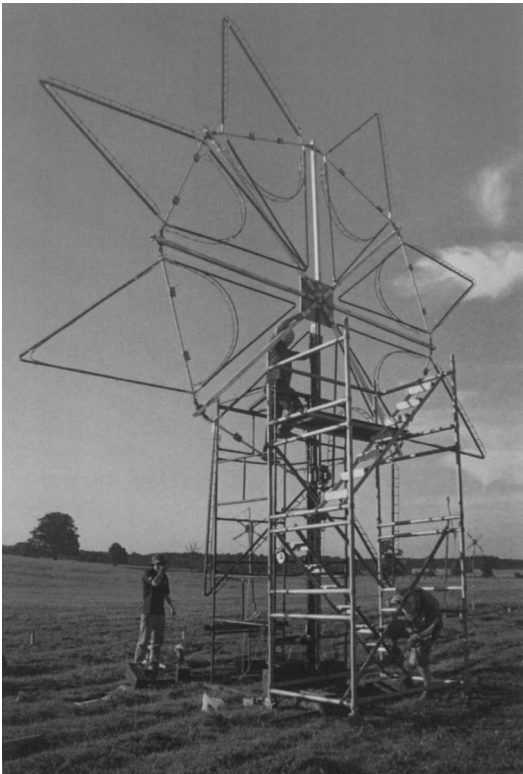


Figure 9.3 Maltese Wheel.
(Courtesy of Pains Fireworks Ltd.)

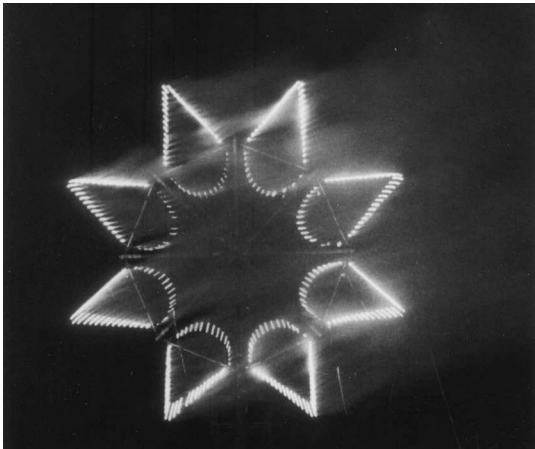


Figure 9.4 Wheel displaying Maltese Cross.
(Courtesy of Pains Fireworks Ltd.)

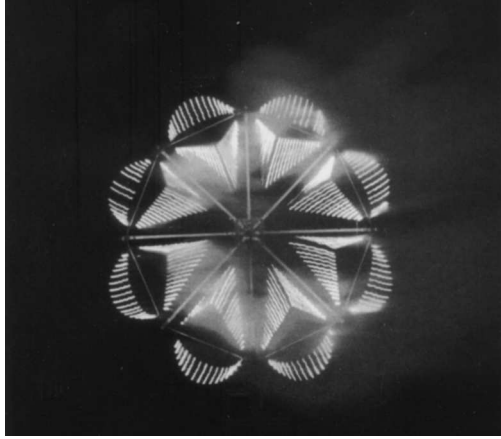


Figure 9.5 The same wheel displaying the diamond facets.
(Courtesy of Pains Fireworks Ltd.)

Unlike conventional fireworks, the platform and wheel are formed from sections of aluminium tubing (and are hence re-usable) while rotation of the wheel itself is effected by virtue of an electric motor powered by portable batteries, to give about 20 revolutions of the wheel per minute.

CHAPTER 10

Special Effects

Having introduced the basic types of firework, from rockets to gerbs and wheels, it remains to consider the special effects that are essential features of large display fireworks and, indeed, of many of the smaller ones.

Aspects of special effects described in this chapter include fuses (quickmatch and plastic fuse), lances (small coloured flares), set-pieces and devices (assemblies consisting of various types of fireworks linked together), flash, bang and whistle compositions and daylight fireworks (smoke puffs and coloured smokes). Finally, the electrical firing of firework displays is discussed.

QUICKMATCH

Early fuse trains consisting of loose trails of gunpowder were dangerous in that a spark could jump ahead of the advancing flame front and create a second flame front, thus shortening the fuse. The use of quickmatch overcomes this problem somewhat, the gunpowder simply being glued onto a supporting cotton yarn using an adhesive, such as gum arabic, to form a string-like fuse.

The speed of burning of quickmatch is related to the chemical composition and the mass of the composition on the string. The linear burning rate equation enables a crude estimate of the speed of burning to be made. For example, a typical relationship already seen for gunpowder is given by equation (10.1),

$$R_B = 3.5p^{0.5} \quad (10.1)$$

where R_B is the rate of burning in mm s^{-1} and p is the ambient pressure in psi. Assuming a pressure of one atmosphere or 14.7 psi gives a linear rate of burning of 13.4 mm s^{-1} . This translates to a theoretical burning time of 74 s m^{-1} . In fact, the burning of a typical quickmatch fuse is faster, at around 40 s m^{-1} , this being due to heat effects associated with the construction of the fuse where all three types of heat transfer (radiation, conduction and convection) are present and superimposed on each other.

PIPED MATCH

Whilst quickmatch can be used to form simple fuses for fireworks, both internally and externally, a burning time of some 40 s m^{-1} is too long in instances when a more or less ‘instantaneous’ ignition is required. Also, quickmatch is rather fragile and tends to kink or lose powder unless it is coated in some way.

Piped match is merely quickmatch that has been enclosed within a paper pipe (Figure 10.1). The paper pipe serves to trap some of the evolved gases and increases the ambient pressure, thereby significantly increasing the rate of burning as well as affording the fuse some protection against mechanical damage.

If one recalculates the rate of burning using equation (10.1) with a revised ambient pressure of, say, 100 psi to reflect conditions inside the

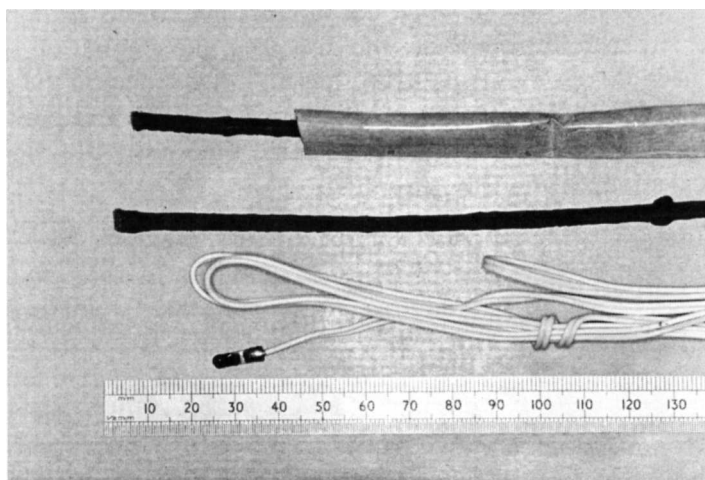


Figure 10.1 Wirebridge fusehead (bottom), quickmatch (middle) and piped match (top).

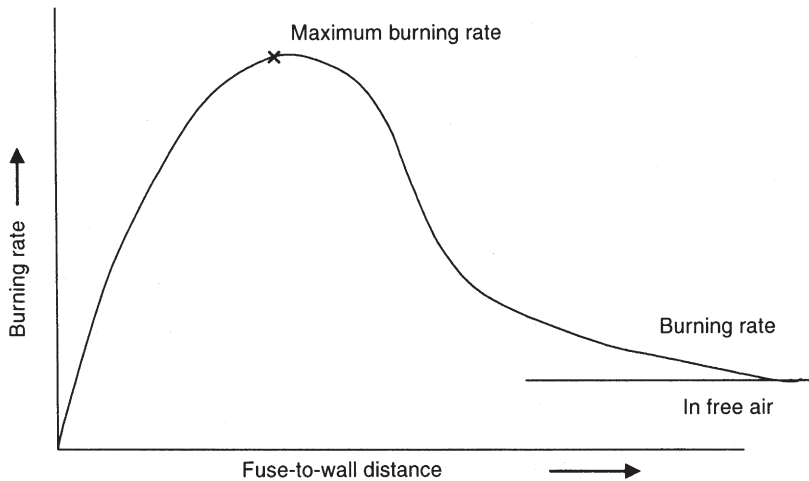


Figure 10.2 Diagram showing the variation of the burning rate of quickmatch with fuse-to-wall distance.

paper pipe, a rate of 35 mm s^{-1} is obtained which corresponds to a theoretical burning time of 28 s m^{-1} . But as with quickmatch, other effects play an important role, and the actual burning rate rises to at least 4 m s^{-1} (0.25 s m^{-1}), this high velocity being brought about by the chemical composition of the gunpowder, and the fact that the 'pipe' serves to confine the flame and provides a 'fire path' whereby hot gases and sparks are forced along the surface of the match. It has also been shown that a tightly fitting match will result in burn rates that are no quicker than quickmatch in free air. Similarly, slow burn rates are seen if the match is too loose a fit or if the pipe is fired with its ends closed. Obviously, the flame must be free to travel within the confines of the pipe but at a rate which produces an acceptable pressure increase without bursting the pipe.

Experiments have confirmed that there is an optimum fuse-to-wall distance in piped match where the burning rate is at a maximum, and this effect is presented graphically in Figure 10.2.

PLASTIC FUSE

Plastic Igniter Cord (PIC) is a modern version of quickmatch in which the gunpowder is replaced by a delay composition, consisting essentially of lead dioxide and silicon, while the support material is aluminium or iron wire. A plastic tube encloses the fuse, as in the manner of electrical

wiring, but in this case the outer tube has no influence upon the burning rate. The outer plastic serves to colour-code the fuse and contain the pyrotechnic composition, while at the same time imparting flexibility, mechanical strength and waterproofing.

The rate of burning of plastic igniter cord is primarily governed by the chemical composition of the pyrotechnic and the rate of heat transfer along the support wire.

A typical fuse composition reacts exothermically according to reaction (10.2):



The above reaction produces little gas and the rate of burning is relatively free from the effect of gas pressure. However, at high temperatures it is quite surprising how much gas can be produced by a composition which is, at first glance, considered to be gasless. The products of reaction in equation (10.2) are both solids at room temperature, but at the reaction temperature of around 2000 °C, significant amounts of vapour are produced.

Plastic fuse is routinely used as a fuse extension to quickmatch or piped match, especially when firing rockets, mines or shells. In the latter case, the piped match fuses from a crate of, say, ten shells connected *via* a single length of plastic fuse which will burn progressively to ignite each of the ten shells in turn.

On the other hand, if a salvo of rockets is required, a fast-burning PIC can be uncoiled into the bottom of a flight-box (which is a box with a wire mesh floor containing rockets, whereby the sticks or tails protrude downwards). On ignition, the plastic fuse rapidly ignites each of the quickmatch fuses protruding from the nozzles of the rockets.

The timing of the above effects is achieved by selecting an appropriate grade of PIC according to types listed in Table 10.1.

Table 10.1 Grades of plastic igniter cord that are commercially available.

<i>Type</i>	<i>Colour code</i>	<i>Burning speed (s m^{-1})</i>	<i>Carcass strength</i>
Slow	Green	30	High – iron support wire
Slow	Yellow	33	Nil – no support wire
Slow	Blue	49	Low – aluminium support wire
Fast	Brown	3.3	Nil – no support wire

PYROCLOCK

A more recent and improved means of timing the ignition of piped match is provided by an Italian product called PYROCLOCK. This is a modular system containing vented delay elements with burn times of 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 seconds.

The construction of these delays is such that they can be joined in tandem to give extended delay times beyond those specified above.

Each water resistant tubular unit contains an open ended piped match holder, a time delay element and a holder at the opposite end of the tube for an electric igniter (or a second PYROCLOCK element).

LANCES

Lances may be used in conjunction with any of the aforementioned fuses.

A lance is a firework that is about the size of a small pencil that functions in the manner of a flare (Figure 10.3). Thus, the theory of coloured flame production, as presented in Chapter 8, applies equally to the lance.

In a firework lance (for example with a yellow flame), we are observing the collective effects of electrons gaining energy and then returning to lower energy levels, shedding energy in the form of photons (coloured light) of certain discrete wavelengths.



Figure 10.3 Portfires and lances.

Yellow flames for lances may be derived from compositions based on sodium nitrate or sodium oxalate, together with magnesium as fuel and a binder such as linseed oil.

The yellow flame colour is due to atomic emission from sodium where the spectrum is dominated by a broad emission centred on 590 nm (the resonance transition is that from the ground state to the lowest energy excited state in absorption and the reverse will apply in emission).

The high efficiency of the Mg/NaNO₃ system at producing light has been ascribed to a chemiluminescence interaction between excited Mg atoms and ground state Na atoms. It is also possible that the surplus Mg burns in air increasing the total available energy.

Lines due to Mg atomic emissions and to emissions from gaseous MgO molecules can also be detected in most yellow flames based on Mg as fuel.

The burning lance (or similar firework) reactions can be pictured as occurring in five zones as shown in Figure 10.4. The bottom zone (No. 1) is essentially the preheat zone where the lance composition is being heated to the NaNO₃ melting point. Based on the thermal conductivity of Mg/NaNO₃ /binder composition it is possible to estimate the thickness of this zone to be about 1 mm.

Zone 2 is the preignition reaction zone where the NaNO₃ and binder react producing gases which drive the Mg particles from the lance surface into zone 3, the ignition zone.

Zone 4 is the main combustion zone which also produces the majority of the visible emissions. By Zone 5, the magnesium has all been combusted and the hot gases cool down, mixing with air in the process. Light emission falls rapidly with decreasing temperature, the visible edge of the flame also failing along the surface where the temperature is about 900 °C.

In Figure 10.4 an attempt has been made to indicate the energy balance (*i.e.* the difference between internally generated energy and that received from adjacent zones) for each zone.

The chemistry associated with each zone has been summarised schematically in Figure 10.5. This has been simplified by ignoring the many equilibria that can occur between the binder combustion products and by discounting the fact that Mg will react with other species such as H₂O, CO, CO₂ and even N₂ at 2700 °C.

Other coloured flames follow similar physico-chemical phenomena but operate in different regions of the spectrum. Consequently, the maker of the coloured lance has at his disposal copper salts for blue, strontium salts for red, sodium salts for yellow and barium salts for green, as shown in Table 10.2.

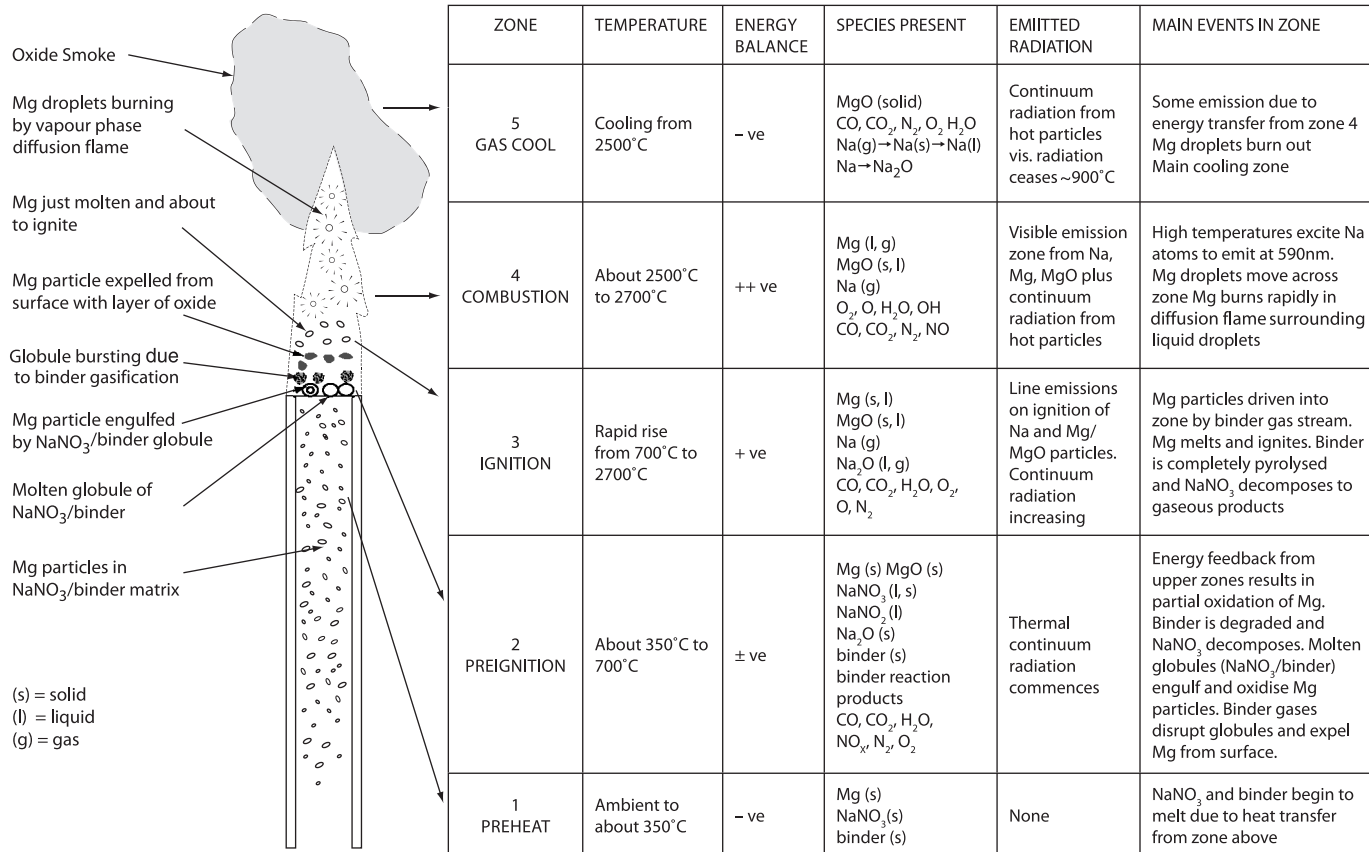


Figure 10.4 The combustion process in lance (or similar firework) yellow flames.

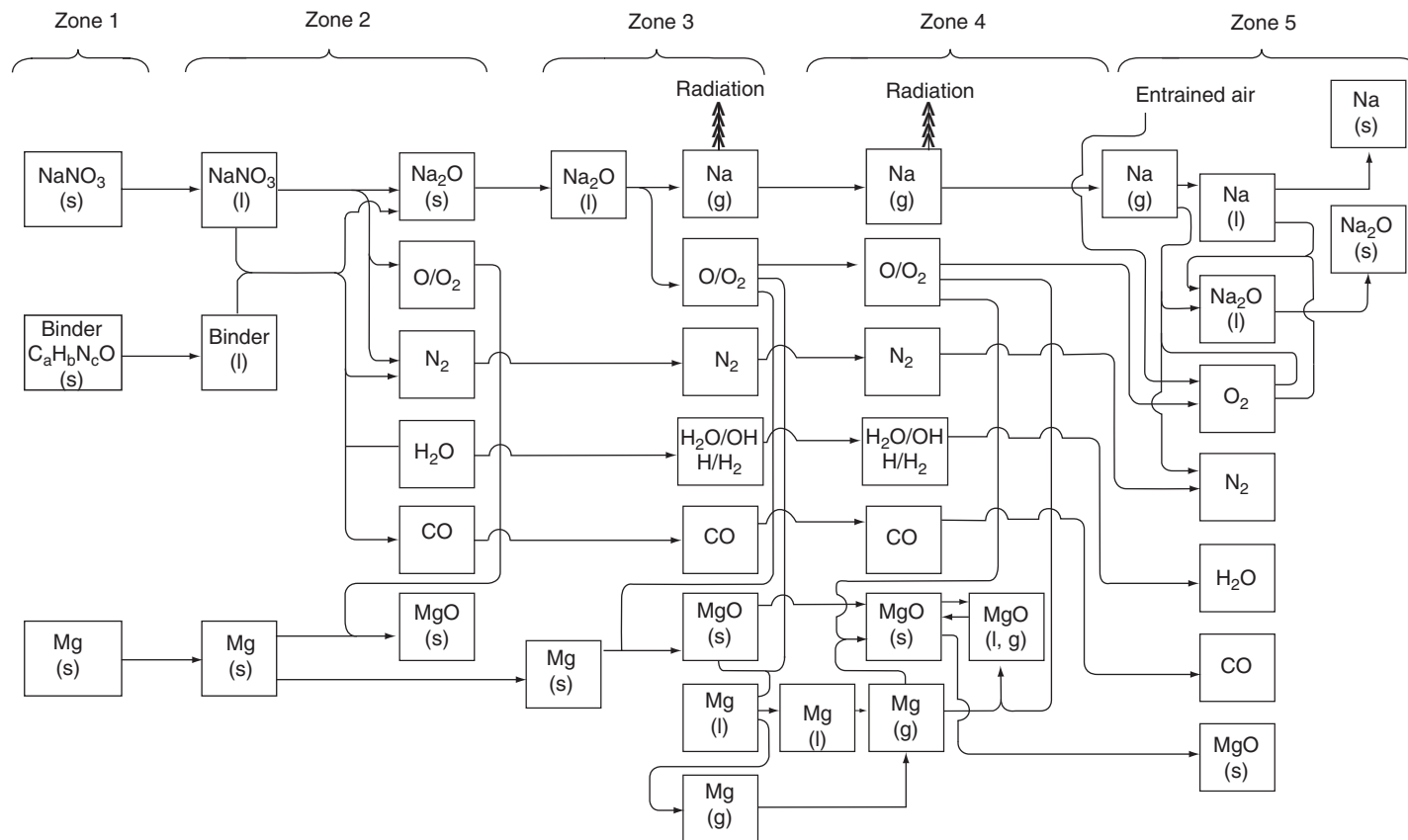


Figure 10.5 Simplified summary of the chemistry involved in yellow lance combustion.

Table 10.2 Commonly-used colour agents.

<i>Name</i>	<i>Formula</i>	<i>Effect</i>
Barium carbonate	BaCO ₃	Green, neutraliser
Barium nitrate	Ba(NO ₃) ₂	Green
Barium sulfate	BaSO ₄	Green
Calcium carbonate	CaCO ₃	Reddish orange
Calcium sulfate	CaSO ₄	Reddish orange
Copper(II) carbonate	CuCO ₃	Blue
Copper(I) chloride	CuCl	Blue
Copper(II) oxide	CuO	Blue
Copper(I) oxychloride	CuCl ₂ · 3Cu(OH) ₂	Blue
Cryolite	Na ₃ AlF ₆	Yellow
Sodium disilicate	Na ₂ Si ₂ O ₅	Yellow
Sodium nitrate	NaNO ₃	Yellow
Sodium oxalate	Na ₂ C ₂ O ₄	Yellow
Sodium sulfate	Na ₂ SO ₄	Yellow
Strontium carbonate	SrCO ₃	Red
Strontium nitrate	Sr(NO ₃) ₂	Red
Strontium sulfate	SrSO ₄	Red

SET-PIECES

The most common set-piece involving lances that one is likely to encounter at a fireworks display consists of a wooden frame measuring about 2 m × 1 m with latticework to support the lances. In fact, the lances are not fixed directly to the lattice but are instead attached to a special form of bamboo that can be softened by soaking it in water and then shaping it to form letters of the alphabet. The bamboo letters are held in position by nailing them to the lattice, after which the letters are picked out using lances that are pinned and glued to the bamboo at intervals. Ideally, the spacing of the lances is about 10 cm. At closer spacing, smoke obscuration and flame overlap can become a problem, whilst more open spacing results in poorly-depicted letters.

The lances are then ‘matched’ using interconnecting piped match and plastic tape or wire, taking care to ensure that each section of piped match directly above a lance is pricked to create a vent-hole. Otherwise, the force from the ignition of the match can blow it clear of the lance before the firework has been successfully ignited.

Finally, the piped match is fitted with a plastic fuse extension for ease of lighting. In operation, the set-piece is positioned above the ground by lofting on poles 2 m in height. Usually reserved for the end of the display, the set-piece being described here is ignited in a prominent position to display the words ‘GOOD NIGHT!’.

Obviously, the number of fire messages and designs achievable in this way is almost infinite – examples are given in Figures 10.6 and 10.7 – and for romantic or other special occasions, outlines depicting hearts and flowers can be set against a lucky couple's initials, while the frame of the

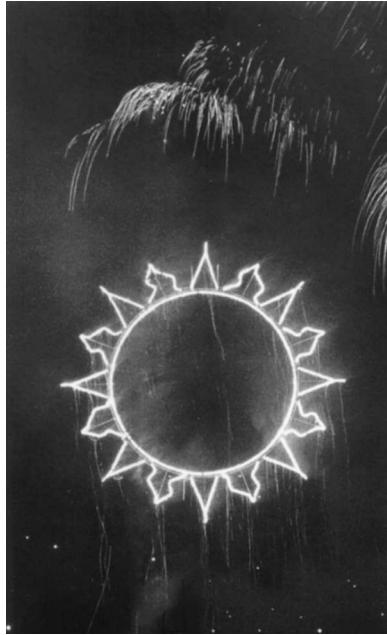


Figure 10.6 Yellow lances forming a 30 metre diameter Rising Sun help to ensure a win for Pains Fireworks at the Montreal Festival, 2007.



Figure 10.7 Set-piece constructed by the author for the occasion of his daughter's wedding.
(Courtesy of David Rushbrook.)

set-piece is adorned with gentle glitter fountains of floral bouquets of silver and gold.

For children who are too young to appreciate (or read) love letters in fire, a set-piece called 'the skeleton' might be more entertaining. This firework features the outlines of a skeleton and delights the audience by waving its arms and nodding its head. In this particular case, the lattice work is hinged so that animation can be produced by the pulling of ropes attached to the hinged sections by (unseen) operators.

DEVICES

If the lances are supplemented by other special effects, exotic devices can be made that provide a theme or highlight to a firework display. 'The Battle' is always a popular device and, as the name suggests, the audience can thrill to the spectacle of ships, tanks or aircraft doing battle across a 40 metre 'no man's land'. The device is, in reality, two devices set the required distance apart with the 'guns' facing each other and the audience watching from one side. Timing of the ignition is critical and two operators must simultaneously ignite the piped match on the two devices. Then it is a case of retiring to a safe distance while the adversaries lob stars and shells and bombs at one another amidst a glorious racket of gunfire and explosions. Usually, the opponent who burns the longest is deemed to be the winner.

Another device that requires a lengthy operating distance is called the 'flying pigeon'. Not too popular with firework operators because of the potential for getting it wrong, a successful firing sees a demented 'pigeon' flying at racing speed across a 40 metre void, shrieking and whistling emphatically until it reaches the other end. The surprise comes when the 'bird' reverses direction and repeats the performance. The errors come if the rope that carries the firework between stout posts becomes too slack or if the firework is lit at the wrong end (the end with the blue dot on it being the 'driver' end).

FLASH AND NOISE EFFECTS

Although gunpowder and its congeners can be successfully used to produce the noise effects of a device such as 'The Battle', there are occasions when a more pronounced flash and bang are required such as, for example, during daylight or when firing a maroon to signal the start (or finish) of a firework display.

In order to produce satisfactory effects a more powerful oxidiser than potassium nitrate is used together with more calorific fuels than sulfur or charcoal. In general, for a given oxidation reaction the heat evolved depends upon the oxidiser anion in the following decreasing order.



Also, for a given oxidiser anion, copper salts yield more heat than lead compounds, which in turn yield more than sodium, potassium, calcium or barium compounds. In practice, copper salts are not commonly used because of the difficulty involved in their ignition. However, the choice of oxidants and fuels for pyrotechnic effects is extensive, as shown in Tables 10.3 and 10.4.

Most flash and loud report effects are produced by using a relatively powerful oxidiser such as potassium perchlorate (which has a high available oxygen content), together with a finely-divided metal fuel (M) that can react according to reaction (10.3).



Such a reaction is capable of producing over 10 kJ g^{-1} in terms of evolved heat.

If one fills the flash composition in a loosely-packed condition into a strong container it will explode violently on ignition, producing a bright flash of light lasting for about a second and accompanied by a loud bang. Pressure build-up accelerates the reaction while rapid energy release produces the flash.

However, a word of caution is needed here because some of the best flashes and bangs are the results of the careful use of some quite powerful and hazardous compositions. For example, the maroon that is often used to signal the start or finish of a fireworks display is loaded with a 'flash' composition containing oxidisers and metallic fuels that must be mixed using remote-controlled machinery.

THE WHISTLE EFFECT

The 'active' ingredients in pyrotechnic whistle compositions are invariably based on aromatic compounds such as gallic acid (10.1) or the salts of aromatic acids including sodium salicylate (10.2) and potassium benzoate (10.3).

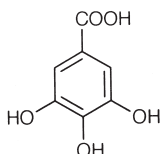
Table 10.3 Properties of inorganic oxidants.

Name	Formula	Molecular weight	Density (g cm^{-3})	Mp ($^{\circ}\text{C}$)	ΔH_f^{\ominus} (kcal mol^{-1})	Total oxygen (% wt)	Available oxygen (% wt)	Reaction
Ammonium perchlorate	NH_4ClO_4	117.50	1.95	d	78.3	54.4	34.2	$2\text{NH}_4\text{ClO}_4 \rightarrow 3\text{H}_2\text{O} + \text{N}_2 + 2\text{HCl} + 2\frac{1}{2}\text{O}_2$
Ammonium nitrate	NH_4NO_3	80.05	1.73	170	87.93	60	19.5	$2\text{NH}_4\text{NO}_3 \rightarrow 4\text{H}_2\text{O} + 2\text{N}_2 + \text{O}_2$
Lithium chlorate	LiClO_3	90.40		125	87.36	53.1	53.1	$2\text{LiClO}_3 \rightarrow 2\text{LiCl} + 3\text{O}_2$
Lithium perchlorate	LiClO_4	106.40	2.43	236	106.13	60.1	60.1	$2\text{LiClO}_4 \rightarrow 2\text{LiCl} + 4\text{O}_2$
Potassium chlorate	KClO_3	122.55	2.32	368	89.87	39.2	39.2	$2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$
Potassium perchlorate	KClO_4	138.55	2.52	610	99.24	46.2	46.2	$2\text{KClO}_4 \rightarrow 2\text{KCl} + 4\text{O}_2$
Potassium nitrate	KNO_3	101.10	2.11	334	118.78	47.4	23.7	$4\text{KNO}_3 \rightarrow 2\text{K}_2\text{O} + 4\text{NO} + 3\text{O}_2$
Sodium chlorate	NaClO_3	106.45	2.49	250	82.34	45.1	45.1	$2\text{NaClO}_3 \rightarrow 2\text{NaCl} + 3\text{O}_2$
Sodium perchlorate	NaClO_4	122.45		d482	100.60	52.2	52.2	$2\text{NaClO}_4 \rightarrow 2\text{NaCl} + 4\text{O}_2$
Sodium nitrate	NaNO_3	85.01	2.26	307	106.6	56.4	28.2	$4\text{NaNO}_3 \rightarrow 2\text{Na}_2\text{O} + 4\text{NO} + 3\text{O}_2$

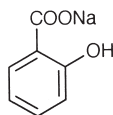
d = decomposes.

Table 10.4 Fuels commonly used in fireworks.

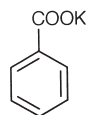
<i>Name</i>	<i>Formula</i>	<i>Notes</i>
Aluminium	Al	
Antimony trisulfide	Sb ₂ S ₃	
Charcoal	C	ca. 85% carbon
Graphite	C	
Hexamine	C ₆ H ₁₂ N ₄	Hexamethylene tetramine
Iron	Fe	
Lactose	C ₁₂ H ₂₂ O ₁₁ · H ₂ O	
Lamp black	C	
Magnesium	Mg	
Magnalium	Mg/Al	Typical alloy 50:50
Silicon	Si	
Sodium benzoate	NaC ₇ H ₅ O ₂	
Sodium salicylate	NaC ₇ H ₅ O ₃	
Stearic acid	C ₁₈ H ₃₆ O ₂	
Sulfur	S	
Titanium	Ti	



(10.1)

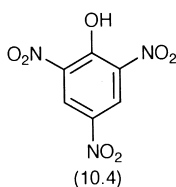


(10.2)



(10.3)

Originally, salts of picric acid (**10.4**) were used.



(10.4)

All whistle compositions are hazardous to handle, but those containing picrates and gallates are also shock-sensitive with a tendency to explode. Picric acid (2,4,6-trinitrophenol) is, in fact, classed as a high explosive.

In forming whistling fireworks, the aromatic compounds described above are mixed with oxidisers such as potassium nitrate or potassium perchlorate and pressed into tubes. On combustion, a loud whistling sound is produced, whose pitch is related to the length and diameter of the tube.

It is generally agreed that the sound originates from oscillations during burning, when the aromatic compounds create small 'explosions' or 'decrepitation' on the burning surface which results in a change in pressure of the out-streaming gases. A resonating standing wave is created inside the tube whose wavelength increases as the length of tube above the burning surface increases. An increase in wavelength is associated with a lowering of the frequency of the whistle, the effect progressing as the burning composition is consumed and free space increases within the confines of the tube.

SMOKE PUFFS

Bursts or puffs of smoke are produced by explosively-dispersing very fine particles (aerosols), either in the form of combustion products or as inert, solid ingredients. These effects are seen in daylight pyrotechnics displays or when firing 'blanks' from artillery pieces. In the latter instance, a brass case loaded with grain gunpowder is fired from the breech to give white smoke, which is in fact an 'aerosol' of mainly potassium carbonate particles. Alternatively, if a bag of fine powder such as charcoal dust is inserted into the muzzle, together with a small bursting charge of 'flash' powder, a black smoke is discharged.

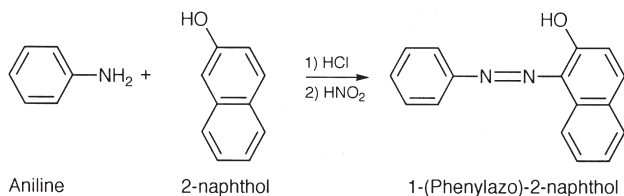
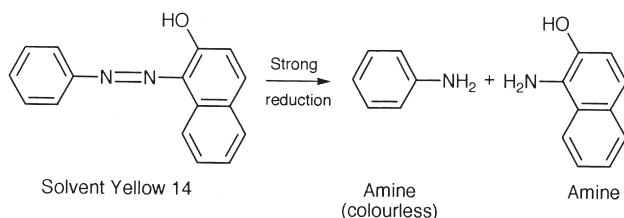
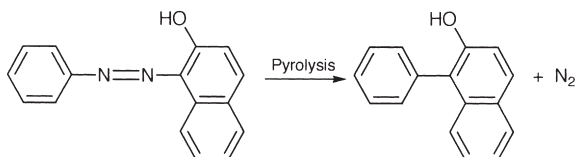
For coloured smoke puffs, pigments based on metal chromates are utilised, the pigment being intimately mixed with a fuel such as magnesium. On combustion in free air, a smoke cloud is produced that has residual colour due to the chromate.

COLOURED SMOKES

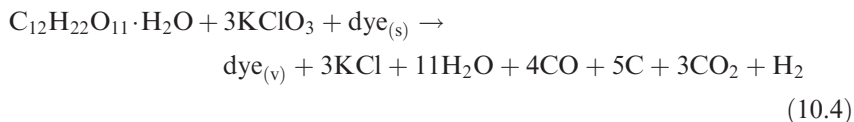
As well as using inorganic pigments in the production of transient smoke effects, a more sustained release can be brought about by using compositions based on gas-producing pyrotechnic ingredients together with readily sublimable organic dyestuffs. In this way, slow-burning 'candles' are produced whose range of colours is limited only by the number of heat-resistant dyestuffs that are commercially available.

One of the simplest, and hence cheapest smoke colouring agents is an azo dye known as 1-(phenylazo)-2-naphthol which is bright orange in colour and also used as a pyrotechnic 'distress' signal. The dye is made by a diazotisation process involving aniline and 2-naphthol as shown in Scheme 10.1.

Any gas-producing pyrotechnic compositions must be both hot enough to melt and volatilise the dye and gassy enough to disperse the

**Scheme 10.1****Scheme 10.2****Scheme 10.3**

dye particles. Commonly, a mixture of potassium chlorate (oxidiser) and lactose (fuel) is used in a reaction represented in a simplified form by reaction (10.4):



For example, the dye, Solvent Yellow 14 has a sublimation temperature of about 125 °C whereas its melting point is 134 °C. The reaction temperature of the chlorate–lactose composition is in excess of 500 °C, which often results in chemical reactions bringing about the destruction of a large proportion of the dye. For example, strong reduction brings about cleavage as shown in Scheme 10.2, whereas pyrolysis leads to decomposition as in Scheme 10.3: Hence, a typical orange smoke composition contains up to 50% of dyestuff in order to offset losses due to the above reactions.

The loss in colour is due to a loss in conjugation of the aromatic molecule. Dyes absorb light in the visible region of the electromagnetic spectrum by virtue of transitions between electronic energy levels.

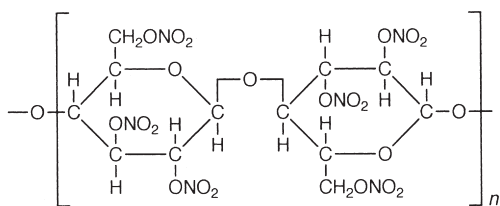
A dye appears coloured because one or more components of the light falling upon it are absorbed so that the reflected light is deficient in certain colours. The wavelength of absorption is dependent upon the degree of conjugation (*i.e.* the number of alternate single and double bonds within the molecule).

It can be shown that increasing conjugation causes a shift to longer wavelengths. For example, dyes from orange to green can be made from increasingly conjugated anthraquinones, as presented in Table 10.5.

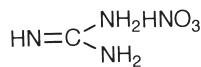
Although blue dyes usually appear to be blue-black in bulk, a blue colour is seen when they are viewed at the edge of a smoke cloud. This is related to the spectral characteristics, concentration and particle size of the dye.

A cooler-burning pyrotechnic composition based on cellulose nitrate and guanidine nitrate has been developed which produces reaction temperatures of less than 500 °C, thus causing less destruction of the dye.

Cellulose nitrate (**10.5**) is a common component of propellant compositions because the fuel and oxygen are combined within the same molecule, whereas guanidine nitrate (**10.6**) is rich in nitrogen and is an efficient gas producer.

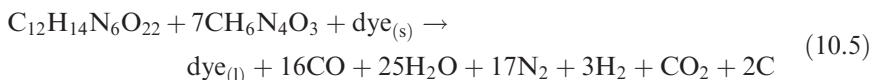


(10.5)



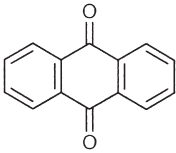
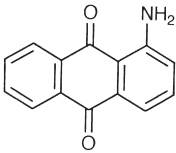
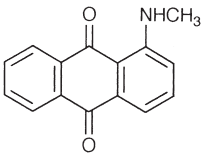
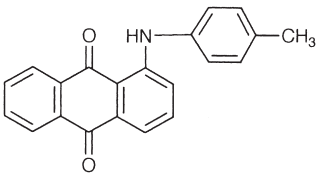
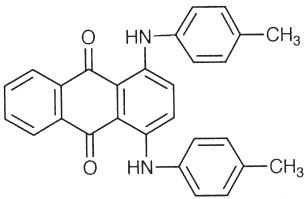
(10.6)

The reaction of the two compounds can be expressed in a simplified form by reaction (10.5):



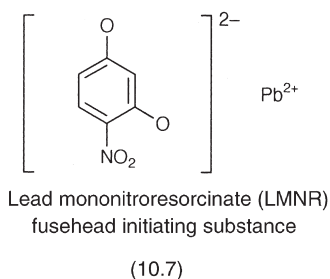
The pyrotechnic composition described above will also contain plasticisers, stabilisers and combustion moderators, thus complicating the overall reaction.

Table 10.5 Variation of colour with increasing conjugation of anthraquinone dyes.

<i>Material</i>	<i>Colour absorbed</i>	<i>Colour seen</i>
 <p>Anthraquinone (colourless)</p>		
 <p>1-amino-anthraquinone</p>	Greenish	Orange
 <p>Disperse Red 9</p>	Blue-green	Red
 <p>Disperse Blue 180</p>	Yellowish orange	Blue
 <p>Solvent Green 3</p>	Red	Bluish green

FIRING ELECTRICALLY

Most fireworks can be initiated electrically, and moving to the subject of electric igniters brings us into the 21st century with regard to explosives. The wirebridge fusehead (or electric match as it is more commonly known) consists of a small bead of explosive held on a support which is essentially a pair of conducting foils separated by an insulating wafer as shown in Figure 10.8 (and earlier in Figure 10.1). The foils terminate in a bridgewire (or fusewire) that is embedded in the explosive bead. Relatively few explosives function satisfactorily from the transient hot glow of a bridgewire and the one most commonly employed is the lead salt of an organic substance known as lead mononitroresorcinate (LMNR) (10.7).



When used in conjunction with more conventional oxidisers and fuels the fast deflagration (burning) from the LMNR ignites the surrounding composition to produce a spurt of flame. Thus the 20 mg or so of explosives in a typical wirebridge fusehead ignite within about 4 ms (depending upon the applied current) and may be used against conventional piped match to ignite shells or any other 'matched' firework.

Provided that the operator has enough connecting wire, a plentiful supply of fuseheads and a firing box, the fuseheads can be connected in series (like the lights on a Christmas tree), each fusehead being securely taped inside a length of piped match to form an ignition train leading to the firework.

Connecting in series has the advantage that the electric circuit can be tested for defective fuseheads or loose connections by doing simple resistance checks. Obviously the current needed to operate a number of fuseheads connected in series is greater than that required for a single device. However, if the applied current is above a certain minimum value, the collective excitation time (during which the bridgewires heat up to the ignition temperature of the LMNR) is shorter than the lag time

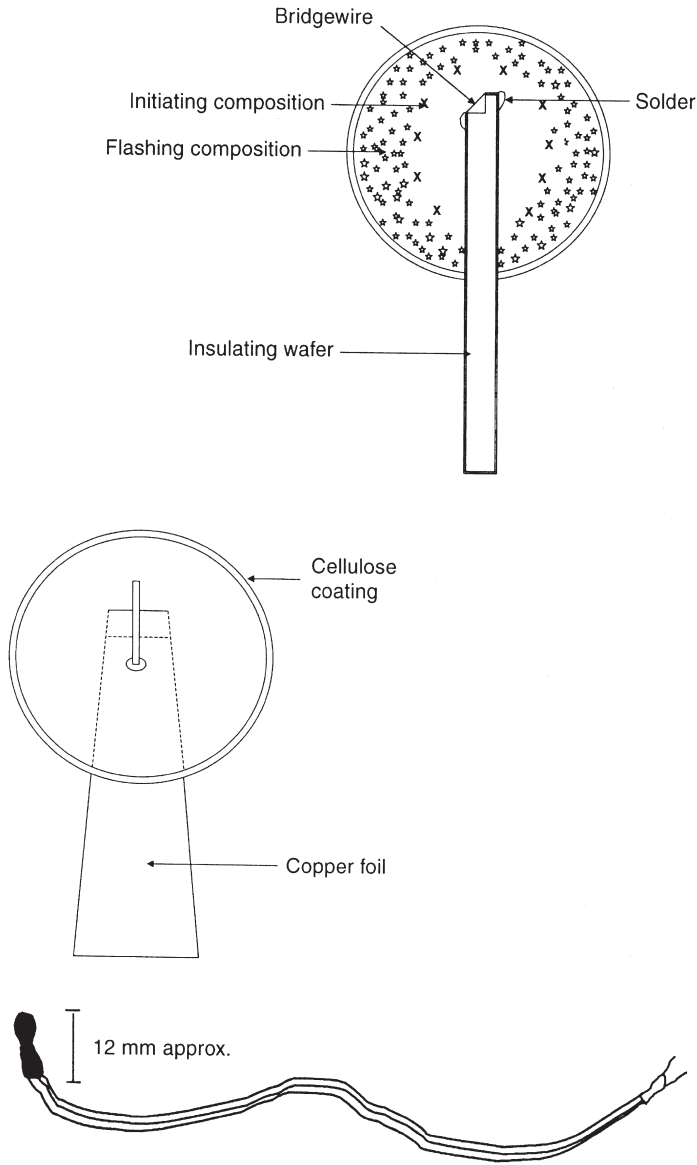


Figure 10.8 Wirebridge fusehead.

(when the fusehead ignites and the bridgewire breaks) and a successful multiple firing will result.

The rather complicated setting up of electrically-fired displays is more than compensated for the split-second timing that is achievable. This is especially important when large displays are fired to accompany music, which might be the way of all firework displays in the future.

CHAPTER 11

Fireworks Safety

The subject of safety is obviously of paramount importance, and this chapter might be used as reference long after the history of fireworks and Vieille's Law have been forgotten.

Fireworks, when not properly handled, can result in injury, loss of life and property damage. The problems of safety are in many ways different from those of most explosives and propellants. In general, the sensitivity of fireworks to shock and impact is considerably less than that of many explosives and propellants. On the other hand, most fireworks are more sensitive to sparks and flame than most other explosive materials.

RADIO HAZARD

When fired electrically, fireworks are connected to wirebridge fuseheads. The fuseheads can inadvertently ignite if subjected to radio hazard (RAD HAZ) when in the vicinity of radio frequency sources such as cellular (mobile) telephones or walkie-talkie radios. Further advice on this should be sought from the makers of the wirebridge fuseheads and of the communication equipment because the characteristics of all these items can vary to some extent.

PUBLIC SAFETY

It can be taken as axiomatic that every person in the fireworks industry recognises that they are dealing with potentially dangerous substances

and articles, and that in this regard they will strive to reduce the hazard to themselves and the general public to the absolute minimum.

While it is recognised that there is a continuing emphasis towards large, organised displays, in Great Britain the inhabitants have the freedom of choice between purchasing and lighting their own fireworks or leaving it to the professionals. It must be said that where fatalities do occur, they tend to be at the hands of private individuals who are handling powerful fireworks recklessly or who are unaware of the dangers.

So far as public safety is concerned, the fatalities due to fireworks in a typical year amount to fewer than 1 in 10 000 000 of the population. On the same terms, this statistic can be contrasted with deaths from infection in hospital (1996) 1000; road deaths (DoT, average 1995–96) 660; accidents in the home (average 1990s) 650; drug-related deaths *ca.* 2000; suicide 86; arson 14; and homicide 130 per 10 000 000 of the population.

Thus, in perspective, the journey by road to any firework display might well be significantly more dangerous than the display itself. However, in order to maintain this high standard of safety it is important to educate, so far as is possible, anybody who is even remotely associated with the handling of fireworks.

First, it must be understood that all fireworks and pyrotechnic compositions are classed as explosives. It is both dangerous and illegal (a) to manufacture gunpowder or pyrotechnic compositions, (b) to assemble such compositions into fireworks, (c) to dismantle (unmake) fireworks or (d) to import fireworks without giving required information to the Commissioners of Customs and Excise.

Anybody who has responsibility for the handling of fireworks, either privately with a modest sparkler or professionally with gigantic shells, should be aware of the safety aspects as they relate to a particular situation. Generally, if a box or a packet of fireworks is purchased privately there is a list of safety instructions included, in addition to the label on each firework that is mandatory under BS 7114. You should read them because the first line of defence against accidents is information and education. This can be enhanced by adopting a safety philosophy, attending firework operator training courses where necessary, communicating with others, and by planning, example, thought and deed.

In the case of sparklers they should not be handled by small children who might chew at the live composition, poke the wires into their eyes, burn themselves with sparks or pick up the burnt-out wires while still hot. Sparklers should not be handed around while burning, they should not be used near animals, the eyes, flammable materials or other fireworks.

Any remaining sparklers should be kept covered and away from burning fireworks. Anybody who takes all these precautions will have

made a safety assessment, either consciously or sub-consciously, and the risk of accident will be minimised.

ORGANISED DISPLAYS

In the broader context we must consider safety as it applies to a long list of topics. For every firework display there is the safety of the general public to consider. Equally important is the safety of the spectators, stewards and attendants, not forgetting the operators themselves. The list should also take account of the safety of animals and property, including buildings, vehicles and personal effects. An ill-aimed rocket can quite easily penetrate a bathroom window and continue burning once inside the room.

A diligent operator must also be concerned with the quality of the fireworks and equipment; that there are no obvious flaws or deficiencies. The frames and timber should be given close scrutiny, as should the conveying vehicle.

Once on-site, the operator must judge the weather. Is it too wet or windy and is the wind in the right direction? Will the sparks from the bonfire blow onto the assembled fireworks? Will the smoke and fall-out be taken towards the spectators?

Communication with the display organiser, hereafter known as the 'customer', should clarify the situation with regard to crowd control, emergency services, first-aid and other amenities. The site must be inspected for obstacles, ground condition, power lines, animals, neighbouring buildings and the fall-out area. If any of these aspects are not acceptable on safety grounds, then the operator has every right to modify or to cancel the display. Obviously, it is helpful if an inspection of the site can be made before the display day, but this is not always possible.

The operator's first point of contact is the customer. After providing proof of identity, essential questions must be asked such as what are the arrangements with stewards, security and emergency services? Are the police and near neighbours aware of the display? Where is the nearest telephone and emergency exit? Are there any first-aid or other facilities?

Inspection of the site and an assessment of the wind direction enables an informed judgement to be made regarding the position of the fireworks in relation to the spectators. If necessary, the positions must be adjusted (or even reversed) so that members of the audience have their backs to the wind so far as is possible. It is absolutely vital that smoke and debris do not drift towards the audience. If necessary: maximise the distance from the audience for fallout; remove items from the display; or cancel the display.

Rockets fired vertically will track into the wind and can be carried hundreds of metres down-range before the burnt-out motors and sticks return to earth. Similarly, in high winds, the debris from shells can carry considerable distances and scatter over a wide area. The fall-out area must therefore be inspected, as must the positions of any bonfires on the site.

Assuming that the operator and his colleagues have permission to take their vehicles across the site and that the ground is suitable for vehicular access, an approach can now be made to the firing area.

When the operator looks at the firing area, one of the factors to be considered is the safety distance from the spectators to the first line of fireworks. This is dependent upon the type and size of the fireworks of course, but as an absolute minimum the distance should be 25 metres. Ideally, the ground should be soft enough to accept stakes or digging in of the largest mortars, but if not, sandbags must be used. If the ground is not level, the degree of slope must be taken into account when the frames are erected and when the crates of mines and shells are set up. Rough ground can present problems if the display is to be fired electrically when smooth runs of wire are required and also if cakes are to be used.

Having inspected the firing area, the fall-out area and the spectators' enclosure, it is time to consult the check-list and to commence the unloading of the fireworks. It is prudent to place 'NO SMOKING' signs within 50 metres of all fireworks, and mobile communication equipment should be banned from the vicinity because of the radio hazard if the display is to be fired electrically.

Trained operators know that the fireworks should be unloaded in small quantities at a time. This not only prevents human ruptures but minimises the danger from inadvertent ignition. Similarly, the 'matching' of shells should be done well away from the main supply of fireworks. Mines and shells are especially dangerous and accidents have been caused by joining pieces of piped match using metallic staples. The correct procedure is to tie the match or fuse in place using string and then to lap the join with tape in order to protect the match against sparks from other fireworks. The shell should be carefully lowered into its mortar tube only after the tube has been positioned ready for firing. Once inside the tube, the head and other parts of the human body should be kept well clear of the muzzle. In the event of a misfire, shells, and indeed all fireworks, should be left for at least 20 minutes before dousing with water. Fuses should never be re-struck if there is the slightest possibility of injury to the operator or others from an uncontrolled ignition.

If a mine or shell is too tight for the mortar tube (assuming that it is of the correct calibre), it should on no account be hammered or crushed to

make it fit. Gunpowder is friction-sensitive and it is better to omit the firework from the display rather than have it explode in one's face.

Although professional operators tend to use the same set of mortar tubes on more than one occasion, it is safer to use them once only, particularly during a display because the act of reloading is hazardous if there is any smouldering debris or 'afterglow' from the previous shots within the tube into which a fresh shell is inserted.

In the absence of crates or sandbags, each mortar tube should be partially buried in the ground. In this event, care must be taken that there are no stones or other loose objects in the vicinity that might become missiles in the event of an unscheduled explosion. Having placed all mines and shells at the extreme rear of the firing area it is necessary to ensure that any racks or crates of mortar tubes are positioned perpendicularly or end-wise to the audience so that, in the event of a container tipping over, the contents are not left pointing towards the audience.

Rockets should similarly be located at the rear of the site, along with other aerial fireworks such as crown wheels and maroons, again in positions of safety with respect to the spectators.

Roman candles, set-pieces, wheels and other devices are normally secured to stakes placed in the ground. This is a safe practice so long as the stakes are positioned between the firework and the audience, whereby any loosely-held firework cannot tip towards the audience.

The most favoured knot when tying posts to stakes is the clove hitch. With practice, this knot is quickly effected and easy to undo. However, when tying candles, care should be taken so that the knot is not over-tightened, otherwise crushing of the firework tube might occur which could interfere with the ejection of the stars.

The use of nails in place of rope or string poses additional hazards. Although wooden frames can be securely fixed to posts using nails there is always the problem of protruding nails on dismantling after the display. Perhaps more serious is the danger from flying sparks if a hammer and nails are used, because fireworks are sensitive to sparks as mentioned at the beginning of this chapter.

Bundles of miniature candles packed into circular or square boxes are known as 'cakes' for obvious reasons. They are the simplest of fireworks to set up because one merely places them on level ground, on a waterproof sheet if necessary. However, the fuse that connects all of the tubes runs in a spiral inside the base of the box, and the end that terminates on the outside wall of the box can be difficult to locate (especially in the dark) and be rather slow in operation. Some tens of seconds might elapse before the first tube ignites, but do not be tempted to return to the

firework once the fuse is lit. As always. It is a matter of ‘light the blue touch-paper’ and ‘retire immediately’.

Finally, the question of safety can be addressed to portfires. These are the long, pencil-like fireworks that emit a shaft of flame for a few minutes and are used to light the fuses of the display fireworks. Obviously, for any display lasting for more than a few minutes, a number of portfires are required. It might be tempting to carry these spares in a pocket but remember the sensitivity hazard. A flying spark could set them off. The correct procedure is to carry one portfire at a time in a gloved hand, along with a box of matches to provide a re-light if necessary. Spares should be stored under cover, at some convenient position in the firing area. The composition inside a portfire is somewhat loosely pressed which means that, on occasion, an air gap can develop in the column of burning ingredients that will be enough to put the flame out. In order to guard against this the portfire is tapped (gently) in a ‘nose down’ position to close any gaps before lighting.

After the display, any burning embers should be doused with water, while fireworks that have failed in any way should be segregated from spent fireworks, labelled as MISFIRES and packaged separately. On no account should spent cases or live or faulty fireworks be thrown onto the bonfire. Mortar tubes should be inspected for glowing embers, which should be extinguished before transporting. Misfires should be returned to the point of sale.



Figure 11.1 Author's daughters Claire and Jane exhibit ear protection before a display.

Any remaining portfires or other live fireworks should be returned to their original packaging, and ideally packaged so that they cannot rattle or shift about in transit. Any spilled powder should be washed away with copious quantities of water. Ear defenders are always a good idea and these can take the form of large plastic “bins” (or muffs) or small plugs held on a semi-circular head support (Figure 11.1). Separate plugs are equally beneficial but these are easily lost.

Enjoy your fireworks but remember that failure to act safely and responsibly can lead to accidents; just as it will with the ubiquitous garden barbeque. The motor vehicle is still ahead on points though – in 1997 there were over 65 000 fires in vehicles resulting in some 100 deaths.

CHAPTER 12

Fireworks Legislation

THE EXPLOSIVES ACTS

The important subject of legislation applied to the explosives industry, including fireworks, commenced in the form of the Explosives Acts of 1875 and 1923.

Nowadays, regulatory provisions are applied, and those governing health and safety fall into four categories: (a) Acts of Parliament, (b) Regulations made under those Acts, (c) Codes of Practice, and (d) Guidance Notes.

When a Bill has been debated in Parliament and received Royal Assent it becomes law; regulations made under the Acts also become law. The Factories Act of 1961 and the Health and Safety at Work Act of 1974 must be obeyed because they are part of criminal law.

The fireworks industry in the UK is too small to warrant continuous attention by Parliament, but two corporate bodies have been established in accordance with the Health and Safety at Work Act that control safe practices within factories, including fireworks factories, and this, in turn, ensures a safe standard of products that reach the general public.

THE HEALTH AND SAFETY COMMISSION

The Health and Safety Commission (HSC) consisted of a Chairman appointed by the Secretary of State for Employment, and not fewer than six and not more than nine other members drawn from industrial

organisations, local authorities and professional bodies. As of April 2008 the HSC was abolished and the HSE became the sole controlling body.

THE HEALTH AND SAFETY EXECUTIVE

The Health and Safety Executive (HSE) is a statutory body co-ordinated by a Director General and two other people appointed by the Executive.

Health and Safety Inspectors (including Explosives Inspectors) are appointed by the HSE to ensure compliance with the relevant statutory provisions. The inspectors have very wide ranging powers, and this is another factor that contributes to fireworks safety.

A welcome addition to the controls imposed by the HSE which relate to the manufacture, keeping, safe conveyance and importation of explosives, including fireworks, is the British Standard BS7114. This standard applies specifically to consumer fireworks and was promulgated in 1988 in order to deal with aspects such as the categorisation, performance testing, quality control and labelling of all types of fireworks.

Amazingly, no such protocol existed in the UK before 1988, when it was difficult to prevent dangerous, imported fireworks from reaching the shop shelves. Thus, unsuspecting consumers could, in theory at least, purchase items containing prohibited mixtures of, say, sulfur and potassium chlorate and drop them onto the back seat of the family saloon where they could ignite without warning.

Anybody who studies the legislation will see that BS7114 makes a notable addition to the Explosives Acts of 1875 and 1923, the Fireworks Act of 1951, the Health and Safety at Work Act of 1974, the Consumer Protection Acts of 1978 and 1987, and the Classification and Labelling of Explosives Regulations of 1983.

Hitherto, imported fireworks were subject to licensing and a 'spot check' by the HM Explosives Inspectors, while labelling was evaluated on the basis of common sense and past experience.

On the other hand, fireworks manufactured within the UK were controlled by factory licensing and statutory inspections by the Explosives Inspectors.

In the absence of any approved official standard, procedures for quality control, overseas manufacture and importation were tenuous to the extent that it was often unclear as to whether some fireworks were suitable for sale to the general public or whether they should be used by a licensed importer or manufacturer.

A published specification was thus called for in the form of a British Standard.

BRITISH STANDARD FOR FIREWORKS

British Standards are created by a committee that includes representatives from those involved in the manufacturing industry, and in this case the result was BS7114 which is divided into three parts: Part 1, Classification of Fireworks; Part 2, Specification of Fireworks; and Part 3, Methods of Test of Fireworks.

In Part 1, fireworks are divided into four categories that relate to where the products are used and the level of associated hazards.

- Category 1 fireworks are suitable for use inside houses and include toy caps, ‘party poppers’, cracker snaps, throwdowns, smoke devices and sparklers (both hand-held and non-hand-held). They are often used by children under adult supervision and are either hand-held or designed to function quite close to a person. Factors such as the flammability of clothing materials and other household effects and the possible injury, particularly to the eyes, face and hands, are taken into account when assigning a firework to Category 1. The potential hazards to consider include excessive flame or explosion, hot particles, hot slag and sharp fragments.
- Category 2 fireworks are intended for outdoor use in confined areas, such as small gardens, where spectators are expected to be at a distance of at least five metres when the firework is functioning. The person lighting the firework is also expected to retire to a safe distance and so the fusing of the firework (blue touch-paper) becomes important. Examples of fireworks in this category include fountains, Roman candles, mines, wheels, rockets and large sparklers (both hand-held and non-hand-held). The main hazards associated with Category 2 fireworks are ejected debris, burning matter and erratically-flying rockets.
- Category 3 fireworks are designated for outdoor use in large open spaces such as parks, sports fields and open land, and spectators are expected to be at least 25 metres away when the firework is functioning. This category includes the proportionately larger fountains, Roman candles, mines, wheels, rockets, non-hand-held sparklers and combinations such as devices. Again, the main hazards are ejected or burning matter and erratically-flying projectiles.
- Category 4 fireworks are of such design that they are not intended for use by the general public and therefore do not feature significantly in BS7114.

Part 2 of the British Standard lists all of the main types of firework within Category 1, Category 2 and Category 3, and provides specification requirements by which the construction and performance of these fireworks can be controlled. Aspects that are addressed include means of ignition, projection of burning matter, projection of debris, principal pyrotechnic effects and the angle of flight of rockets.

The important subject of labelling is addressed in some detail because Categories 1, 2 and 3 all have labelling requirements that apply to the packaging as well as to individual fireworks. In general, the phrases on the label are selected from standard lists that ensure conformity and unambiguity. Thus, the labelling must be in English, in letters of a specified type and size, and all fireworks must be labelled with their intended use and type name. The auxiliary verb 'must' is chosen deliberately here to express necessity or obligation. A correctly labelled fountain in Category 2 will have 'GARDEN FIREWORKS', 'FOUNTAIN', together with the appropriate warnings, instructions and effects, followed by the name and address of the manufacturer or importer. Any fireworks that are deficient as regards labelling should not be purchased. The words 'complies with BS7114: Part 2, 1988' must also be present on the label.

Part 3 of BS7114 is concerned with the methods of testing of fireworks and certain items of auxiliary equipment such as rocket launchers. In essence, the standard calls up chemical and physical test methods that are applied to all types of firework, from toy caps to large rockets. Fireworks that are incomplete or not intended for sale to the general public are excluded.

Physical testing includes a primary examination of the packaging and the fireworks within. A note is made of the general condition of the firework and the presence of any defects such as loose powder. The firework is weighed and, if required, the weight of explosives inside is also determined. In performance testing, the firework is made to function and a note is made of effects such as the fuse burning time, the number of explosions, the ejection of incandescent matter or debris and the orientation of the firework whilst functioning.

Chemical testing is carried out in an approved laboratory because the firework must first be dismantled. 'Wet' methods of analysis are applied that involve analytical grade reagents to detect, in particular, the presence of chlorates in admixture with elemental sulfur. Sulfur-chlorate mixtures are banned in the UK, and one use of sulfurless gunpowder is in fireworks where chlorates are also present.

UK LIST OF CLASSIFIED AND AUTHORISED EXPLOSIVES

Fireworks that meet the requirements of BS7114 must also be included in a publication called the UK List of Classified and Authorised Explosives (LOCAE) and more recently by LOCAF (the UK List of Classified and Authorised Fireworks 1999). These lists originate from the Explosives Acts and relate to civilian rather than to military explosives. Thus, the 1994 edition of LOCAE contains articles ascribed to Kimbolton, Pains and Le Maitre. For example, included in the FIREWORKS columns, will be found STANDARD – SET PIECE. For this particular entry, the United Nations Serial Number is given as 0336, the Hazard Code is 1.4G, the UK Class and Division is 7.2, while the Competent Authority (HSE) Reference is GB 72411.

What do all of these terms mean? Well, the UN serial number 0336 applies to a particular group of fireworks, and acts as an aid to international identification. The HSE or MoD, as part of the process of classification of a product, assigns the most appropriate of these four-digit numbers, taking cognisance of the hazard classification code and security requirements.

Upon classification, all explosives (including fireworks) are assigned to dangerous goods Class 1 in accordance with the Classification and Labelling of Explosives Regulations 1983 (CLER). Class 1 explosive substances and articles are then further classified according to their respective hazards.

The United Nations recommendations provide six sub-divisions (Division 1.1 to Division 1.6). They are defined according to the different types of hazard:

- Division 1.1
Substances and articles which have a mass explosion hazard. (A mass explosion is an explosion which affects almost the whole load of explosives virtually instantaneously).
- Division 1.2
Substances and articles which have a projection hazard but not a mass explosion hazard. (*e.g.* 50 mm and 60 mm candles).
- Division 1.3
Substances and articles which have fire hazard and either a minor blast or minor projection hazard or both, but not a mass explosion hazard. (*e.g.* medium sized rockets and shells).
- Division 1.4
Substances and articles which present only a slight risk in the event of ignition or initiation during carriage. The effects are largely

confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package. *e.g.* 20 g rockets and small firecrackers.

- Division 1.5

Very insensitive substances having a mass explosion hazard which are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions of carriage.

- Division 1.6

Extremely insensitive articles which do not have a mass explosion hazard. The articles contain only extremely insensitive detonating substances and demonstrate a negligible probability of accidental initiation or propagation.

Fireworks are mainly classified as Hazard Division 1.4 (meaning substances and articles that present no significant hazard, *e.g.* small display fireworks) or Hazard Division 1.3 (meaning substances and articles which have fire hazard and either a minor blast or minor projection hazard but not a mass explosion hazard, *e.g.* large display fireworks). There are increasing numbers of fireworks classified as 1.1 or 1.2 (mass explosion or projection hazard). This explains the 1.4 Hazard Division of the STANDARD – SET PIECE, but what does the ‘G’ mean?

Well, the UN also acknowledge that the safety of substances and articles is best assured by keeping each generic type separate. This is not always practicable, however, and if there has to be a degree of mixing of various explosive substances and articles, then the extent of such mixing is determined by the compatibility of the explosives. Explosives are considered to be compatible if they can be transported (or stored) together without significantly increasing either the probability of an accident or, for a given quantity of explosives, the magnitude of the explosion.

The UN Compatibility Groups are represented by letters from A to S, but omitting I, M and O.

Compatibility Group G comprises any substance which is an explosive substance because it is designed to produce an effect by heat, light, sound, gas or smoke, or a combination of these as a result of non-detonative, self-sustaining, exothermic chemical reactions, or an article containing such a substance or an article containing both a substance which is explosive because it is capable by chemical reaction in itself of producing gas at such a temperature and pressure,

and at such a speed, as could cause damage to surroundings and an illuminating, incendiary, lachrymatory or smoke producing substance (other than a water-activated article or one containing white phosphorus, phosphide or a flammable liquid or gel).

That is what ‘G’ means, and I hope you will agree that it applies to fireworks!

The UK Class and Division for fireworks is 7.2. This should not be confused with the UN dangerous goods Class 1 to which all explosives are assigned.

Class 7, Division 2 relates to manufactured fireworks consisting of any classified explosive and any classified firework composition, when such explosive or composition is enclosed in any case or contrivance, or is otherwise manufactured to form a squib, cracker, serpent, rocket (other than a military rocket), maroon (including signalling maroons), lance, wheel, Chinese fire, Roman candle, or other article specially adapted for the production of pyrotechnic effects, or pyrotechnic signals or sound signals. Provided that a substantially constructed and hermetically closed metal case containing not more than 1 lb of coloured, fire composition of such a nature as not to be liable to spontaneous ignition shall be deemed to be a manufactured firework.

Class 7, Division 1 relates specifically to firework compositions (such as flash powder) and these are referred to as ‘substances’ rather than manufactured ‘articles’.

Other regulations control the packaging and storage of dangerous goods, the transportation by sea, air, rail and road, the training of drivers, the licensing of explosives factories and magazines, and limitations on quantities. (See for example: CDGUTPER 2007, 2005; COER 1991; COMAH 1999; Fireworks Act 2003; DSEAR 2002). The general public are free to purchase certain types of fireworks or do-it-yourself display kits, without licence, from reputable suppliers.

In summary, fireworks legislation is necessary and is designed to prevent accidents and to reduce risk to the absolute minimum. To this end, the HSE helps to ensure:

- (1) sufficient knowledge of the properties of compositions being manufactured and hence of the precautions which should be taken;
- (2) adequate working instructions and safe systems of work;
- (3) planned maintenance of equipment, facilities and buildings;
- (4) compliance with advice given by HSE inspectors.

While compliance with a British Standard does not of itself confer immunity from legal obligations, the net effect to the consumer or spectator has been a reassuring increase in the standard of safety of both the fireworks and the people responsible for them. The current trend towards organised displays has not been at the expense of the availability of garden or indoor fireworks, however, and the increasing legislation is mainly the concern of those in the industry who are involved with the importation, manufacture, retail or safe operation of fireworks.

RECENT LEGISLATION

More recently, the Fireworks (Safety) Regulations of 1997, on Consumer Protection, has prohibited the supply of certain fireworks to the general public. These include bangers, fireworks containing bangers, aerial shells and maroons, and shells- or maroons-in-mortars. However, such fireworks are still available to professional operators for firing at organised displays.

The Carriage of Dangerous Goods (Amendment) Regulations of 1999 provide an update on the Classification, Labelling, Packaging and Carriage of Dangerous Goods Regulations (including explosives) published between 1983 and 1997.

Further details of the current legislation are included in the Bibliography that follows this chapter, while full details are available from HSE Books, Sudbury.

THE FIREWORKS REGULATIONS 2004

The latest Fireworks Regulations came into force on 7th August 2004 having been issued as a Statutory Instrument in conjunction with the DTI.

These Regulations provide some useful definitions (“interpretations”) as well as setting out a list of “prohibitions,” the first of which states that persons under the age of eighteen years are not allowed to possess an “adult firework” in a public place.

Category 4 fireworks are now banned to the general public but exclusions exist which include their use in organised displays or by members of recognised establishments or Government departments.

The Regulations go on to say that no person may supply excessively loud Category 3 fireworks, while “adult fireworks” must be clearly advertised as such at the point of sale.

There is also monitoring of the import of fireworks and prohibitions on the use of certain fireworks at night. The law now prohibits the use of fireworks between the night hours (11 pm and 7 am) except on the following nights: Bonfire Night (Midnight to 7 am), Chinese New Year, Diwali and New Years Eve (1 am to 7 am).

THE MANUFACTURE AND STORAGE OF EXPLOSIVES REGULATIONS 2005

The Manufacture and Storage of Explosives Regulations (MSER) and Approved Codes of Practice (ACoP) were issued by the Health and Safety Commission, and came into effect on 26 April 2005, having largely replaced the Explosives Acts 1875 and 1923.

MSER covers the manufacture, storage and handling of all explosives (*e.g.* ammunition and blasting explosives) and there is specific reference to fireworks, fusing fireworks and assembling fireworks displays from components.

Thus anybody involved in the manufacture, storage, or professional use of fireworks should at least be familiar with the scope of the 2005 Regulations and of the fact that the Code of Practice has special legal status *i.e.* a court would find you at fault if it is proved that you did not follow relevant provisions of the Code.

Although the Regulations are both extensive and detailed, sound advice will be found on matters such as firework fusing and the prevention of accidental initiation which might occur *e.g.*

- (a) from not using sharp cutting tools made from non-sparking materials or from stapling fuses directly into place
- (b) by friction when inserting fuse or fuseheads into sensitive exposed composition.

In all there are seventeen Guidance precautions listed in ACoP with regard to fusing as included in Regulation 4 (Safety Requirements).

It should also be noted that the Regulations apply to the manufacture and storage of explosives whether this is for work or non-work purposes. This means that they would apply to anyone storing explosives for personal recreational use, or to clubs or societies storing for firework displays or re-enactment events.

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