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Speculation on the Effects of Gunshot or Explosive Residues on Historic Silk Flags

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ABSTRACT

Historic battle flags and uniforms are collected by museums, and many have significance as icons representative of their owners as well as historic context. The effects of battle, both mechanical and chemical, have an impact on the projected lifetimes of these objects in museums. Modern air quality, as well as the type of display, is important. Pyrotechnic displays using Black Powder can also produce considerable amounts of particulates and gases and, if near museums, may be a significant source of damage to a museum's collection.

Keywords: gunshot residue, explosive residue, silk flag, Black Powder

Introduction

This paper was presented in November of 1989 as an informal lecture at a one-day working session on Weighted Silk Research at the Conservation Analytical Laboratory (now the Smithsonian Center for Materials Research and Education). The discussion centered on the possible effects of gunpowder (explosives) residue on historic silk flags, primarily those from 18th and 19th century battlefields. Silk flags of this type are often found in a highly deteriorated condition, from both mechanical and chemical damage. This lecture was intended to provide background material and speculation on the effects of this hostile chemical environment on the eventual stability of these flags.

Black Powder and Its Residues

Black Powder was introduced into Western Europe around the 13th century and was used in military applications from the 14th century. It was the universally used explosive until about 1870, being in part replaced by nitroglycerin and/or nitrocellulose in various forms. Black Powder is still used in large quantities even today. Other propellants and explosives were developed in the 19th century: nitrocellulose (guncotton) introduced as the first successful smokeless powder by Schultze in 1864 and dynamite (nitroglycerin based) by Nobel in 1867.

Black Powder is a mechanical mixture of potassium nitrate, charcoal and sulfur. There are many formulas for this mixture but in general they fall into the following weight ranges:

Potassium nitrate	70–80%
Sulfur	5–18%
Charcoal	9–19%

Sodium nitrate was used in some formulations as an explosive in mining.

British Government powder in the early 19th century was composed of potassium nitrate, 75%, sulfur, 10%, and charcoal, 15%.[1] By the mid-19th century the "ideal" composition was potassium nitrate, 74.9%, sulfur, 11.8%, and charcoal, 13.3%.[2] The volume of gas produced by this mixture was 296 times that of the unexploded powder.

Black Powder was used in propelling projectiles from small arms, cannons, and mortars. It was used as well in rockets, in hand grenades, and in other types of bombs.

After ignition, Black Powder mixtures produce about 45% gaseous products with the remainder as solids in the barrel of the weapon or as particulates in the air. The bulk of the gases are carbon dioxide, carbon monoxide and nitrogen with some hydrogen, methane, water and hydrogen sulfide as minor constituents. It should be noted that charcoal might contain

substantial constituents other than carbon. For all varieties of Black Powder, the largest volume of gas produced is carbon dioxide, followed by nitrogen and then by carbon monoxide.

A complicated and impressive empirical equation for describing the combustion products of Black Powder is given in the *Encyclopedia of Chemical Technology*:[3]

$$74\ KNO_3 + 16\ C_6H_2O + 32\ S \rightarrow$$
$$35\ N_2 + 56\ CO_2 + 14\ CO + C +$$
$$19\ K_2CO_3 + (NH_4)_2CO_3 + 3\ CH_4 +$$
$$7\ K_2SO_4 + 8\ K_2S_2O_3 + 2\ KSCN +$$
$$2\ K_2S + 2\ H_2S + 3\ S + 4\ H_2$$
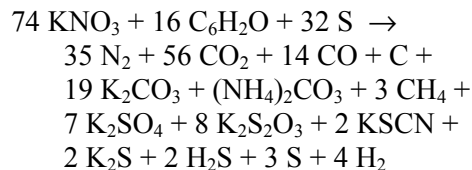
The formula is a general one and the specific products may change depending upon the powder's composition and impurities as well as temperature and moisture.

The solid residues after Black Powder ignition are often found to be:

> potassium sulfate
> potassium carbonate
> ammonium carbonate
> potassium sulfide
> potassium thiocyanate
> potassium thiosulfate
> carbon

with some unconverted potassium nitrate, sulfur and charcoal. With moisture and time these residues may be converted to other compounds.

Large amounts of Black Powder were often used in 19th century combat. In the Napoleonic Wars, at the siege of Ciudad Rodrigo (Jan. 1812), cannons and mortars consumed 74,978 pounds (34080 kg) of powder in less than 31 hours. Similarly at Badajos an enormous 228,830 pounds (104000 kg) of powder were used. At the first and second sieges of San Sebastian 502,110 pounds (228232 kg) of powder were consumed.[4] Battlefields were often clouded with these gunpowder particulates whose weight totaled thousands of pounds.

Metal or Metal Ions from Projectiles

Historically lead has been the metal used in projectiles from small arms, while iron and steel were used in larger weapons such as artillery and mortars. Copper-, nickel-, and steel- covered lead projectiles are also known. Projectile residues are often found on fabrics. Oxidation of many of these metals along with water vapor or liquid water can lead to discoloration at best and decomposition of the fibers at worst. Metals will often catalyze the hydrolysis and sometimes the oxidation of proteins such as silk.

Heavy metal salts have been used in percussion caps and cartridge primers since the 19th century. Some of the materials used were:

> antimony sulfide
> barium nitrate
> barium carbonate
> barium peroxide
> calcium silicide
> copper thiocyanate
> lead thiocyanate
> lead trinitroresorcinate
> mercury fulminate
> quartz
> glass

Early primers also contained potassium chlorate, which—on detonation—produced potassium chloride. Potassium chloride was determined to be a serious source of corrosion in rifle barrels. Other primer constituents were nitrated organics such as picric acid, trinitrotoluene (TNT), gums, and nitrated guanidine compounds. Since primer compounds are only a small proportion of gunshot residues, their effect would probably be small on flags or historic textiles. Brass is an integral part of many primers, and particles of brass are sometimes associated with primer residues. Brass is a common component of cartridge cases and brass particles are often ejected from modern auto loading weapons.

Methods of Deposition

Two principal modes of depositing gunshot residues on flags would seem likely.

First, the particles could attach themselves either directly from the force of the weapon's discharge (under 3 ft (1 m) or so from small arms) or through gravity and wind currents in the atmosphere. Of course, projectiles going through a flag will generally leave some residues. People handling the flag with residues on

their hands may also transfer that residue to the flag as well. Deposited materials can pick up water with time and attack both the fibers and dyes. High humidity or cleaning may reactivate particles dormant after deposition.

Second, dissolution or mechanical transfer of gunshot chemical species by rain may affect the condition of the flag. Large amounts of particulates in the air over battlefields have been postulated as the cause of rain following battle. Rain would dissolve, or force to earth, many particles or gases formed by gunshot, and solutions of these salts would chemically attack fabrics and dyes.

Chemical Reactions

Certain reaction products from gunpowders can react with moisture and oxygen in the environment to produce further reactive species. For example, nitrogen oxides and moisture can produce nitric and nitrous acids. Thiosulfate ion can react in an acid environment to produce sulfur or sulfur oxides. Reactions with water vapor or liquid water complicate the issue further. Attempts to clean a silk flag with water may dissolve particulates and increase the possibility and extent of damage.

Hydrolysis is an important reaction in the degradation of silk. Any compound that will alter the pH significantly or catalyze the hydrolysis reaction is dangerous to the silk.[5] Black Powder reaction products and their derivatives that are known to attack silks include:

nitrous and nitric acids (from reaction of nitrogen oxides with water)
sulfate ion
hydroxide ion (alkali medium from carbonate solutions)
formaldehyde
heavy metal ions (lead, mercury, copper, etc.)

Most dyes are susceptible to color changes with changes in pH, and some will regain their original color when the pH is changed back. Others have labile chromophoric groups that will react with acids or bases to change color or become colorless, irreversibly. Reaction products from Black Powder that can react with dyes include:

nitrous and nitric acids
sulfur dioxide, sulfurous acid
formaldehyde
potassium salts such as nitrate, thiocyanate, sulfide, nitrite

Examination of Flags

Non-destructive evaluation of residues on textiles can be conducted in several ways. Infrared imaging can disclose many types of residues and x-ray photography can also locate many of the denser residues. Visual examination at 5× to 50× can disclose most residues but will certainly be quite tedious on an object the size of a flag. There are also several wet chemical techniques, which are probably not suitable for historic objects. The forensic literature contains a considerable number of papers on the subject of gunshot residues.[6]

Conclusion

In addition to the obvious mechanical effects in war, chemical damage occurred from the active particulate debris and gases produced on the battlefield. Without proper stabilization and storage this residual debris continues its slow decomposition of the silk flags. Improper cleaning can accelerate the damage by activating residues with water (moisture).

Pyrotechnic displays, although only infrequent events, can also produce considerable amounts of similar particulates and gases. If conducted near museums, these may be a significant source of damage to a museum's collection. The effects of nearby fireworks displays can be reduced by closing air intakes (if this is not possible, filters can be added) until the particulates and gases have dissipated.

References

1) John A. Braddock, *Memoir on Gunpowder*, J. M. Richardson, London (1832).

2) Henry Watts, "Gunpowder", *A Dictionary of Chemistry and the Allied Branches of Other Sciences*, Vol. II, Longmans, Green,

and Co., London (1875) pp 956–960.

3) Kirk-Othmer, "Explosives", *Encyclopedia of Chemical Technology*, 2nd ed., Vol. 8, John Wiley & Sons, Inc. (1965) p 650.

4) John Scoffern, *Weapons of War: A History of Projectiles and Explosive Compounds*, 3rd ed., Ward and Lock, London (1854).

5) M. S. Otterburn, "The Chemistry and Reactivity of Silk", *Chemistry of Natural Protein Fibers*, R. S. Asquith, Ed., Plenum Press, New York (1977) pp 53–80.

6) See, for example, *Journal of Forensic Sciences*, *Forensic Science International*, etc. Also, S. S. Krishnan, "Detection of Gunshot Residue: Present Status", *Forensic Science Handbook*, R. Saferstein, Ed., Regents/Prentice Hall, Englewood Cliffs, NJ (1982) pp 572–591.

Errata

Issue 11, Summer 2000

Title page, 1st article should have read:

A Labscale Hybrid Rocket Motor **f**or Instrumentation Studies

Title page, 6th article should have read:

Forensic Testimony: **"**Matches", An Over-Inference of Data? A *Giglio* Obligation?

Table of Contents, 3rd article, the 4th author's name—A. E. Webb— was omitted.

Table of Contents, Communications, 2nd article, the 2nd author's name—J. E. Fletcher—was omitted.

Additionally, there were numerous errors in the article by Dr. Kubota. Apparently an earlier draft was used for the final copy. This article will be reprinted and distributed to recipients of Issue 11. Our sincere apologies to the author and our readers.

Pyrotechnic Particle Morphology—
Low Melting Point Oxidizers

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ABSTRACT

The morphology (size, shape and surface features) of the constituent particles in a pyrotechnic composition affects its performance. While this is particularly true for high melting point fuels and oxidizers in the composition, to a lesser extent it is also true for those with low melting points. Particle morphology also constitutes an important part of establishing the likelihood of a forensic match between evidence and materials of known origin. This article catalogs and briefly discusses some morphologic features often associated with some of the most commonly used low melting point oxidizers in pyrotechnic compositions.

Keywords: morphology, oxidizer, forensics, pyrotechnics, potassium nitrate

Introduction

The term morphology is one borrowed from biology, where it is used to describe the appearance of organisms. In pyrotechnics and forensics, the term is often used to denote information about the size, shape, and surface features of particles, where knowledge of these attributes is often important. In pyrotechnics, particle morphology generally influences such things as the ease of ignition and the burn rate of a composition.[1] Large particle size, rounded shape, and smooth surface features all tend to make ignition more difficult and burn rates lower. While this is especially true for those compo-

nents with high melting points (e.g., metal fuels and high melting point oxidizers), to a lesser extent it is also true for those components with low melting points (e.g., organic fuels and low melting point oxidizers). It is less important for these particles because of their tendency to have begun to melt (or decompose) below the ignition temperature of the composition. See Table 1 for melting points of some common pyrotechnic oxidizers and metal fuels.

An important aspect of forensic science is the identification of materials, often for the purpose of determining their source. Typically this would be accomplished by attempting to "match" one material (or its components) with other material(s). In attempting to determine whether two materials match, various attributes of the two are compared. The degree of certainty of the match is a function of the number of attributes compared and the degree to which they are identical.[4] For pyrotechnic compositions, one important part of the matching process should be a comparison of the morphologies of the materials. Probably the best known and most complete work on this subject are the writings of McCrone and Delly.[5] This multi-volume treatise provides extensive overall information. However, of necessity for chemicals, it tends to only include a few of the most common chemicals, and then in only one form (e.g., individually grown crystals). Their atlas emphasizes the identification of the nature of the chemical. This is valuable information but it falls short of what is needed to determine whether a firm match exists between known and evidentiary materials.

Table 1. Examples of Melting Points (in °C) of Some Common Pyrotechnic Components of Forensic Interest.

Metal Fuels	T_m	High T_m Oxidizers	T_m	Low T_m Oxidizers	T_m
Aluminum	660	Barium sulfate	1580	Ammonium perchlorate	d ~ 150
Boron	2300	Copper(II) oxide	1326	Barium peroxide	450
Iron	1535	Iron(II) oxide	1565	Potassium chlorate	356
Magnesium	649	Lead chromate	844	Potassium nitrate	334
Silicon	1410	Lead(II) oxide	886	Potassium perchlorate	d ~ 400
Titanium	1660	Potassium sulfate	1069	Sodium nitrate	307

Note: The symbol T_m is the melting point in degrees Celsius; values are taken from references 2 and 3.

The symbol d indicates that the oxidizer decomposes before melting and is followed by the approximate decomposition temperature.

This article is the second in a series on the subject of pyrotechnic particle morphology.[6] Whereas the initial article examined a number of different chemicals (metal particles), the current article considers only one. This was done for brevity and to emphasize the wide range of possible oxidizer particle morphologies for a single chemical. Potassium nitrate, the oxidizer in Black Powder (gun powder) and used extensively in fireworks, was chosen because it is probably the most frequently used pyrotechnic oxidizer. However, the information presented for potassium nitrate is generally applicable to other members of that much wider class of common oxidizers, alkali-metal and alkaline-earth nitrates, perchlorates and chlorates.

Two sources of potassium nitrate were used in this study. One source was analytical reagent (AR) grade[7] with an initial average particle size of approximately 6 to 60 mesh (3400 down to 250 microns), see Figure 1 for a somewhat typical example of its initial morphology. The other source was an agricultural prill[8] (AgP) with an initial average particle size ranging from approximately 18 to 150 mesh (1000 down to 100 microns), see Figure 2 for a somewhat typical example of its initial morphology.
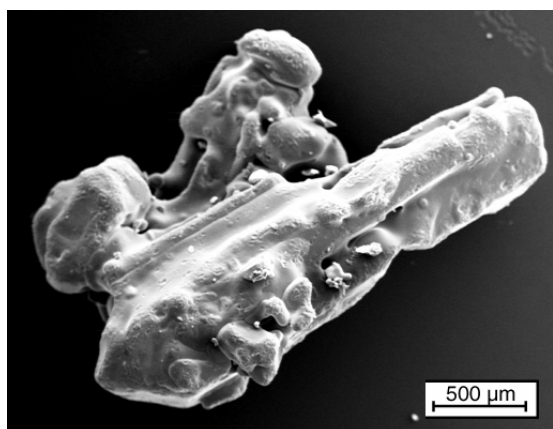
Figure 1. Micrograph of a somewhat typical initial particle of analytical reagent (AR) grade potassium nitrate (35× magnification).
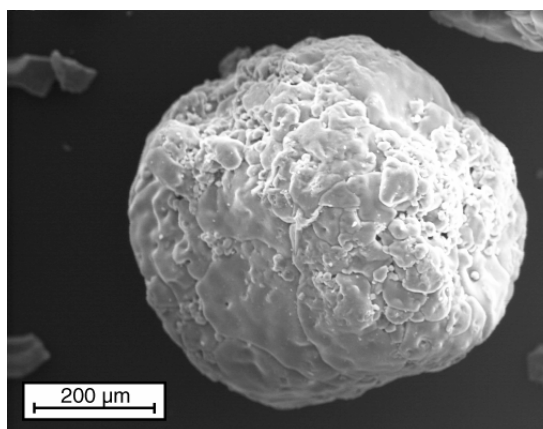
Figure 2. Micrograph of a somewhat typical initial prill of agricultural (AgP) grade potassium nitrate (100× magnification).
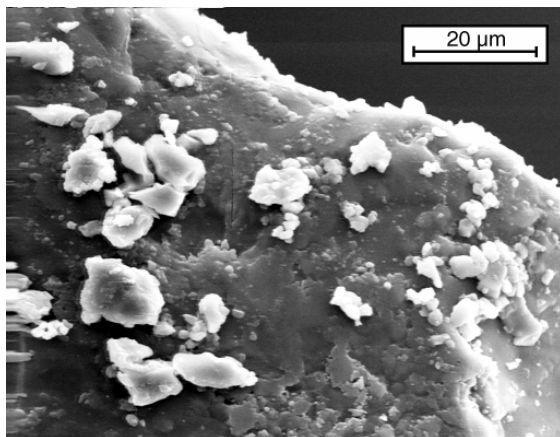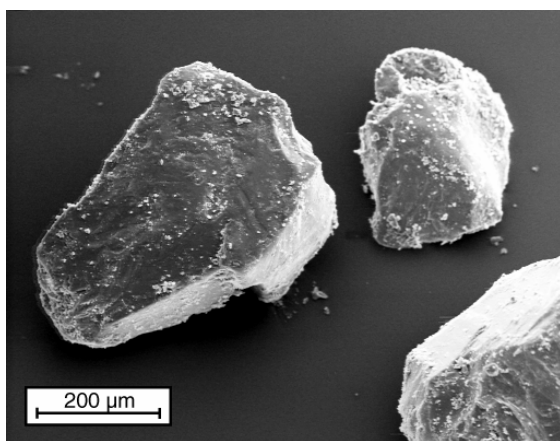
Figure 3. Two images of potassium nitrate, 60 to 100 mesh (150–250 micron) particles produced using a rotating disk mill. This documents the presence of many tiny particles adhering to the surface of larger particles. Upper, 100× magnification; lower, 1000× magnification.

Particle Size

For low-temperature oxidizers, ones that have melting points (or have begun to decompose) at temperatures below approximately 700 °C, particle size is of less importance than it is for higher melting point components. Nonetheless, relatively small particle size remains important to achieve an intimate mixing of the components of a pyrotechnic composition, and the degree of mixing plays an important role in determining burn rate and other properties of pyrotechnic compositions. Accordingly, even for low temperature oxidizers, it is common for

Table 2. Mesh Fractions of AR Grade Potassium Nitrate Produced by Grinding.

Mesh Range (a)	Particle Size (microns)	Fraction (per-cent)
+60	>250	1
−60 to +100	250 to 150	16
−100 to +200	150 to 74	31
−200 to +400	74 to 37	28
−400	<37	24

a) Mesh numbers are for US Standard sieves. Mesh number is the number of standard diameter wires per inch of wire mesh. A plus sign (+) means larger than or fails to pass through the specified sieve. A minus sign (−) means smaller than or passes through the sieve.

their particle size to mostly fall in the range of 60 to 200 mesh, corresponding to particles ranging from about 250 down to 74 microns. (Of course, for high temperature oxidizers, such as some of those listed in Table 1, small particle size is even more important.[1])

Two competing processes that significantly widen the 60 to 200-mesh range of particle size. One is the diminution process, where most commonly some type of crushing or grinding is used to reduce the particle size to smaller than 60 mesh. In this process, as the large oxidizer crystals are broken, in addition to producing particles in the range of 60 to 200 mesh, many much smaller particles are also produced that range down to a few microns and below. For example, when a portion of AR grade potassium nitrate was processed to produce −60 mesh particles by grinding in a rotating disk mill, many particles in the 0 to 20 micron range were also produced, see Figure 3. (Note: the mill was a 4-inch (102-mm) diameter stone mill, similar to a flourmill.) The upper micrograph is at a magnification of 100×, and the lower micrograph is a portion of one of the same particles at 1000×. Notice that adhering to the surface of the larger particle are some of the very tiny particles that were produced. Table 2

presents the results of a sieve analysis of this ground material. Note that while 99 percent of the larger particles were reduced to smaller than 60 mesh (250 microns), 52 percent of those particles reduced to smaller than 200 mesh (74 microns).

The other process affecting the range of particle size is agglomeration, the fusing together of smaller particles to form larger particles. This process is aided by the presence of moisture and time. (In pyrotechnics this process is often referred to as "caking".) An example of this was observed when a portion of AR grade potassium nitrate was ball milled for 12 hours, without first drying the material; eventually most of the smallest particles agglomerated into a few large masses inside the mill. (Note: the milling media consisted of ceramic cylinders, 0.5 inch (13 mm) diameter by 0.5 inch long, weighing 5.5 grams.) At that time, the particles had not yet fused solidly together, and they still could be fairly easily broken apart when minimal finger pressure was applied to the lumps during sieving. See Figure 4 for examples of the appearance of the agglomerated particles (upper and middle micrographs) and the smaller particles from which they were formed (lower micrograph). When viewed with a visible light microscope, these large agglomerated particles have an opaque white appearance much like a snowball.

From a pyrotechnic performance standpoint, compositions prepared using solidly agglomerated particles of low melting point oxidizers are expected to behave somewhat differently than those made using individual solid particles. This is because the increased permeability and porosity of the agglomerated particles should affect their ignition and burning characteristics, as well as their physical properties, such as when being compacted (rammed).

Forensically, while oxidizer particle size distribution can provide potentially useful information, care must be exercised because of the possibility that agglomeration has occurred to differing extents for known and suspect materials. Accordingly, for materials such as low melting point oxidizers, a sieve analysis should be augmented with a microscopic inspection.
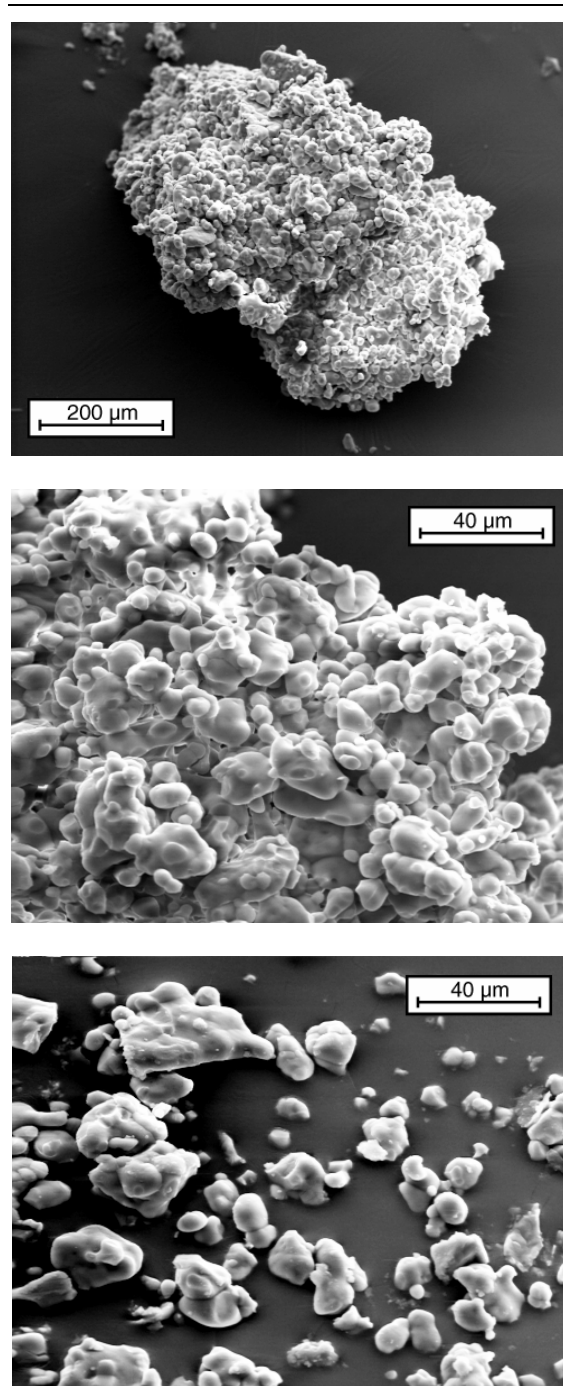
Figure 4. Two mesh fractions of undried AR grade potassium nitrate produced by ball milling for 12 hours. Upper, a particle in the range of 60 to 100 mesh (250–150 micron) at 100× magnification; middle, the same particle at 500× magnification; and lower, –400 mesh (<37 micron) particles at 500× magnification.

Figure 5. AR grade potassium nitrate particles from the –400 mesh (<37 micron) fraction produced by ball milling for two hours (500× magnification).

Particle Shape

Particle shapes tend to fall into two basic categories, rounded particles and sharp angular particles. Rounded particles may have been formed that way, such as the agricultural prill shown in Figure 2. (Prill is formed by spraying a hot concentrated solution of the chemical species into the top of a tower, where the droplets assume a fairly spherical shape when they cool and solidify as they fall.) Particles that are less spherical, but still quite rounded, can be produced during ball milling. In this case, even though the milling media chips-off and crushes particles that must initially be relatively sharp and angular, they quickly lose those features during the milling process as the particles abrade against each other. Figure 5 demonstrates the effect of even fairly short duration (two hours) ball milling. Note that while these –400 mesh (37 micron) particles are not as small or rounded on average as those shown in the lower frame of Figure 4, where the milling continued for several more hours, they are already fairly small and quite rounded.

Particles reduced in size by grinding predominantly have sharp angular features. Whether the grinding was accomplished using a motorized disk grinder or by hand using a mortar and pestle, the result is essentially the same. The similarity in particle size distribution and angular features of the –400 mesh (37 micron) parti-
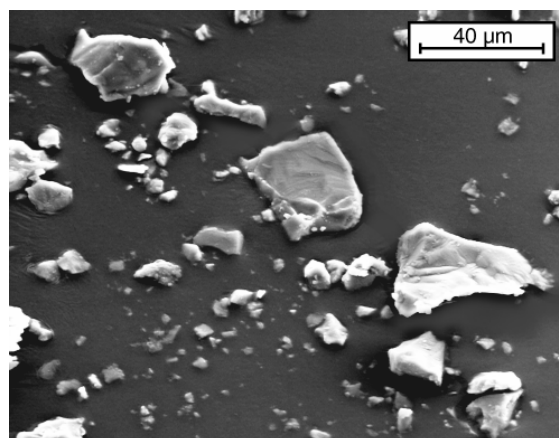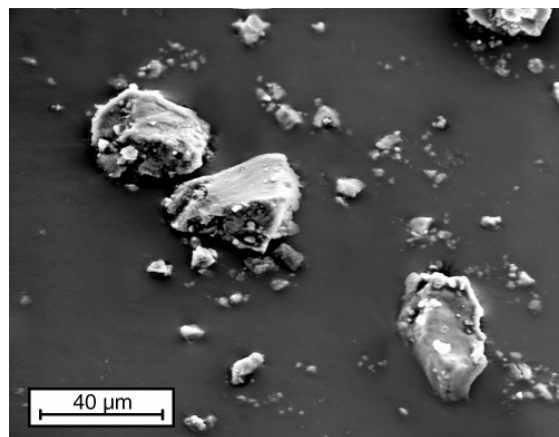
Figure 6. AR grade potassium nitrate particles from the –400 mesh (<37 micron) fraction produced by grinding (500× magnification). Upper fraction, produced using a rotating disk grinder; lower fraction, produced using a mortar and pestle.

cles can be seen in Figure 6, in which the upper micrograph is of particles produced using the rotating disk grinder, and the lower micrograph is of particles produced using a mortar and pestle. These fairly sharp angular particles can be contrasted with those of the same size but with rounded features seen in Figures 4 and 5.

Another process that may be used for particle size reduction is coacervation. (This is sometimes known as the CIA method, because of its purported use in the CIA's field expedient method for the manufacture of Black Powder.) In this process, large size particles are dissolved in water to make a nearly saturated solution, usually at an elevated temperature to increase
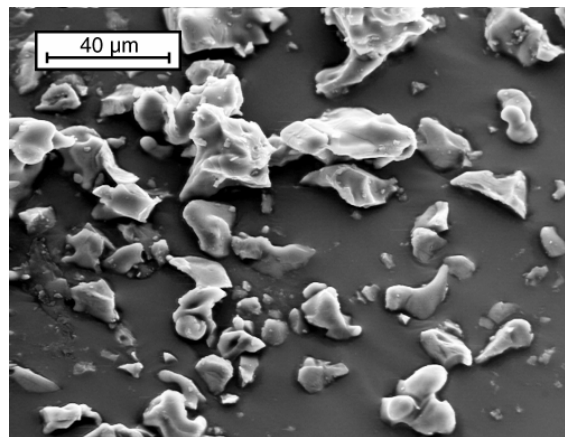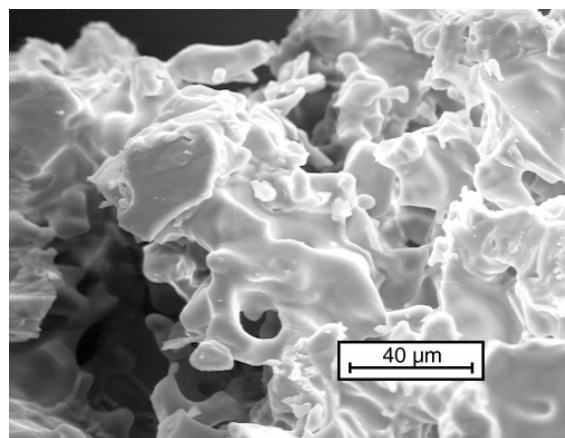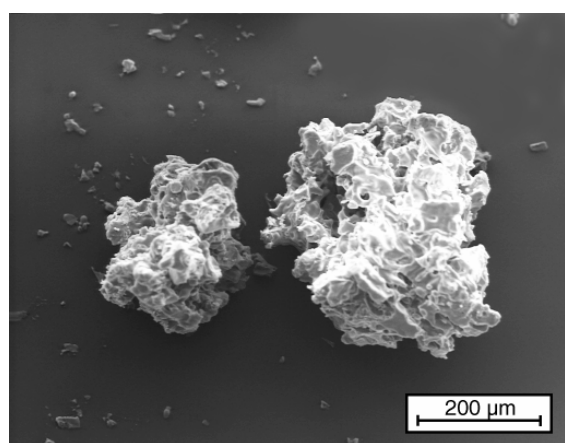
Figure 7. *Particles from two mesh fractions of AR grade potassium nitrate produced by hot coacervation with rapid stirring. Upper, 60 to 100 mesh (250 to 150 micron) particles at 100× magnification; middle, a portion of one particle at 500× magnification; lower, –400 mesh (<37 micron) particles at 500× magnification.*

Figure 8. *Comparing the sharpness of –400 mesh AR grade potassium nitrate particles. Upper, coacervated particles at 2000× magnification illustrating features that are sometimes quite rounded (A) and other times fairly sharp and angular (B); lower, mortar and pestle produced particles at 2000× magnification.*

the amount of material that can go into a solution. Then alcohol is added, usually quickly and while stirring vigorously. The alcohol acts to displace the dissolved material from the solution because the alcohol has a much greater solubility, and to some extent also by cooling the solution. In this process tiny particles are formed, many of which fuse together to form larger particles. Figure 7 documents the appearance of these particles, where the upper and middle micrographs are views of a particle, in the 60- to 100-mesh (250 to 150 micron) fraction, at 100× and 500× magnifications. The lower micrograph is of the –400 mesh (<37 micron) particles at 500× magnification. The larger particles are clearly agglomerations; however, their

appearance is substantially different than that seen for the caked particles in Figure 4. The constituent particles are angular as opposed to being rounded and the agglomeration is fairly open as opposed to being relatively tightly packed. Many of the –400 mesh particles are as angular as the ground and crushed particles seen in Figure 6; however, many others are quite rounded. This can be seen more clearly in Figure 8, which compares –400 mesh coacervated particles with those produced with a mortar and pestle, both at 2000× magnification.

When coacervation is carried out with the rapid addition of the alcohol and vigorous stirring from a near saturated—but cool—solution, the appearance of the particles is substantially similar to those for a hot solution like those particles seen in Figure 7. However, when the alcohol is added slowly and mostly without stirring, some of the particles produced have a somewhat rod-like shape that is characteristic of potassium nitrate crystals, see Figure 9.

Surface Features

Surface features and texture can significantly affect the reactivity of some pyrotechnic materials (e.g., so called titanium sponge ignites easier than solid titanium particles of the same size). However, for compositions made with low melting point oxidizers, except for particles that are agglomerations of a large number of much smaller particles, surface features are not expected to noticeably affect the ignitability and burn rate of pyrotechnic compositions. However, surface features are an important part of forensic materials comparison.

Some of the possible particle surface features have already been mentioned. For example, particles can be agglomerations of smaller particles that have characteristic shapes, and the agglomerations can be densely packed or have relatively open structures, see Figures 4 and 7. However, there are other characteristic surface features that should be mentioned. When particles are crushed, noticeable fracture patterns can be produced. These particles have concave particle surfaces and deflection fracture marks, sometimes called "whiskers". (Whiskers are somewhat parallel ridges on the fractured sur-
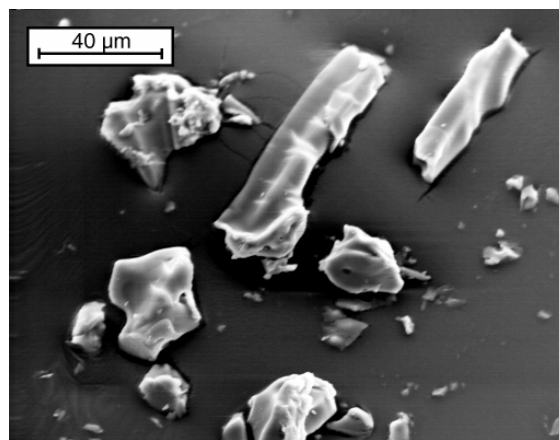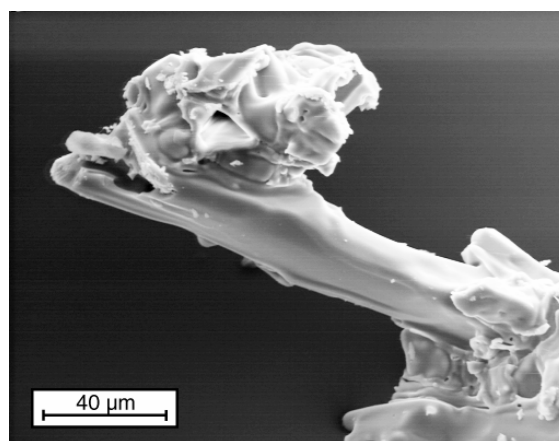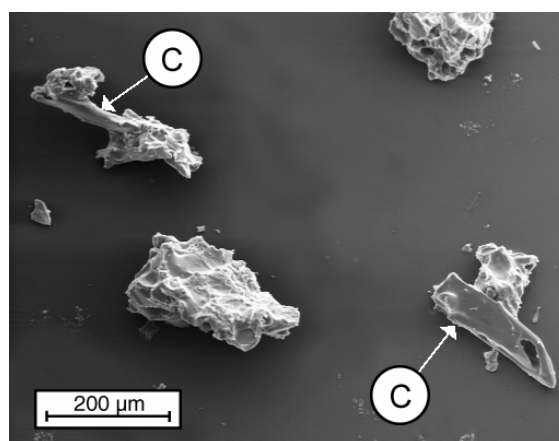
Figure 9. Particles with some rod-like characteristics (C) are produced by slow coacervation. Upper, 60 to 100 mesh (250–150 micron) particles at 100×magnification; middle, a portion of one particle at 500×magnification; lower, –400 mesh (<37 micron) particles at 500×magnification.
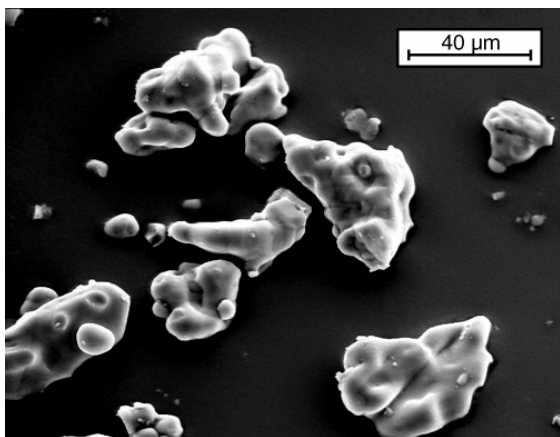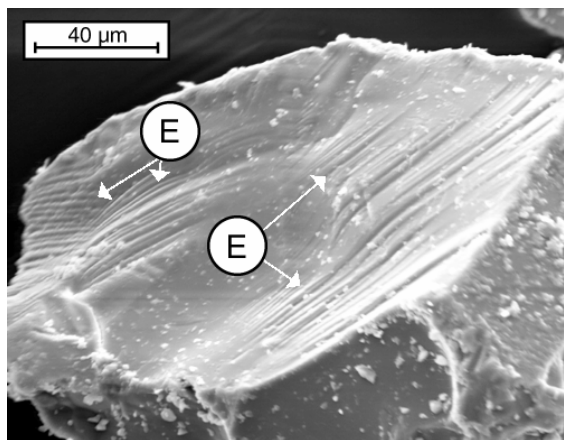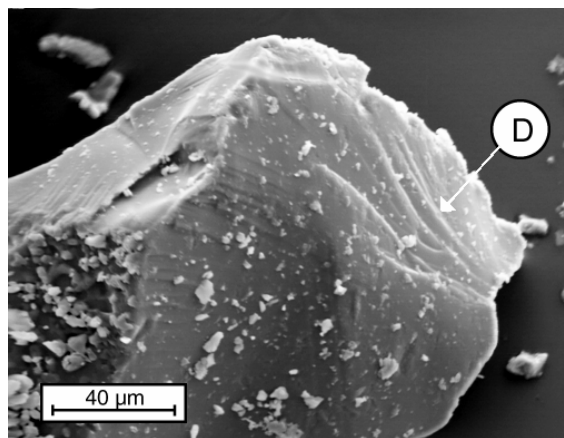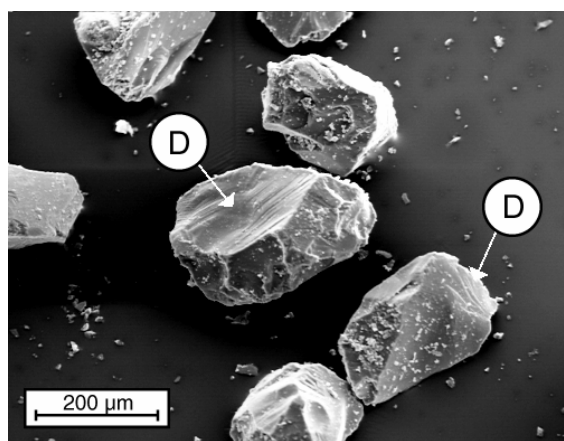
Figure 10. Particles of AR grade potassium nitrate produced by hammer milling. Upper and middle, demonstrating fracture patterns (D) (100× and 500× magnification, respectively); lower, a rather extreme example of "whiskers" (E) (500× magnification).

face). When particle diminution is accomplished by hammer milling, where high speed rotating blades impact and shatter the particles, the num-
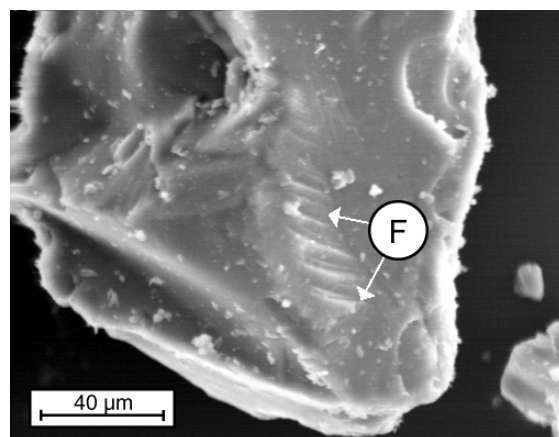
Figure 11. Possible example of tool marks (F) produced during hammer milling AR grade potassium nitrate (500× magnification).

ber and degree of fracture patterns observed can be significantly greater than those patterns produced by crushing and grinding, see the upper and middle micrographs in Figure 10. The lower micrograph in Figure 10 is a rather extreme example of fracture features formed when this particle was smashed. The degree to which fracture patterns are produced during milling ranges from modest (for rotating disk mills) through moderate (for mortar and pestle) to substantial for hammer milling. Also, on rare occasion, a hammer-milled particle may exhibit what appear to be tool marks (mostly straight parallel grooves) from a blade scraping across the particle, see Figure 11.

When particles have been ball milled, the large number of impacts can leave the larger particles with a pitted surface texture; see Figure 12. These micrographs illustrate the typical appearance of the 60 to 100 mesh (250–150 micron) particles of AR grade potassium nitrate after having been ball milled for 2 hours. At first glance and under minimum magnification, the particle may appear somewhat like the agglomerated particle in Figure 4. However, under higher magnification the difference is obvious. Using the visible light microscope, the difference in appearance between the agglomerated and pitted particles is even more readily apparent. Particles such as those in Figure 12 are translucent and are definitely single particles, appearing much like lightly frosted glass. To the
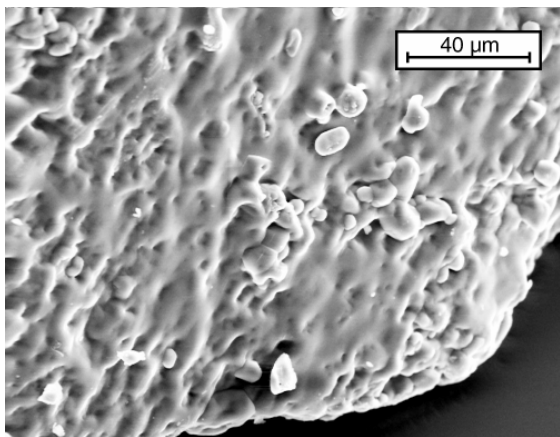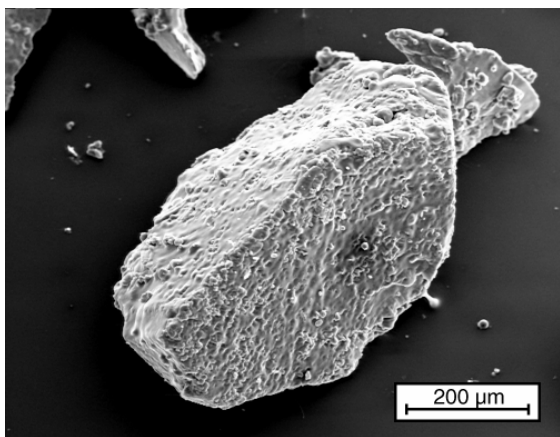
Figure 12. Particle of AR grade potassium nitrate produced by ball milling for 2 hours, illustrating the pitted surface of the 60 to 100 mesh particles. Upper, 100× magnification; lower, 500× magnification.

Figure 13. Particle of AgP grade potassium nitrate produced using a mortar and pestle, illustrating the presence of numerous occlusions. Upper, 100× magnification; lower, 500× magnification.

contrary, particles such as those in Figure 4 are opaque white, appearing much like snowballs.

Holes or voids, though not uniquely surface features, are sometimes discernable on the surface of particles. This is especially the case for agglomerated particles (see Figure 4), coacervated particles (see Figure 7), and particles produced from prilled chemicals (see Figure 13). However, it should be noted that holes and voids were also occasionally observed in particles produced from potassium nitrate that was slowly recrystallized from an aqueous solution and from potassium nitrate that solidified from high temperature melts.

A definite surface feature, but one that is not characteristic of unexamined potassium nitrate

particles, is illustrated in the lower micrographs of Figure 14. The thermal expansion and fissuring of the particle's surface is an artifact introduced during the examination process itself. Specifically this is a result of particle heating when the specimen absorbs the energy of the electron beam of the scanning electron microscope. (For a more complete discussion of possible causes of thermal expansion and some steps to help limit the problem, see reference 9.) The possibility of causing beam-induced artifacts becomes a greater problem at higher magnifications, when the electron beam is more concentrated (the same beam current is spread over a smaller area). The upper micrograph of Figure 14 is the initial image of an uncoated AR grade potassium nitrate particle at 2000× magnification. The middle and lower micrographs
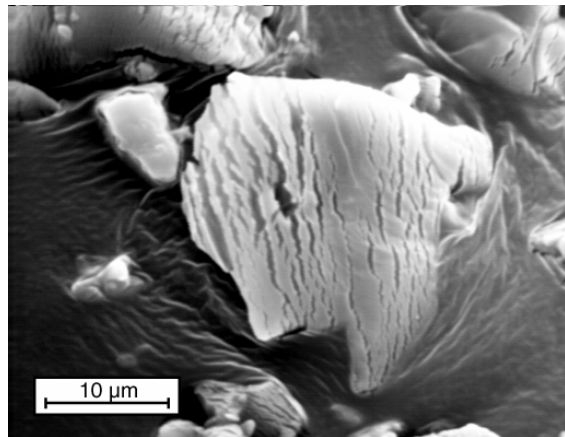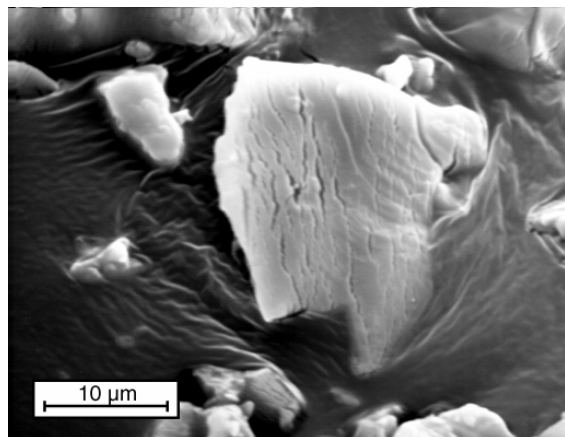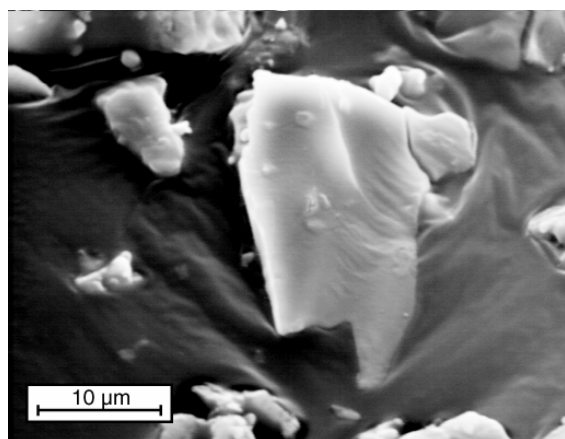
Figure 14. Illustration of SEM beam-induced surface damage (thermal expansion) to AR grade potassium nitrate particles under high magnification (2000✕) as a function of time. Upper, initial image; middle, image recorded after approximately one minute; lower, image recorded after approximately three minutes.

were recorded after approximately one and three minute exposures to the beam of the SEM,
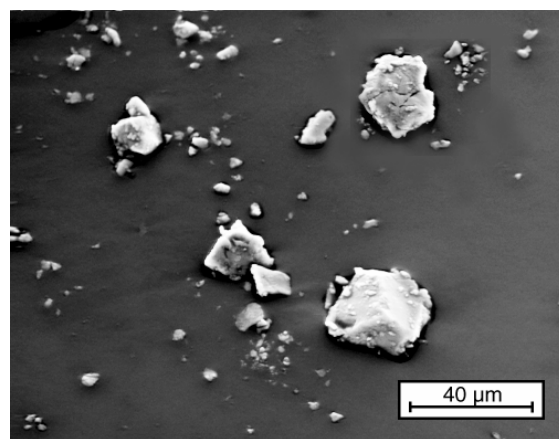
Figure 15. Micrograph of the –400 mesh (<37 micron) fraction of AgP potassium nitrate produced by ball milling for 12 hours (500✕ magnification).

and they demonstrate the progressive development of the fissures in the particle's surface. For these AR grade potassium nitrate particles, essentially no further surface damage was observed after approximately three minutes.

Conclusion

Particle size, shape and surface features of low melting point oxidizers are not as critically important in determining the ease of ignition and burn rate of pyrotechnic compositions as they are for many other components in these mixtures. Nonetheless, knowledge and control of these attributes is necessary to maintain consistent performance of pyrotechnic devices. Further, from a forensic standpoint, an investigation of these attributes can be an important part of establishing reliable matches between known and evidentiary materials. (Unfortunately, the converse is also true, i.e. failing to consider detailed particle morphology makes any claim of a match less credible.)

As a note of caution for the forensic analyst, it is important to avoid over-inferences based on a limited investigation of particle morphologies. Specifically, while it is true that the method of particle size reduction plays a major role in determining particle morphology, so do many other things. Accordingly, one should resist the temptation to use particle morphology

as the sole basis to infer the method of production of the material. For example, consider the potassium nitrate particles shown in Figure 15. These particles definitely have sharp angular features. Based on the information presented in this article, one might be tempted to conclude that the method of their production was by crushing or grinding, see Figure 6. Similarly, one might be tempted to exclude the possibility that this material was produced by extended ball milling, see the lower micrograph of Figure 4. However, if either conclusion were reached, it would be erroneous. Figure 15 is the –400-mesh (<37 micron) fraction of AgP potassium nitrate produced by 12 hours of ball milling. The rather extreme difference in particle morphology, when compared with that seen in Figure 4, is simply due to differences in the physical properties of the AR and AgP grades of potassium nitrate.

Acknowledgments

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A Survey of Analytical Tools for Explosion Investigation

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ABSTRACT

Practical analytical techniques that have been found to be useful in explosion investigation include: timeline analysis, experimental data comparisons, thermochemical code analysis, TNT and other air blast equivalency techniques, ground shock analysis, dynamic gas concentration estimates, simple fuel/air explosion codes, damage pattern analysis and system safety analysis methods. An example application of existing analytical tools to an explosion investigation is presented. Exotic analytical techniques are available but are not justified unless the loss is very large. Methodology is reviewed for completing a reasonable explosion investigation, including essential items from NFPA 921. Needs are addressed for desired technology advancements.

Keywords: explosion investigation, thermochemical equilibrium, blast equivalency, system safety analysis, ground shock

Introduction

The investigation of explosions can be an extremely complex task depending on the nature of the incident. Evidence is often destroyed by the forces involved or subsequent fires. The evidence may be spread out over an extremely large area. Fuels and oxidizers involved may or may not be easily identified. Pyrotechnic and explosive materials involved will generally be consumed in the event, and the materials that remain after and incident may be misleading. Fuel gases involved in a fuel-air explosion are often dissipated before any investigators are on the scene. The explosion origin can be difficult to pinpoint due to a lack of explosion seating (e.g., the absence of a crater). Propagation patterns may be lacking or conflicting in some cases. Ignition sources may be extremely difficult to identify, due to problems in establishing the origin, or perhaps in sorting out the source from a plethora of viable sources.

A basic knowledge of the chemistry and physics of explosions is necessary for an intelligent evaluation of an accident scene. Several specialized experts might necessarily be involved depending on the kind of answers that are desired. Typical questions that need answers are:

Where was the origin of the explosion?

What material exploded?

How much material exploded?

How was it initiated?

What was the extent of damage/injury?

How can it be prevented from recurring?

The best pathway to answering these questions is the scientific method. This paper is an overview of analytical tools that have proven to be useful in facilitating the scientific method in explosion investigations.

Conducting the Explosion Investigation

An explosion investigation and analysis is a complex endeavor that needs to be approached in a systematic manner using the scientific method. The initial steps will include securing the scene to prevent spoliation of evidence, assessment and documentation of the scene, and collection and preservation of evidence. This will be combined with other relevant data collection and interviews of witnesses. The data is then inductively analyzed and a hypothesis developed. The hypothesis is then deductively tested by comparing it to all known facts. If the hypothesis is inconsistent with the known facts, it should be discarded and another hypothesis examined. This may identify the need to collect additional data or perform other analyses.

Of course, the extent of an investigator's involvement may vary with his assignment and may only cover part of the overall investigation. In some cases an investigator's involvement may even occur several years after the incident.

Additional details of the investigation methodology are given in Chapters 2 and 13 of *NFPA 921, Guide for Fire and Explosion Investigation*.[1] The analytical tools described in this paper can be used to assist in both the development and testing of hypotheses, which is the essential element of the scientific method in explosion investigation.

Useful Analytical Tools

There are a wide variety of analytical tools for possible use in explosion investigation. These may range from simple fluid dynamic expressions for estimating leak rates, to complex three-dimensional computational fluid dynamic models for estimating explosive reaction propagation through a structure. Quite often design-basis tools are too conservative for use in evaluating explosions. That is because engineering design-basis tools are usually standardized to assume idealized phenomena and incorporate large safety factors to insure public safety. Although the typical accidental explosion is far from ideal, some design-basis explosion mitigation guides can be utilized in a reverse-engineering fashion to be useful to the investigator. Other tools borrowed from fire investigation techniques and systems safety science are extremely valuable.

Analytical tools that have proven especially useful in practice are listed below. Many of these tools may be incorporated in future editions of NFPA 921.

Timeline Analysis

A timeline is a graphical or narrative representation of the events related to the incident that are arranged in some chronological order. The events included in the timeline may occur before, during or after the incident. This valuable investigative tool can show relationships between events, identify gaps or inconsistencies in information and sources, assist in witness interviews, and otherwise assist in the analysis and investigation of the incident.

The value of the timeline is dependent on the accuracy of the information used to develop it and the interpretations of the person assembling it. One example of a complex timeline diagram is shown in Figure 1 from reference 2.

Early Fire Spread in Batch Dryer and Process Building

Early Ignition Sequence

Figure 1a. Pepcon fire spread diagram.

Fire Spread throughout Remainder of Plant

From Figure 1a

```
Explosion occurs
in poly drum or
batch dryer
```

11:50 AM **Initial Explo-sion**

```
Burning particles
raining down in
process building
area
```

Dominant fire spread NE through plant aided by wind → Area 7 SSD rows of poly drums

Dominant fire spread NE through plant aided by wind → Dryer building → Poly drum rows in areas 8, 9, 10 → **C**

Fire spread W through plant → Crystallizer building → Area 2 storage

Fire spread SE through plant → Through drums at SE corner of batch dryer (area 4) → Blender building → Steel drums area 11

Blender building → Poly drums in area 12

Fire spread S hampered by wind → Area 5 storage → Reprocess area 5 storage

Fire spread to sections of plant by burning drum projectiles → To middle of lot A in poly drum and bag storage area in front of adm. bldg. → N to empty poly drums in front of adm. bldg. → Admin. building

To middle of lot A in poly drum and bag storage area in front of adm. bldg. → S, W, and E through storage field

Fire spread through bulk storage is about 3.5 ft/sec

Flame height during main NE fire spread along poly drums varies from about 100 to 270 ft tall

C → Anode building

C → SW corner of lot A → Fireballs in lot A and poly drum rows coalesce to form a single 270 ft high fireball

C → Chlorate building

Major Explosions

11:53 AM
```
First major
explosion
(lot A)
```
→ 11:53:01.11
```
Explosion in
crystallizer/dryer
building
```
→ 11:53:01.40
```
Explosion in
chlorate
building
```
→ 11:53:32
```
Large fire plumes
suppressed due to
upheaval (radiation
attenuated)
```

11:55 - 11:57
```
Several small explosions

Explosion near coordinate
354/85 at 11:55:23.81

Bin explosion on loading
dock at 11:55:31.71

Bin explosion on loading
dock at 11:55:36.87
```
→ 11:57 AM
```
Second major
explosion (lot B)

Ground flash near
coordinates 354/65-85
0.03 seconds earlier
```
→ 11:57:15 AM
```
Gas pipe rupture
fire apparent
```

Figure 1b. Pepcon fire spread diagram (continued).

Experimental Data Comparisons

Useful experimental data for explosion investigation covers a broad range of topics. These can include data on minimum ignition energy of dust clouds, maximum explosion pressure of a mixture of gases, maximum explosion pressure under specified vented conditions, explosion limits of fuel gases, critical diameters of solid explosives, explosion air blast or TNT equivalency, etc. Each investigation is unique and requires data sources unique to the relevant issues. Sources of such data are much too numerous to list here, but some useful tabulations are found in references 1, and 3–7.

An important point regarding the use of such data sources is that much of the tabulated data is derived from standard tests, and caution should be exercised in their use. These data sources are usually developed to result in conservative values so that their use will always err on the side of safety. Often times these data do not adequately fit the accident scenario of interest.

For example, the high and low strength enclosure venting data models in NFPA 68[3] are too conservative for many cases where less than the worst-case scenario is evident. Thus, it is usually quite difficult to use NFPA 68 venting guides to help in the analysis of an accidental building explosion. This is because the strength of the structure and explosion vent parameters is often unknown. In addition, information on the fuel-gas mixture content and concentration generally are lacking.

The use of ASTM E 1226[8] test data involving maximum pressure development for dusts is another example where the source data do not adequately fit the scenario. The standard test requires sieving the dust sample to 200 mesh. This gives conservative results in most cases, even though the fines are more easily lofted than coarse particles, they generally dominate the explosion effects. Due to the sieving, the test does not consider the agglomeration of particles with, for example, wood dusts in high humidity or plastic dusts in low humidity (due to electrostatic forces).

Fuel/Air Explosion Models

There are simplified methodologies for predicting maximum pressure development in a vented enclosure as well as flame speed and shape. However, these quasi-empirical methods require input such as burning velocity, turbulence factors, enclosure geometry, and physical vent parameters. Some of these methods are summarized in reference 9 or listed in NFPA 68.[3]

It should be noted that the present state-of-the-art in explosion science does not allow one to reliably predict diffuse fuel explosion pressure development within an enclosure, using any methodology. Computational Fluid Dynamics (CFD) is beginning to provide major improvements in the analytical prediction of the effects of volumetric explosions (i.e., gas, dust and hybrid explosive systems). A range of CFD computer codes exist, and many of these codes are commercially available, some examples are the commercial FLUENT code, the KIVA code[10] and the IIT code.[11,12] These codes clearly demonstrate that CFD technology is very close to providing a valuable tool for explosion investigation, but at least three problems remain before this analysis tool can be practical. First, to represent realistic configurations the geometry is generally complex. In some cases two-dimensional analysis may be sufficient, but many times three-dimensional computations are appropriate. In addition, the analysis probably requires a fine numerical grid in at least some locations, and as a consequence a full evaluation generally requires substantial computer running time. Often a simplified configuration is adequate and can go a long way toward making the analysis more practical. Second, for explosion analysis the numerical method must have the ability to resolve shock waves. This requires special numerical schemes such as Godunov, Van Leer, Flux Corrected Transport (FCT), Total Variation Decreasing (TVD), and others.[13–25] Third, the reaction kinetics must be represented realistically. One approach, given in references 11 and 12, uses the reaction kinetics in Arrhenius form. Generally major simplifications in the kinetics scheme are made in analyses of this type.

The work presented in references 11 and 12 was in support of experimental detonation tube studies of a wide variety of pyrotechnic formulations being evaluated for landmine neutralization and other applications for the Army. Formulations evaluated included particulate explosives (e.g., TNT and RDX), particulate ammonium perchlorate (AP), atomized and flaked aluminum, and other constituents dispersed in air and nitrogen (e.g., reference 26). Although the work was not directly in support of process accident investigation, the results of both the analytical and experimental investigations are potentially useful in understanding explosion effects from a dispersed pyrotechnic in a process accident.

Usually an analysis involving major effort, such as a detailed CFD model is only justified in cases of very large losses. Although the accuracy might not be improved by such an analysis (e.g., overpressure prediction), the insight into the physics involved might be greatly enhanced. For these reasons, there is still a strong reliance on measurements from large-scale experiments. Although large-scale experiments are costly, these experimental results are more easily accepted than are predictions based upon analysis.

TNT Equivalency and Other Equivalency Methods

TNT equivalency or other equivalency methods are particularly useful for the analysis of large-scale accidents with high overpressures at the origin (e.g., vapor cloud, condensed explosive, and some pyrotechnic material accidents). In TNT equivalency methods, the available explosion energy in the accident is converted to the equivalent mass of TNT. Thus, explosion effects, particularly overpressure as a function of distance, are then basically a function of the TNT equivalent mass. Explosion effects for TNT are well known and available in various references (e.g., see references 5 and 27–30).

The TNT equivalency approach is discussed in the context of chemical process explosions in Perry's *Chemical Engineer's Handbook*.[31] Pyrotechnics manufacturing operations are in fact chemical process plants, with specialized aspects due to the reactive nature of the final products and many of the in-process material

forms. Of particular concern in the general chemical process industry are chemical reactor runaway reactions, inert pressure vessel explosions, and pressure vessel explosions involving flash vaporizing liquids. For pressure vessel explosions involving compressed gas, the equivalent mass of TNT is computed by assuming isentropic expansion of the gas from the initial vessel pressure to ambient pressure and dividing by the detonation energy of TNT. The resultant energy is partitioned into 30% for blast, 40% for fragments, and 30% for other dissipative mechanisms. For diffuse fuels such as flammable vapor clouds, a yield factor is typically applied to the calculation to account for inefficiencies in explosive combustion, mainly due to inhomogeneities in fuel-air mixing. This factor usually ranges from 1 to 40% depending on the circumstances. TNT equivalency methods are generally thought to be satisfactory as long as the far-field potential is the major concern. In the near field, where there can be significant distortion of the blast, then either numerical modeling or simulation experiments must be conducted.

Other equivalency methods have evolved in recent years for systems such as flammable vapor clouds. The multi-energy method has received wide acceptance for use with unconfined vapor cloud explosions. In this method, potential sources of strong blast are identified, energies are computed, and the relative blast strength is estimated. Strong blast sources generally correspond to locations where there is partial confinement or where the cloud is congested with obstacles that produce turbulence. Sachs-scaled blast parameters are utilized to determine blast variables of interest as a function of distance. Blast variables generally include peak overpressure, positive phase impulse, time of arrival, positive phase duration, and shock velocity. A good compilation and discussion of these methods is listed in reference 32.

Ground Shock Analysis

After an accidental explosion occurs, there are generally numerous reports of damage to surrounding property. This damage is many times attributed to air blast or ground shock. For air blast damage, the TNT equivalency methods

described above can be used to evaluate which of these claims are credible. An extension of the air blast methods can be employed to evaluate ground shock damage, as well. Ground shock analysis methods have been used for the design of structures to resist accidental explosions in pyrotechnics manufacturing and storage facilities, and to design structures to resist weapons effects in military applications. Ground shock can be evaluated as having two contributing parts: the air blast induced ground shock and the direct induced ground shock. The air blast induced ground shock is (as the name implies) the ground shock disturbance that follows the air shock as it propagates outward from the explosion center. The direct induced ground shock is the disturbance that passes from the explosion directly into the ground medium. This component depends on the coupling of the explosion to the ground at the source. Many times the explosion is not in direct contact with the ground surface, and the resulting direct induced ground shock is substantially diminished because of this poor coupling. To conduct a ground shock analysis, the characteristics of the soil medium (e.g., seismic velocity and density) and characteristics of an underlayer such as the water table or a rock layer must be known.

Sources of information on this subject can be found in references 28–30. These are each in a workbook form, which aid in their application by a knowledgeable practitioner. Each of the references were developed for different specific purposes, and their domains of applicability must be considered by the user. The Pantex Manual[28] concentrates on buried explosions, either in direct ground contact or within an underground cavity. Since the explosions are buried, no air blast induced ground shock is considered. TM 5-1300[29] is concerned with designing structures against accidental explosions. It considers both air blast induced ground shock and direct induced ground shock. These methods do not directly include an underlayer. TM 5-855-1[30] is concerned with designing structures against conventional weapons. To use this approach for an above ground accidental explosion, an equivalent TNT hemisphere is assumed to sit on the ground surface. The height of the burst is not automatically taken into account for ground shock. An underlayer can be consid-

ered. These references provide the procedures to conduct a good assessment of the effects of ground shock on structures, based on predicted maximum displacement, velocity and acceleration. A criterion used frequently for the threshold of damage is a maximum velocity of 2 inches (51 mm) per second. A more comprehensive approach is to conduct a structural analysis for a specific structure, given the predicted ground shock characteristics.

Dynamic Fuel Concentration Modeling

The analysis of flammable gas concentrations has been used to evaluate whether a gas leak could have been responsible for a fire/explosion incident and to assist in determining the source of the gas. These models can be used to calculate the gas concentration as related to time and elevation in the space, and they can be correlated with explosion damage. Models may range from simple exponential mixing calculations in a control volume, to detailed computational fluid dynamic (CFD) models incorporating diffusion, turbulence and gravity effects.

Flammable gas concentration modeling, combined with an evaluation of explosion/fire damage and the location of possible ignition sources, can be used to establish whether or not a suspected or alleged leak could have been the cause of an explosion/fire and to determine what source(s) of gas or fuel vapor was consistent with the explosion/fire scenario, damage, and possible ignition sources. Useful sources of information on this topic include references 9, 33, and 34.

Thermodynamic Chemical Equilibrium Analysis

Fires and explosions that are suspected of being caused by reactions of known or suspected chemical mixtures can be investigated by a thermodynamic analysis of the probable chemical mixtures and potential contaminants. This type of analysis can be used to help answer causal investigative questions such as: What reaction(s) could have caused the fire/explosion? Was the reaction spontaneous or did it require an outside source of energy? Was there an improper mixture of chemicals or a contamination? Did a chemical or chemical mixture overheat? Was

there a vapor release followed by an outside ignition?

Thermodynamic reaction equilibrium analysis requires tedious hand calculations or the use of a complex computer code. Several of these thermodynamic codes that are available are reviewed in reference 35. These computer programs usually require the input of material and the material's properties that include the chemical formula, density, mass, entropy and heat of formation. Sources for this information include the JANAF tables,[36] Chemical and Chemical Engineering Handbooks, published papers, material safety data sheets, and the NIST Chemistry WebBook.[37]

The state of the art of equilibrium thermochemical codes for explosion analysis is represented by the CHEETAH Code.[38] This code was developed by Lawrence Livermore Laboratory. It is an improved version of the TIGER Code.[39] The Code is quite easy to use—it is user friendly. However, this code is currently available only to the government and government contractors working on government projects. To use the code properly, the user should have a reasonable understanding of how equilibrium thermochemical codes work. For example, there are several options for equation of state and species libraries, each of which has certain domains of applicability. There are a number of state characterizations to choose from. The primary application of this code is for the characterization of condensed explosive and pyrotechnic propellant formulations, but diffuse fuel-air applications are easily handled. Because of the limited availability of this code, other codes such as NASA-Lewis and others (see reference 35) should be employed where necessary.

Damage Pattern Analysis

Damage pattern analysis usually includes analysis of debris and structural damage. Often, it is very useful to prepare diagrams showing relative damage patterns. Debris patterns often can show the direction and relative force of the explosion. However, different drag or lift forces of various fragment shapes will tend to favor some shapes continuing on further trajectories. These factors must be considered in relative force comparisons. Quite often, investigators erroneously assume that the fragments that have gone the furthest are representative of the strongest force and direction of the explosion. References 27 and 32 aid in this type of analysis.

Structural damage analysis usually involves the estimation of overpressures and sometimes the impulse necessary to produce the damage. Several generalized overpressure damage listings are compiled in the literature (see references 1, 9, 27, 31, and 32). These are quite useful for making quick estimates. These lists are usually derived from data where explosive impulse is very high at a given overpressure, where the overpressure approximates a static application. Thus, such data can be quite useful for applications involving fuel, gas or dust explosions, where such an approximation is usually valid.

If needed, various structural computer programs can be used, however, sometimes a structural damage expert will be necessary. Some examples of practical computer programs are listed in reference 40.

Systems Safety Analysis

Systems Safety Analysis (SSA) techniques are particularly useful for explosion investigations. They can help identify potential causes of an explosion, and they can indicate where further analysis should be directed. A formalized SSA is generally most useful in a large and/or complex incident. It can be very effective in identifying all factors, both physical and human, which did or could have contributed to the cause of the explosion. Similarly, it can be helpful in eliminating potential causes of an explosion.

These techniques include Failure Modes and Effects Analysis (FMEA), Fault Tree Analysis, HAZOP Analysis, What-If Analysis, etc. In general, these tools provide a systematic method for analyzing large complicated systems to determine hazards or faults. The tools can utilize either qualitative or quantitative formats. Hazard probabilities or failure rates can be factored in when using quantitative formats. Some of the more common techniques—failure mode and effects analysis and fault tree analysis—are described below.
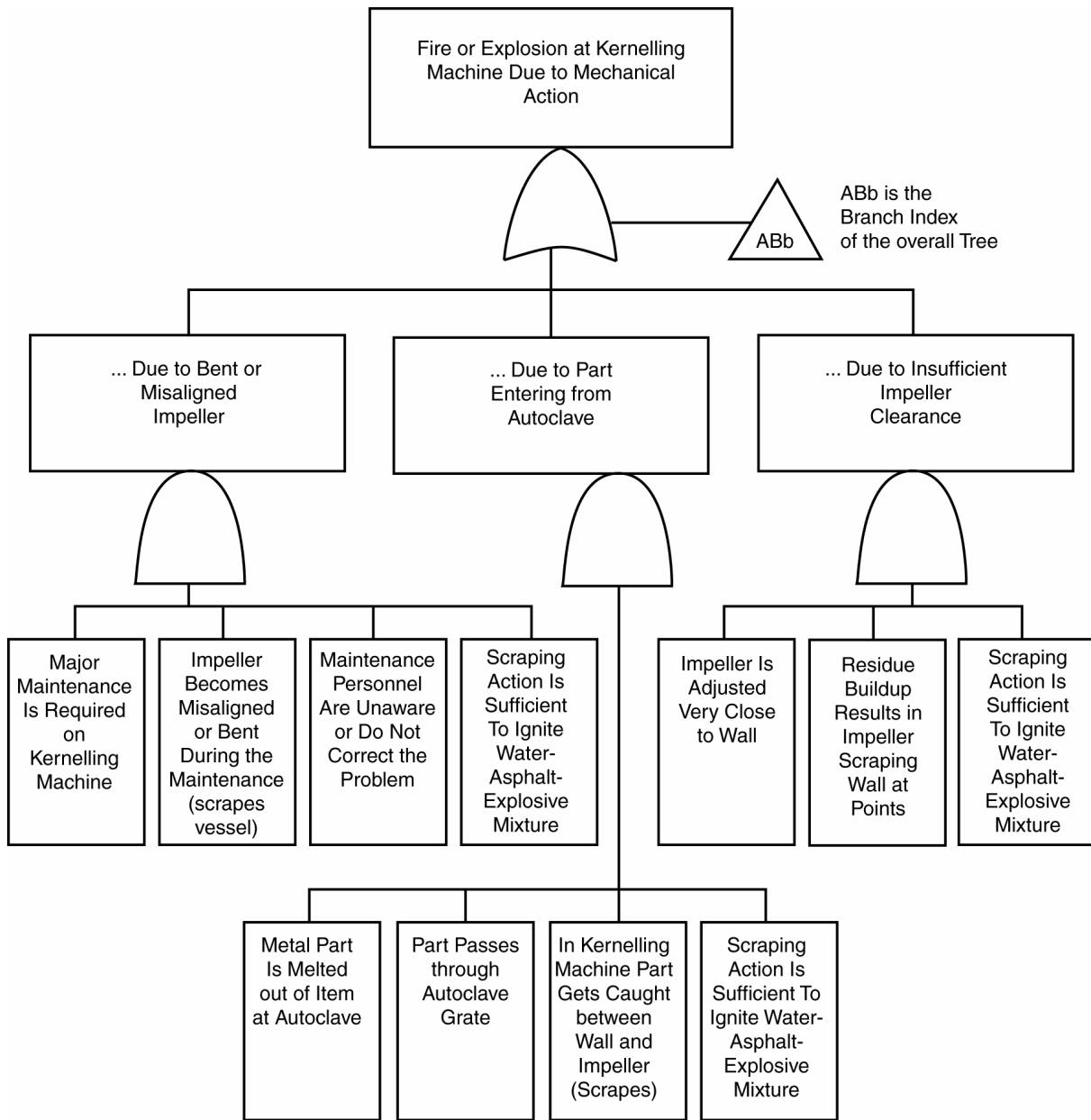
Figure 2. Fault Tree Example.

Failure Modes and Effects Analysis

A FMEA is a relatively simple and straight-forward technique to identify basic sources of failure within a system and to follow the consequences of these failures in a systematic fashion. In fire/explosion investigations, the purpose of the FMEA is a systematic evaluation of all equipment and/or actions that could have contributed to the cause of the incident. A FMEA is prepared by filling in a table with row headings such as those shown in the example in Table 1.

Table 1. Example Failure Mode and Effects Analysis.

Item No.	Part Name	Operating Mode	Failure Mode	Est. Prob.	Failure Effects	Hazard Description	Haz. Cat.	Recommended Controls	Remarks
301	Cellulose hoppers (not enclosed)	Normal abnormal	Conveyor control failure, hopper overfills	Low	Fire or dust explosion if initiation source present	Flammable cellulose material present in unwanted areas due to hopper overfill	II	• Level sensor in hopper interlocked with conveyor power • Sprinkler system • TV surveillance • Consider dust collection system at conveyor transfer point • Inspection ports	Cellulose fire is likely to be a smoldering type
			ESD at hopper discharge	High	Fire or dust explosion if ESD is sufficient	Cellulose discharge process generates ESD	II	• Design unit to minimize problem using conductive materials and proper grounding and bonding	
			Severe friction in hopper auger	Low	Fire in cellulose; possible spread to other parts of the process	Cellulose in presence of frictional heat source	II	• Design unit to minimize problem • TV surveillance	
302	Weigh conveyor (enclosed)	Normal abnormal	Mechanical or control failure, overfills nitrator	Low	Fire or dust explosion if initiation source present; or denitration/fire/explosion if cellulose not wetted properly in nitrator causes hot spots	Flammable cellulose material spilled in unwanted areas due to nitrator overfill, and improper wetting of cellulose in nitrator	II	• Consider non-water fire supression system • TV surveillance • See recommended controls for nitrator	Minimize possibility of water introduction into nitrator

The row headings and format of the table are flexible, but at least three items are common: the item (or action) being analyzed, the basic fault (failure) or error that created the hazard, and the consequence of the failure. Additional rows are added by the investigator as needed for the particular investigation at hand. An assessment of the likelihood of each individual failure mode is frequently included. Also, it is sometimes helpful to assess the severity of a given failure. Also, it is sometimes helpful to assess the severity of a given failure relative to the fire/explosion. FMEA tables can also be catalogued by item and serve as reference material for further investigations.

When filling out the table, the investigator should consider for each item/action the range of environmental conditions and the process status (i.e., normal operation, shutdown, startup, etc.). Qualitative or quantitative values can be assigned as probabilities of occurrence. Then, when a sequence of failures is required for an incident to occur, the probabilities can be combined to assess the likelihood that any given sequence of events led to the incident.

The usefulness of FMEA is limited by the ability of the investigator to identify all system components (or human actions) that may have contributed to the incident. Furthermore, the evaluation of the likelihood that a given sequence of events caused the incident is only as good as the ability of the investigator to assign accurate probabilities to each of the individual failure modes that contributed to the sequence.

Fault Tree Analysis

A fault tree is a diagram used to analyze an undesired event. The undesired event is placed at the top of the diagram, and all the causes that can lead to the event are grouped below. This approach is repeated for each cause and continues until the desired level of detail is reached or the root causes of the event are determined. The diagram takes the form of an inverted tree. The relationships between the events leading to the undesired event are described by the use of "AND" and "OR" gates at the junction(s) leading to the next level of the event. An example diagram is shown in Figure 2.

Once a complete fault-tree is developed for an undesired event, an investigator can look at each of the root causes of the undesired event and all of the steps necessary for the event to happen. If any of the necessary steps did not occur, the root cause associated with that particular path can be eliminated.

It is possible to assign values associated with the probability of occurrence to the root causes and other independent aspects of the fault-tree. The probability of each path leading to the undesired event can then be evaluated. The investigator will find that information on the probability of the occurrence of causes is difficult to find or not available. In most cases the assignment of a probability of occurrence will be based on experience, engineering judgment, tests, incident reports, models or published data. Any time probabilities are assumed, the sensitivity of the outcome to the assumed value should be determined by reevaluating the outcome with slightly modified values.

Reference 41 provides additional guidelines for conducting these and other types of systems safety analyses.

Example Application

The use of some of these tools is illustrated for the Pepcon explosion investigation.[2] This incident originated as a fire in a large ammonium perchlorate (AP) plant located in Henderson, Nevada. The fire quickly spread through most of the facility by means of thermal radiation, firebrands, a continuous (linear) source of fuel, and some natural self-propelled missiles. Two large explosions occurred during the fire, each equivalent in energy to a few hundred tons of TNT. The explosions claimed two lives, injured 372 people and damaged plant buildings and nearby residential buildings. Some of the tools used in the analysis are illustrated below, in limited detail.

A videotape of the event from a nearby mountaintop permitted advanced reconstructive techniques, such as superimposing CAD outlines of the plant on video records. This, together with witness accounts, greatly aided in constructing a detailed timeline of events from ignition, through various modes of flame spread through the plant, to the two large explosions (see Figure 1). The
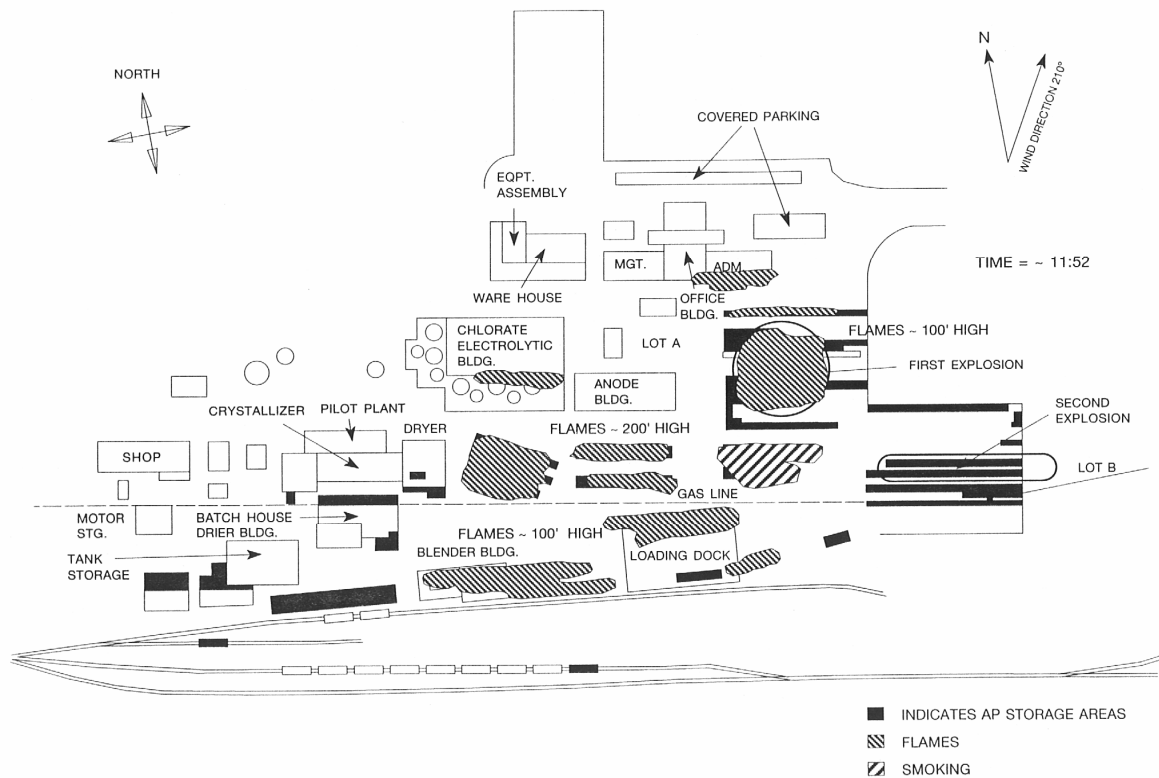
Figure 3. Pepcon Fire Progress at 11:52 AM

size and shape of the extremely large fire plumes advancing through the plant were determined. Graphical plot plan diagrams of the fire/explosion progress were prepared for different time slices (one example is shown in Figure 3).

Thermal radiation heat transfer calculations aided in the determination and confirmation of the flame-spread theories. A radiant heating model was constructed that showed that significant preheating of drums/bins of AP in storage lots near the huge fire plumes had occurred before initiation of the detonation. The model consisted of a marching/growing radiant plume model coupled with a one-dimensional conduction heat transfer model of a bin. Due to the large size of the bins and their orientation with respect to the immense fire plumes, an assumption of modeling the bin as a semi-infinite solid was appropriate. This analysis was very useful in predicting that pyrolysis of AP in strongly preheated bins would cause them to burst and disperse some of their contents onto nearby fuels, providing a more-easily initiated explosion layer, which could serve as an explosive booster to the drums and bins.

Explosion dynamics estimates aided in determining the locations of the initial small explosions and in estimating the amount of product involved in the large explosions as sympathetic detonations. Experimental data on AP and AP/fuel explosion characteristics provided guidance for possible modes of explosion initiation and propagation. A thermodynamic equilibrium analysis was done to determine the energy release from AP and different fuels at the plant. Structural damage data helped assess the overpressures experienced in the area.

Possible causes of the initial fire were ascertained, and the most probable was related to welding sparks coming into contact with contamination-sensitized AP. The official cause remains undetermined. Conclusions were formulated regarding major factors involved in the ignition, the extreme rate of fire spread, and the explosion initiation and propagation.

Summary

Currently the engineer investigator has a range of practical analytical tools for effective investigation of explosions. These "tools" can be applied to the investigation of incidents in pyrotechnics manufacturing facilities. Most of the tools require that accurate data from the incident be available. Thus, data gathering activities are crucial to a successful investigation.

Although many analytical methods are available, desirable advancements in the area of explosion science to aid in such investigations include: verified field modeling of vented explosions in enclosures, a wider range of data and models for estimating vented explosion external pressures, more refined models for gas mixing, additional experimental investigation and modeling for estimating cascade fuel/air explosion overpressures in successive compartments, and verified field modeling of explosions in highly elongated geometries.

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An Introduction to Chemical Thermodynamics
Part 2—Entropy, Molecular Disorder,
and the Second and Third Laws

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ABSTRACT

This is the second in a series of articles, prepared at the request of the publisher of this Journal, presenting an introductory outline of chemical thermodynamics and chemical kinetics, with emphasis on those aspects of particular relevance to pyrotechnics. The First Law of Thermodynamics, which was the subject of the first article, cannot explain the direction of change in the physical world. The Second Law of Thermodynamics states that spontaneous change is always associated with an increase in the entropy of the universe. The universe is simply the system of interest plus its surroundings, assumed to be isolated from external influences, while the entropy is a thermodynamic state function. Much of this article is taken up by a discussion of entropy. The relationship between entropy and spontaneous change is clarified when entropy is interpreted as a measure of molecular disorder. The Gibbs Free Energy is a thermodynamic state function that allows the entropy change in the system and its surroundings to be predicted from the thermodynamic properties of the system alone. It provides the basis for predicting the direction of change in chemical systems. Finally, the Third Law of Thermodynamics states that the molar entropy of a pure substance is zero at the absolute zero of temperature. This is developed from Boltzmann's relationship between entropy and the number of molecular arrangements consistent with the properties of a system. It is shown how the Third Law permits the calculation of absolute values for the molar entropies of pure substances.

Introduction

The first article in this series[1] showed how the *energy changes* involved in a chemical process can be calculated from the standard enthalpies of formation of the reactants and products. The energy change, however, does not tell us whether or not a process will occur. For example, melting ice absorbs energy and freezing water releases energy, yet both processes can occur spontaneously, depending on the temperature.

In this article the thermodynamic properties that allow the direction and extent of change in chemical systems to be predicted will be introduced and explained. Applications of these concepts to chemical systems of interest to pyrotechnists will form the third in this series of articles.

Spontaneous Processes

In chemical thermodynamics a "spontaneous" process means one that will continue to equilibrium *once it has been started*, without further input of external work. This is different from the usage in ordinary speech, where something is said to be "spontaneous" if it happens "of its own accord". The reaction of aluminium with hydrochloric acid is spontaneous in both the conventional and the thermodynamic senses. That between aluminium and potassium perchlorate is spontaneous in the thermodynamic sense, but not in the conventional. The reasons why many thermodynamically spontaneous pro-

cesses are not spontaneous in the conventional sense are dealt with by **chemical kinetics**, to be discussed in a future article in this series.

A New State Function: The Entropy

The First Law summarizes the experience of many generations of scientists and engineers that energy cannot be created or destroyed, but is merely *transferred* in one form or another. If you watch a movie that is being run in reverse, you will see examples of energy being transferred in ways that are completely consistent with the First Law, but which never happen in the real world. Something that could happen in such a movie, but not in the real world, would be a balloon inflating by itself as air rushes into it from the room. A block of ice might emerge from a bucket of hot water, with the water coming to the boil as the ice freezes. Neither one of these processes conflicts with the First Law, but neither has ever been observed. There is clearly a preferred direction of change in the real world.

In the real world, gas at high pressure will spontaneously flow to a region of low pressure, until the pressure in both regions is the same. A cold object and a hot object in contact will come to an intermediate temperature. In each case, the system has come to equilibrium. It has also lost the ability to perform work. A system with gas at different pressures could do work through a fan or turbine placed between the two regions. A system with two bodies at different temperatures could do work through a heat engine placed between the two bodies. In coming to equilibrium*, the system has lost the ability to do work, but the internal energy of the system has not changed*. No work has been done, and no heat has been exchanged with the surroundings, so the internal energy must be the same. Energy that was once available to do work has somehow become unavailable, as the system has come to equilibrium.

In the examples just given, at the beginning of the process some thermodynamic state function was different in various parts of the system. In one case, the pressure was different. In another, the temperature was different. To reach equilibrium, the system changed in such a way that the state functions became equal in all parts of the system. This leads to an important ques-

tion. Is there a state function that can be used to indicate whether or not a *chemical* system is in thermodynamic equilibrium? Clearly pressure and temperature will not suffice. A mixture of potassium perchlorate and powdered aluminium might well be at uniform temperature and pressure, but it is certainly very far from a state of thermodynamic equilibrium. A new state function is needed. To arrive at it, however, requires a measure of the loss of ability to perform work that accompanied the attainment of equilibrium in the two simple examples just discussed.

In the nineteenth century Clausius[2a] introduced a thermodynamic state function called the **entropy** (symbol *S*) that provides just such a measure. The word comes from a Greek word meaning "transformation" or "change".

Recall that for any process the change in internal energy is

$$\Delta U = q - w$$

where ΔU is the change in the internal energy of the system, q is the heat absorbed by the system and w is the work done by the system.

Recall, too, that the *maximum* work done by a system in coming to equilibrium is w_{rev}, the work that is done when equilibrium is reached in a *reversible* process. A reversible, or *quasistatic,* process is one in which all change takes place infinitely slowly, so that the system is in equilibrium at each step in the process. Such processes occur only in the imaginations of thermodynamicists; no natural process takes place in the manner just described. Nonetheless, the concept of a reversible process is important because it allows powerful mathematical tools (the calculus) to be applied to problems that would otherwise be extremely difficult or impossible to model mathematically. For the present discussion, the important point is that the work done and the heat absorbed, in the reversible process taking a system from one state to another, is the *maximum* possible for that change in internal energy.

For each very small step in a reversible process, the First Law of thermodynamics becomes

$$dU = dq_{rev} - dw_{rev}$$

The symbol "d" can be taken to mean "an extremely small change in".

The heat absorbed by the system (dq_{rev}) during this very small change was absorbed at a particular temperature T. Because dq_{rev} is extremely small, T can be taken as constant over the time taken for the change. The ratio dq_{rev}/T, taken at every step during a change from a first state 1 to a second state 2 leads to a new state function called the **entropy.** The change in entropy, ΔS, is *defined* by

$$\Delta S = S_2 - S_1 = \int_1^2 \mathrm{d}\, q_{rev}/T$$

The integral sign $\int$ (the elongated "S") in this equation is simply an instruction to add up ("sum") the quantities that follow. Stated in words, the right hand side of the equation means "the sum of the ratio dq_{rev}/T for every step in the process, starting at State 1 and ending at State 2".

The direction of change in the physical world can be predicted from the entropy change. Change will always occur in such a way that the *entropy of the universe increases*. This is one way of expressing the **Second Law of Thermodynamics**. Recall that in thermodynamics the word "universe" means the system of interest plus its surroundings, and that the system and its surroundings are assumed to be totally isolated from external influences. A thermodynamic "universe" could be, for example, a piece of experimental apparatus enclosed in a perfectly insulated box.

Molecular Interpretation of the Entropy

The entropy, as introduced in classical thermodynamics, is a rather abstract concept. It is not obvious why the ratio of heat absorbed in a reversible process to the temperature at which the absorption occurs should be associated with the direction of change in the physical world. The situation becomes completely different when we think about what entropy means in terms of the behavior of molecules. It is then possible to express the Second Law very crudely, but accurately, as "moving molecules get into a mess".

The Natural Tendency to get into a Mess

It is a matter of personal experience that there is a natural tendency for things to get into a mess.

Everybody knows how difficult it is to keep a kitchen or workshop tidy. Unless you take care to put everything back where it belongs, the place soon gets messed up. Why? Simply because there are *millions upon millions* of ways of putting things in a room that make it look a mess, but *relatively few* ways of arranging things that make it look tidy. That is consistent with the old adage "a place for everything, and everything in its place". According to that rule, there is only *one* arrangement of things that is consistent with the room being tidy. At the other extreme, who could say how many ways there are of putting things in a room that would make the room look untidy?

Sometimes an untidy room is described as "disordered". In thermodynamics "disorder" has a particular technical meaning that is consistent with the common usage of the word, but is more rigorously defined. The amount of disorder (in the thermodynamic sense of the word) associated with a particular state of a room is simply an indication of how many ways of arranging things in the room are consistent with that state. For example, the state described by "a perfectly tidy room" might be consistent with just one possible arrangement; the "degree of disorder" of "a perfectly tidy room" is therefore low; indeed, it could be no lower. At the other extreme, because the description "a very untidy room" would be consistent with countless possible arrangements, the degree of disorder of "a very untidy room" is very high.

Messiness Among the Molecules

Go into a tidy room, pick something up, and then put it down without thinking about where you are putting it, and chances are that it will not land in a place that will make the room tidy. Do that with two or three or more things, and the degree of disorder begins to increase significantly.

Exactly the same sort of thing happens on the molecular scale. With molecules, however, it is necessary to think of different *velocities* as

well as different *positions*. To begin with, it's useful to imagine what would happen if molecules had no tendency whatsoever to stick to each other. At a given temperature (room temperature, for example) such molecules would be continually jostling around, incessantly colliding with each other and rebounding to collide over and over again. Left to themselves, they would spontaneously distribute themselves over a vast number of different arrangements of position and velocity. This is the same as saying that a collection of these imaginary molecules would naturally get into a state of disorder. Having no inherent stickiness, they would have no impediment to getting themselves well and truly mixed up. They would be in that chaotic state that we call a *gas*.

The Effect of Temperature on Molecular Disorder

What would happen if the temperature were to increase? Recall the discussion of the Equation of State of a Perfect Gas in the first article in this series. If the pressure were constant, the gas would expand. More space would be available for the molecules to move around, and they could take up even more different arrangements of their positions. What about their velocities? Obviously, since temperature is a measure of the average molecular kinetic energy, and kinetic energy is proportional to the square of the velocity, the average velocity of the molecules would be greater at the higher temperature. Detailed analysis of the behavior of large collections of randomly colliding molecules[3a] shows that the molecules can have a huge range of velocities, and the way in which they distribute themselves over that range depends on the temperature. At low temperatures most molecules have velocities that are rather close to the average velocity. At high temperatures the distribution of velocities is much broader, with more molecules having velocities very different from the average. A proper treatment of the relationship between molecular velocity and temperature would require a discussion of statistical mechanics,[3b,4] which is beyond the scope of this article. The important point is that an *increase in temperature* means an increase in the *spread of molecular velocities* and thus an *increase in disorder*.[5]

Attractions between Mixing Molecules

So far, the molecules have been imagined to have no tendency to stick to each other. They would spontaneously mix themselves into a state of disorder by their random motion. A world made of such molecules would be completely disordered on the molecular level but completely uniform on the large scale. It would be a rather dull place. Fortunately, real molecules always have a tendency to stick together because of attractive forces arising from electrostatic interactions. If molecules have opposite electrical charges, as for example gaseous sodium and chloride ions (Na^+ and Cl^-) these attractive forces can be very strong indeed. Even the most simple and symmetrical molecules (atoms of helium or argon, for example) have a slight tendency to stick together. The distribution of electrons in each atom is continually changing, and when the atoms are very close, the electrons in each atom come under the influence of the nuclear charge of the other. This results in a small attractive force between the atoms.

These attractive forces make a great difference to the behavior of atoms and molecules at low temperatures. Imagine a collection of atoms, all of the same kind, with each atom having a rather high average kinetic energy. For example, this could be a quantity of argon gas in a container at room temperature. The atoms are continually colliding; as they collide, they have a slight tendency to stick together. The attractive force is very weak, however, and at high temperatures is negligible. Now suppose that the sample of argon is cooled by some sort of refrigerator, to the point where the average kinetic energy of the atoms is so low that colliding atoms can start to stick together and form clumps. If the temperature is low enough, some of the gas will condense into a *liquid*. A more ordered state of matter (liquid) has spontaneously appeared from a more disordered one (gas).

Order Here, Disorder There

It seems that cooling the gas has made the world a more orderly place. This conclusion would seem even more valid if the cooling process were to continue to the point where all the argon condensed to a crystalline solid, with the atoms neatly arranged in a beautifully regular array. That is certainly a more ordered arrangement of atoms than the original chaotic swarm of atoms filling the whole container. There is no doubt that the degree of molecular disorder in the container has been reduced.

In thermodynamics, however, what happens in the container is only part of the story. What about the surroundings? Recall that the sample of gas was originally at room temperature, and a refrigerator was used to cool it. For argument's sake, the refrigerator can be assumed to be perfectly efficient: it simply takes a quantity of energy from the gas, and dumps it into the outside world. On the molecular level, this means that the molecules of the outside world can now move more rapidly and are therefore able to become even more disordered.

As will be shown later, the increase in molecular disorder in the outside world must at the very least equal the decrease in molecular disorder that happened when the gas condensed into a liquid, or when the liquid condensed into a solid. Because of the natural tendency of randomly moving molecules to get mixed up, *the entire physical world tends to become more disordered on the molecular scale*. Parts of the world can be made very orderly, but the ordering process inevitably results in some other part of the world becoming even more disordered.

To return to the example of the untidy room, imagine you are in a small room that is so full of stuff that you are up to your elbows in objects. You try to tidy the room, but as you pick up things and put them where they need to go, your movements stir up all the objects around you, and they get into more of a mess than they were originally. In a room, and in the world at large, there is no way around the fact that objects moved at random are inevitably going to end up in a mess.

It must be admitted, of course, that continuous random rearrangement of a set of objects does have some chance of putting the objects into one of the rare orderly arrangements. That chance would be greater if there were only a few objects being moved around, but even then the objects would remain ordered for only an instant. As the number of objects increases, the number of possible arrangements increases tremendously, and the fraction of time that the objects spend in orderly arrangements becomes completely insignificant compared to the time that they spend in disordered arrangements.

The statement that the world becomes more disordered on the molecular scale is another way of stating the Second Law of Thermodynamics.

The Consequences of Molecular Disorder

What are the consequences of this tendency to disorder? To answer this, it is necessary to look at how molecular disorder shows itself in the everyday world. All substances and systems have their own characteristic properties, which can stay the same only if the positions and velocities of the molecules that make up the substance or system are restricted to a certain range. If that range is reduced or exceeded, the properties of the substance or system will change. For example, the molecules of a crystalline solid must remain arranged in a regular array if the crystal is to retain its hardness and rigidity. To remain in a regular array, the molecules can have only a rather restricted range of positions and velocities.

The degree of disorder depends on the number of possible combinations of position and velocity that are available to the molecules. A substance (or system) has a low degree of molecular disorder if the molecules that make it up can arrange themselves over only a relatively restricted number of positions and velocities. The degree of disorder in a crystalline solid is therefore low. In a liquid, the molecules can distribute themselves over a much greater range of positions and velocities than they can in a crystalline solid. The degree of disorder of a liquid is therefore higher than that of a crystalline solid. The molecules in a gas can spread themselves over a vast range of positions and

velocities. The degree of disorder in a gas is very high.

The natural tendency towards molecular disorder would suggest that a crystalline solid should spontaneously melt, and the liquid should then evaporate and turn into a gas. This certainly happens, but only if the temperature is sufficiently high. Energy has to be absorbed from the surroundings to overcome the forces that hold the molecules together in the solid. The loss of that energy from the surroundings reduces the molecular disorder there. The solid cannot melt until the increase in disorder resulting from its melting at least equals the decrease in disorder in the outside world that comes about by the transfer of energy from the outside to the melting solid.

How something changes, or whether it changes at all, is constrained by two factors: *the total amount of energy in the universe must stay the same*, and *the total amount of molecular disorder in the universe must increase*. The first of these constraints is a statement of the First Law of Thermodynamics, while the second is a statement of the Second Law. The Second Law was previously stated as the *entropy of the universe increases*. This implies that the *entropy is a measure of the amount of molecular disorder*.

The Relationship between Entropy and Molecular Disorder

Recall that in thermodynamics, the disorder of a system is simply the number of molecular arrangements that are consistent with the properties of that system. This number is sometimes called the thermodynamic probability of the system, and is given the symbol W.

In the nineteenth century Ludwig Boltzmann[3c] showed that the entropy S of a system is given by

$S = k \ln W$

where k is a constant (Boltzmann's constant, 1.381×10^{-23} joules per Kelvin), and $\ln W$ is the **natural logarithm** of W (The natural logarithm of any number x is defined as follows: if $x = e^y$, where e is the number 2.71828… then $y = \ln x$).

A Justification of the Entropy Formula

A properly detailed discussion of the mathematical relationship between entropy and molecular disorder[4] is beyond the scope of this article. Nonetheless, it is worth offering a brief justification of the formula for the *change* in entropy.

According to this formula, the entropy change ΔS for a reversible process at constant temperature, such as the melting of ice at 273 Kelvin at a pressure of 1 atmosphere, is given by

$\Delta S = q / T$

where q is the heat absorbed and T is the absolute temperature.

It is easy to see that the absorption of heat would increase molecular disorder, because the extra energy would help to overcome attractive forces that tend to keep molecules close together. Even when attractive forces are negligible, the addition of extra energy gives molecules a broader range of velocities and this makes the system more disordered.

Why is the absorbed heat divided by the absolute temperature? That implies that the same amount of energy produces a greater change in the disorder of a collection of molecules at a low temperature than it does at a higher temperature. Does that seem reasonable? Recall that collections of molecules become more *disordered* as the temperature increases. The same amount of disruption (i.e., added energy) produces a greater *change* in the degree of disorder in a group of molecules that was *less* disordered to start with than it does in one that was more disordered. The analogy with a tidy room is useful. Imagine that you go into a perfectly neat and tidy room, and you throw ten objects about and leave them where they fall. Is it obvious how the state of order in the room has changed? Now go into a really untidy room and do exactly the same thing. Pick up ten objects at random, throw them into the air and leave them where they fall. Are you aware of much difference in the tidiness of the room? The change in orderliness produced by the same amount of disruption (i.e., randomly changing the positions of ten objects) is clearly much greater in a

tidy room than in a room that was already in a mess.

It has already been stated that entropy is a state function; that is, its value does not depend on the path that was taken to arrive at the final state. That makes sense, given that entropy is basically a measure of how many arrangements of molecules are consistent with the properties of the system. A system is characterized by a particular set of state functions, all of which are independent of the path taken to get to that state. Only a certain number of arrangements of molecules is consistent with that set of state functions; there is no reason to think that that number is in any way dependent on the way in which the system came to have that particular set of state functions.

Now, temperature is also a state function, but the heat absorbed is not. The heat absorbed by a system in going from one state to another is not well defined at all. It depends on how much work was done in the process, and this clearly depends on the path taken. However, imagine that the change from one state to another is carried out infinitely slowly, in other words if it is carried out *reversibly*. Then the amount of heat absorbed is well defined, and is the maximum that is consistent with the change in internal energy. The proper definition of the entropy change is therefore

$$\Delta S = q_{rev}/T$$

What happens if the temperature is not constant during the change from one state to the next? In such a case, the process must be thought of as taking place in very small steps. The tiny amount of heat absorbed reversibly by the system during this very small step is dq_{rev}. The temperature at each step is effectively constant for that step. The value of q_{rev}/T is calculated for each step, and then all the values are added to give the entropy change. This is written as

$$\Delta S = \int_{1}^{2} dq_{rev}/T$$

This, of course, is the formula presented in a previous section as the definition of the entropy change that takes place when a system in one state (state 1) changes to another state (state 2).

Entropy Changes in Reversible Processes at Constant Temperature

It is useful to think about entropy changes taking place at a constant temperature. This can be done if the surroundings are imagined to be some sort of huge thermostat, kept at the same temperature T.

In a reversible process, the entropy change *in the system* is given by

$$\Delta S_{system} = q_{rev}/T$$

The heat absorbed came from the surroundings, so the heat "absorbed" by the surroundings is $-q_{rev}$ (the negative sign mean that heat is lost by the surroundings) and the entropy change *in the surroundings* is

$$\Delta S_{surroundings} = -q_{rev}/T$$

The entropy change in the universe is the sum of the entropy changes in the system and the surroundings:

$$\begin{aligned}\Delta S_{universe} &= \Delta S_{system} + \Delta S_{surroundings} \\ &= q_{rev}/T - q_{rev}/T \\ &= 0\end{aligned}$$

The entropy change in the universe in a reversible process at constant temperature is therefore zero. This is consistent with the definition of a reversible process as one in which the system and its surroundings are always in equilibrium. Recall that for a system in equilibrium, the change in any state function is zero.

Entropy Changes in Real Processes

Real processes *always* occur irreversibly. The entropy changes are easily calculated if we imagine that the surroundings are at a constant temperature T, as in the previous example. First, consider the entropy change in the system. Entropy is a state function, so the entropy change in the system is exactly the same as it would have been if the change had been carried out reversibly.

$$\Delta S_{system} = q_{rev}/T$$

The heat absorbed in the real process, however, would have been *less* than q_{rev}. This is

because q_{rev} is the maximum amount of heat that can be absorbed for a given change in internal energy. The quantity of heat absorbed by the system in an irreversible process can be labeled q_{irrev}.

Now consider the entropy change in the surroundings. The heat absorbed by the system, q_{irrev} came from the surroundings, so the heat "absorbed" by the surroundings is $-q_{irrev}$ and the entropy change *in the surroundings* is

$$\Delta S_{surroundings} = -q_{irrev}/T$$

As previously, the entropy change in the universe is the sum of the entropy changes in the system and the surroundings:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$
$$= q_{rev}/T - q_{irrev}/T$$
$$> 0$$

because q_{irrev} is always less than q_{rev}.

The entropy change in the universe in a real, irreversible process is always greater than zero.

Entropy Change in the Expansion of a Perfect Gas

Suppose one mole of a perfect gas with an initial volume V_1 and an initial temperature T_1 reversibly absorbs a small quantity of heat dq_{rev} and expands by a very small volume dV against an external pressure P. The final volume is V_2, the final temperature T_2. The work done by the gas will then be $dw_{rev} = PdV$

From the First Law,

$$dU = dq_{rev} - dw_{rev}$$
$$dU = dq_{rev} - P\ dV$$
$$dq_{rev} = dU + P\ dV$$

From the Equation of State of a Perfect Gas, for 1 mole of the gas $P = RT/V$

$$dq_{rev} = dU + \frac{RT\ dV}{V}$$

Also for 1 mole of gas, the internal energy U is given by the product of the heat capacity at constant volume C_V and the temperature T,

$$dq_{rev} = C_V\ dT + \frac{RT\ dV}{V}$$

Dividing both sides by the temperature T

$$dq_{rev}/T = C_V\ dT/T + R\ dV/V$$

With calculus, this equation can now be integrated to give

$$\Delta S = (C_V\ \ln T_2 + R\ \ln V_2) - (C_V\ \ln T_1 + R\ \ln V_1)$$

because the integral of $dx/x = \ln x$ (the natural logarithm of x).

Since $\ln x - \ln y = \ln x/y$

$$\Delta S = C_V\ \ln(T_2/T_1) + R\ \ln(V_2/V_1)$$

This equation defines the entropy change in terms that are either constants (C_V and R) or state functions (V and T). This shows that entropy is a state function for a perfect gas.

Entropy and the Direction of Change in Isolated Systems

A. The Expansion of a Gas at Constant Temperature

The equation for the entropy change that results from the absorption of heat by a perfect gas allows one to calculate the entropy change associated with the expansion of a certain quantity of gas in an isolated system at constant temperature. As previously,

$$\Delta S = C_V\ \ln(T_2/T_1) + R\ \ln(V_2/V_1)$$

but in this case $T_2 = T_1$ so $T_2/T_1 = 1$. From the definition of the natural logarithm, $\ln 1 = 0$ and so

$$\Delta S = R\ \ln(V_2/V_1)$$

From this equation, if V_2 is greater than V_1, V_2/V_1 will be greater than 1 and $\ln(V_2/V_1)$ (and consequently ΔS) will be positive. If $V_1 = V_2$, then $V_2/V_1 = 1$ and $\ln(V_2/V_1)$ (and consequently ΔS) will be zero. If V_2 is less than V_1, then V_2/V_1 will be less than 1 and $\ln(V_2/V_1)$ (and consequently ΔS) will be negative.

In the real world, a gas in an isolated system at constant temperature always expands to fill

the maximum volume available. This corresponds to an increase in entropy. The process whereby a gas at constant temperature spontaneously collects in a small volume of such a system leaving the rest of the system empty has never been reported. Such a process would correspond to a decrease in the entropy of an isolated system.

B. Transfer of Heat between Two Objects at Different Temperatures

Suppose that an isolated system contains two separate objects, one of which is at a temperature T_1 and the other is at some different temperature T_2. Now suppose that by some unspecified process a very small quantity of heat dq is transferred from the object of temperature T_1 to the object of temperature T_2. The change in entropy of the first object is $-dq/T_1$ (negative, because heat is lost from the object) while the change in entropy of the second object is dq/T_2 (positive, because heat is absorbed by the object). The change in entropy for the whole system is the sum of the individual changes, that is, $dq/T_2 - dq/T_1 = dq\,(1/T_2 - 1/T_1)$. If T_2 is smaller than T_1, then $1/T_2$ will be greater than $1/T_1$ and the entropy change will be positive. If T_2 equals T_1, the entropy change will be zero. If T_2 is greater than T_1, the entropy change for the process will be negative.

Comparing these results to what happens in the real world, one sees again that in an isolated system *the process that results in an increase in entropy happens spontaneously*. Put an object in contact with one at a lower temperature, and energy will be transferred as heat from the object at the higher temperature to that at the lower temperature. If the temperature of the two objects is the same, then they are by definition in thermal equilibrium. If a minute quantity of heat is transferred reversibly from one object to the other, the entropy change is zero. The process for which the entropy change is negative, namely the transfer of heat from an object at a lower temperature to one at a higher temperature, never happens spontaneously in an isolated system. If such a process is to occur, external work must be done to transfer the heat. This is what happens in a refrigerator, where the net effect of the work being done by the

electric motor is to cool the inside of the refrigerator and make the air outside warmer.

The Second Law Restated

The statement that "in isolated systems, processes for which the entropy change is negative are not spontaneous" is yet another form of the **Second Law of Thermodynamics.** Perhaps the most general statement of the Second Law is that "the entropy of the Universe increases". In this instance, where the word "Universe" has a capital letter, the meaning is the conventional one: *everything there is*. This is very different from the thermodynamic meaning of the word "universe" (no capital). As indicated earlier, a thermodynamic "universe" is simply the system of interest plus its surroundings, assumed to be totally isolated from external influences.

The statement of the Second Law with reference to the Universe indicates that there is an inevitable progression in time towards a state of higher entropy *for the Universe as a whole*. When one sees a movie being played backwards, one sees a world in which the entropy of the Universe is decreasing with time. Some processes, such as the swinging of a pendulum, do not look any different. Other processes, such as the dropping of a glass of water onto the floor, look remarkably different. Randomly scattered globs of water and shards of glass miraculously re-assemble themselves into a glass of water. Why, one might ask, is that such an amazing process? Why has such an event never been reported in the entire known history of the human race? After all, on the molecular level all that has to happen is for the molecular motions that took place when the glass was shattered and the water scattered to be precisely reversed. Having stated that, it is immediately obvious why such a process would be amazing. It is not that such an event is impossible. It is just wildly improbable. Of all the ways that the molecules making up a smashed glass of water have of arranging themselves, very, very few correspond to the multitude of successive re-arrangements that would have to take place to re-assemble the glass.

The Driving Force of Change

The Second Law of Thermodynamics states that for a spontaneous process, the entropy of the system and its surroundings must increase. In other words, ΔS *for the system and its surroundings* must be positive. Suppose a process takes place in a system for which the entropy change *in the system* is ΔS_{system} and the enthalpy change is ΔH_{system}

The heat evolved or absorbed by the system in the enthalpy change ΔH_{system} obviously goes into, or comes from, the *surroundings*. This heat will be absorbed (or lost) by the surroundings at a temperature T and the *entropy of the surroundings* will change by an amount $(-\Delta H_{system}/T)$. The negative sign is there because heat *emitted* by the system is *absorbed* by the surroundings.

The total entropy change for the system plus the surroundings is thus

$$\Delta S_{system + surroundings} = \Delta S_{system} - \Delta H_{system}/T$$

This equation gives *the total entropy change for the system and surroundings in terms of changes in thermodynamic properties of the system alone*. This is very important because it provides a way of finding out whether or not a particular process will be spontaneous, using only the calculated changes in the entropy and enthalpy *of the system*.

For a process to be spontaneous, the total entropy change must to be positive. Now, ΔS_{system} and ΔH_{system} can be either positive or negative, but the temperature T is always positive. Multiplying the equation by T,

$$T\Delta S_{system + surroundings} = T\Delta S_{system} - \Delta H_{system}$$

Again, a process will be spontaneous if this quantity is positive or, equivalently, if the quantity $\Delta H - T\Delta S$ is *negative*.

Another State Function: the Gibbs Free Energy

The quantity $\Delta H - T\Delta S$ has the units of energy. Recall that ΔH represents the energy available after allowance has been made for the work $(P\Delta V)$ done in volume changes at constant pressure. The quantity $T\Delta S$ can be thought of as the energy that has been dispersed as random molecular motion and is therefore unavailable to do useful work. The remaining energy, $\Delta H - T\Delta S$, is referred to as the *free energy*, because it is available to perform useful work. The free energy is of such great importance that it is convenient to define a new quantity $G = H - TS$ for which, at constant temperature, (from the definition of Δ)

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

Notice that this quantity G, being made up of the state functions H, T and S, is itself a state function. That is to say, changes in its value depend only on the state of the system before and after a process, and are independent of any intermediate states that the system might have assumed during the process. This new state function is called the **Gibbs Free Energy** (after J. Willard Gibbs).[2b]

This, at last, is the state function that can be used to predict the direction of change in a chemical system.

At equilibrium, the Gibbs Free Energy of the reactants will equal the Gibbs Free Energy of the products. If the Gibbs Free Energy change (ΔG) for a process is *negative*, the *entropy change for the universe will be positive*, and the process will be thermodynamically spontaneous.

The sign of ΔG indicates only whether or not the process will be spontaneous. It does *not* indicate whether the transfer of energy during the process will be from the system to the surroundings, or in the opposite direction. That information is given by the sign of the *enthalpy* change, ΔH, as explained in the first article in this series.[1] A process with a negative ΔG may result in the spontaneous transfer of energy *from the system to the surroundings* (i.e., ΔH is negative). Examples of such a process include the freezing of water in the freezer compartment of a refrigerator, and the combustion of magnesium in a burning pyrotechnic composition. On the other hand, a process having a negative ΔG might well result in the spontaneous transfer of energy *from the surroundings to the system* (i.e., ΔH is positive). Examples of such a process include the melting of ice in a

glass of water, and the decomposition of strontium carbonate in a burning red star.

The Third Law

The entropy of a system, as noted previously, is a measure of the number of molecular arrangements that are consistent with the properties of the system.

Recall that the relationship between the entropy S of a system and the number W of molecular arrangements consistent with the properties of the system was shown by Boltzmann[3c] to be

$S = k \ln W$

This relationship means that the entropy of a system that is consistent with only *one* arrangement of its molecules will be zero, because for such a system $W = 1$ and the natural logarithm of 1 is zero. In other words, Boltzmann's equation implies that *the entropy of a perfectly ordered system is zero.*

If this is correct, then the entropy of a perfect crystalline solid should approach zero as the temperature approaches absolute zero. This trend has been demonstrated experimentally by measurements of heat capacities at very low temperatures.[6] The statement that "the entropy of a perfect crystalline solid is zero at the absolute zero of temperature" is one form of the **Third Law of Thermodynamics**. The importance of this law is that it allows an absolute value to be assigned to the **molar entropy** of a substance. The molar entropy is calculated from heat capacity measurements, starting from zero at 0 K. For example, the molar entropy of a gas at room temperature would include contributions from the heat capacity of one mole of the solid from 0 K to the melting point, including any heat absorbed in any changes between different crystalline states. It would also include the latent heat of fusion of the solid, the heat capacity of the liquid from the melting point to the boiling point, the latent heat of vaporization and the heat capacity of the gas from the boiling point to room temperature. At each stage the entropy would by calculated from $dS = dq/T$ and the total molar entropy would be obtained by summing all these increments dS.

What Next?

The next article in this series will show how the Gibbs Free Energy varies with temperature and pressure, and how this affects chemical equilibrium. It will also show that a number of useful facts about chemical systems can be predicted from the thermodynamic properties of the reactants and possible products. This will be illustrated with examples from pyrotechnics.

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Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 4. Firework Compositions and Investigation of the Sulfur/Chlorate Initiation Reaction

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ABSTRACT

Fireworks formulations were modified to produce compositions containing sulfur/chlorate mixtures, and their thermal stability and mechanical sensitiveness were studied. The results indicate that the presence of sulfur/chlorate mixtures in fireworks compositions reduces the ignition temperatures to values well below those obtained with compositions that do not contain the sulfur/chlorate mixture and generally increases the sensitiveness (this was particularly marked in iron-containing mixtures).

The sulfur/chlorate initiation reaction was examined and the mixture was shown to produce sulfur dioxide on heating. Once formed, the sulfur dioxide quickly causes potassium chlorate to decompose and pyrotechnic mixtures containing potassium chlorate to ignite.

Keywords: chlorate, sulfur, sensitiveness, thermal stability, ignition temperature

Introduction

Previous papers in this series have reported thermal stability and sensitiveness studies on sulfur/chlorate mixtures and the effect of the presence of a third component in the mixtures.[1,2] Part four deals with the effect of sulfur/chlorate in a range of fireworks compositions that were modified to produce this mixture.

Several fireworks compositions were identified[3] as containing either sulfur (Table 1) or potassium chlorate (Table 2). By introducing potassium chlorate into a sulfur-containing composition or *vice versa,* it was possible to investigate the effect of the presence of sulfur/chlorate in mixtures similar to fireworks compositions. This produced a series of mixtures: based on Black Powder containing potassium nitrate and from 3 to 21% charcoal, a flash composition containing potassium perchlorate, and chlorate stars each of which had been modified to contain a sulfur/chlorate mixture.

The effect of contamination of the potassium chlorate was investigated by the inclusion of other salts whose chlorates have been identified[4–6] as being less stable than potassium chlorate.

Table 1. Fireworks Compositions that Contain Sulfur.

	Composition (% by mass)					
Component	Rocket	Gerb	Golden Streamers	Tourbillion	Flash-cracker	Pinwheel
Potassium nitrate	68	57	53	36	—	60
Potassium perchlorate	—	—	—	—	50	—
Charcoal (30–100 mesh)	21	10	3	9	—	20
Sulfur	11	10	14	9	25	10
Aluminium (200 mesh)	—	—	—	—	25	—
Meal powder	—	—	—	32	—	10
Iron filings (fine, untreated)	—	23	—	14	—	—
Dextrin	—	—	3	—	—	—
Sodium oxalate	—	—	27	—	—	—

Table 2. Fireworks Compositions That Contain Potassium Chlorate.

	Composition (% by Mass)	
Component	Red Star	Green Star
Strontium nitrate	38.7	—
Barium nitrate	—	38.7
Potassium chlorate	38.7	38.7
Charcoal	12.9	12.9
Dextrin	3.2	3.2
Shellac	6.5	6.5

Experimental

Flowers of sulfur and AnalaR potassium chlorate were used throughout this series of testing. The charcoal was provided by a UK fireworks manufacturer. The other components were purchased from chemical suppliers and were standard laboratory grade. Prior to use, individual materials were ground and sieved to produce a powder passing through a 125 μm sieve.

Loose Compositions

Loose compositions (2 g) were prepared by weighing and mixing. Thermal stability and sensitiveness testing of the compositions was carried out as previously reported.[1]

Pressed Compositions

Star compositions were additionally investigated as pressed material using a hand-operated pill press. Dry compositions were pressed into two 1 g pellets. Wet compositions had the minimum amount of water/ethanol (50:50) added to form a paste and were then pressed to form 1 g pellets. These were allowed to air dry before being tested. Two 1 g pellets with a thermocouple between them were placed into a cardboard fireworks tube and subjected to heating at 5 °C hr^{-1}.

Compositions Prepared from Co-Precipitated Potassium Chlorate

Wet compositions containing sulfur/chlorate mixtures were prepared, dried and tested to investigate the effect of contamination of potassium chlorate. Similarly, co-precipitated materials were prepared by dissolving potassium chlorate (15 g) and the salt under investigation (2–4 g) in 50 cm^3 of hot water and pouring the solution into 200 cm^3 of acetone to precipitate the salts.

Mass Spectrometer Investigation of Sulfur/Chlorate Pre-Ignition Reaction

A sulfur/chlorate mixture (2 mg, 30% S) was heated at 5 °C min^{-1} in an atmosphere of helium/argon (225 ppm Ar) to just below the ignition temperature (155 °C) determined by differ-

Table 3. Ignition Temperature (°C) of Sulfur-Containing Fireworks Compositions with Added Potassium Chlorate.

Composition	Average Ignition Temperature (°C) for % by Mass of Potassium Chlorate				
	0%	5%	10%	15%	20%
Rocket	>200	142	132	127	123
Gerb	>200	134 exo	120	118	116
Golden Streamers	>200	137 exo	123	117	116
Tourbillion	>200	147	137	133	125
Flash-cracker	>200	119 exo	120	117	115
Pinwheel	>200	157	152	144	136

Note: "exo" means a non-ignition exotherm.

ential scanning calorimetry for a similar 2 mg sample (155 °C). The evolved gases were investigated by mass spectrometry (70 eV ionisation energy) and a time profile generated for the evolved products.

Sulfur Dioxide Activated Reactions

Mixtures containing sulfur/chlorate (2 g) were heated in cardboard fireworks tubes placed in a metal block, and sulfur dioxide was passed through. Times to ignition were measured.

Results

The Thermal Stability of Sulfur-Containing Fireworks Compositions Modified To Contain Sulfur/Chlorate

Fireworks compositions listed in Table 1 were modified by replacing part of the oxidiser with potassium chlorate and were then subjected to slow heating (5 °C hr^{-1}). For most compositions, the ignition temperature was lower with increased potassium chlorate and all compositions ignited when there was 10% potassium chlorate. At 5% chlorate both non-ignition exotherms (noted as "exo" in Table 3) and ignitions were recorded. Table 3 summarises the results.

The Thermal Stability of Chlorate-Containing Fireworks Compositions Modified To Contain Sulfur/Chlorate

The compositions containing potassium chlorate listed in Table 2 were modified by the addition of sulfur and similar tests were performed. The results are reported in Table 4.

Table 4. Ignition Temperature (°C) of Potassium Chlorate-Containing Fireworks Compositions with Added Sulfur.

Composition	Processing		Ignition Temperature (°C) for Quantity of Added Sulfur	
			0%	5%
Red Star	loose	dry processed	>200	163
	pressed	dry processed	>200	152
	pressed	wet processed	>200	148
Green Star	loose	dry processed	>200	159
	pressed	dry processed	>200	152
	pressed	wet processed	>200	152

Table 5. Impact and Friction Sensitiveness of Sulfur-Containing Fireworks Compositions with Added Potassium Chlorate.

Composition	Impact Sensitiveness Limiting Impact Energy (J) for Quantity of Potassium Chlorate			Friction Sensitiveness Limiting Load (N) for Quantity of Potassium Chlorate		
	0%	10%	20%	0%	10%	20%
Rocket	20	15	15	>360	120	40
Gerb	20	>30	≤1	>360	>360	240
Golden Streamers	40	25	30	>360	>360	240
Tourbillion	25	25	2	>360	>360	160
Flash-cracker	7.5	10	25	40	60	40
Pinwheel	30	25	40	>360	>360	360

Table 6. Impact and Friction Sensitiveness of Potassium Chlorate-Containing Fireworks Compositions with Added Sulfur.

Composition	Impact Sensitiveness Limiting Impact Energy (J) for Quantity of Sulfur		Friction Sensitiveness Limiting Load (N) for Quantity of Sulfur	
	0%	5%	0%	5%
Red Star	30	40	360	60
Green Star	50	35	240	60

The Sensitiveness of Fireworks Compositions Modified To Contain Sulfur/Chlorate Compositions

The modified fireworks compositions were also subjected to mechanical sensitiveness testing and the results are reported in Tables 5 and 6. In general, the sulfur-containing fireworks composition became more sensitive (lower limiting loads) as the chlorate proportion by mass increased. Similarly, as sulfur was added (5% by mass) there was a corresponding increase in the sensitivity of the chlorate-containing compositions.

The Effects of Wet Processing of Compositions Containing Sulfur/Chlorate Mixtures

Fireworks composition may be processed in a wet state. To investigate the effect this may have on ignition temperature, a range of materials was added to a sulfur/chlorate mixture (5% sulfur) to replace part of the potassium chlorate. Table 7 lists the ignition temperatures for these mixtures after undergoing wet processing followed by air-drying.

Table 7. The Effect of Wet Mixed Additives on the Ignition Temperature of Sulfur/Chlorate Mixtures.

Additive	Average Ignition Temperature (°C) for % by Mass Additive		
	0%	20%	40%
Potassium nitrate	116	114	126
Barium nitrate	116	115	118
Calcium carbonate	115	115	115
Copper(II) chloride	115	113	114

Table 8. The Effect of Co-Precipitation of Additives with Potassium Chlorate on the Ignition Temperature of Sulfur/Chlorate Mixtures.

Precipitated Material	Average Ignition Temperature (°C) for % by Mass Sulfur	
	5% Sulfur	30% Sulfur
Potassium chlorate	114	110
Potassium chlorate/barium nitrate	99	89
Potassium chlorate/strontium nitrate	91	94
Potassium chlorate/copper(II) chloride	100	98

Thermal Stability of Sulfur/Chlorate Compositions Prepared from Co-Precipitated Potassium Chlorate

A limited number of salts were co-precipitated with potassium chlorate to give a low (but unknown) proportion of the salt in the precipitate. A similarly treated sample of potassium chlorate was also prepared and the materials were formulated into sulfur/chlorate mixtures for use in slow heating experiments. Table 8 lists the ignition temperatures of the resulting sulfur/chlorate mixtures.

Mass Spectrometry Study of the Sulfur/Chlorate Initiation Reaction

A sulfur/chlorate mixture (30:70 flowers of sulfur/AnalaR potassium chlorate), when heated to below the ignition temperature, evolved gases with mass per unit charge (m/e) ratios of 16 (O), 32 (S or O_2), 48 (SO or O_3), 64 (SO_2 or possibly S_2) and 80 (SO_3). Figure 1 illustrates the relative abundance of these ions in a typical mass spectrum from the evolved gas.

Evolution of the gas started at approximately 100 °C and reached a maximum at about 150 °C. Figure 2 illustrates the evolution of the two components of interest (m/e 64 and m/e 80) from the evolved gas (the m/e 64 trace has been scaled to fit).
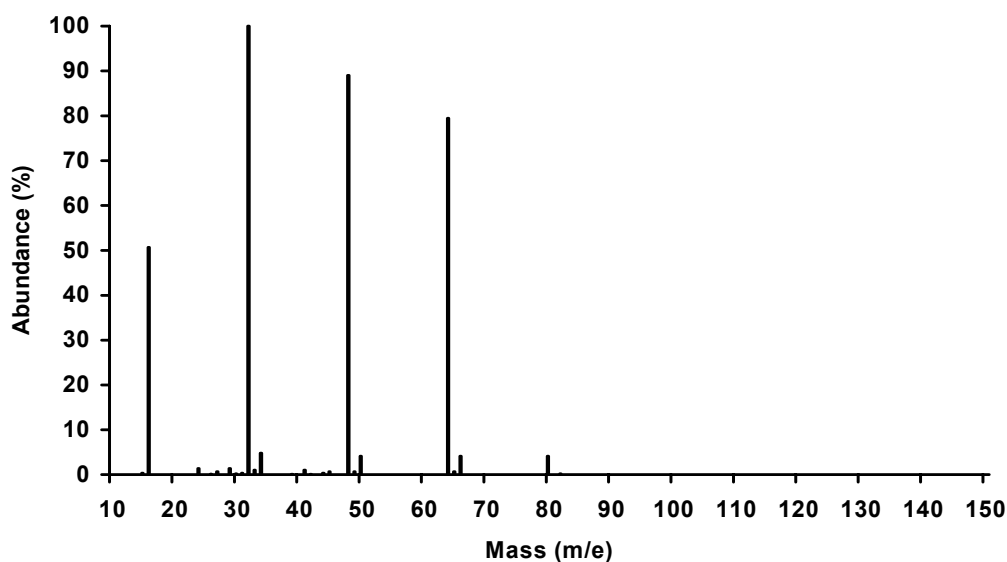

Figure 1. Mass spectrum of gas evolved during thermal reaction of sulfur with potassium chlorate at temperatures below the ignition point.
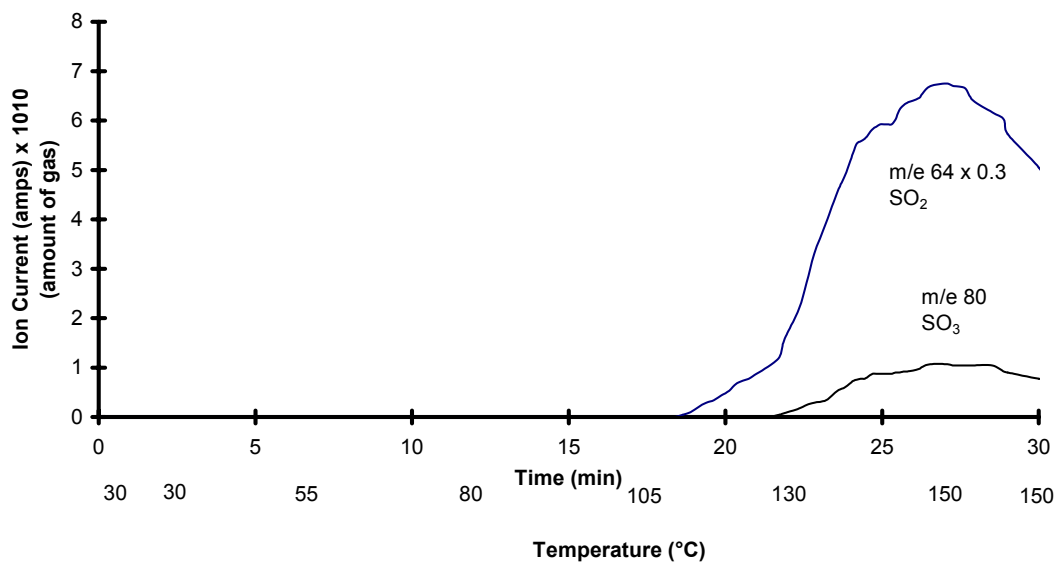
Figure 2. Evolved gas profile for primary gases from heating flowers of sulfur/AnalaR potassium chlorate. Note that the m/e 64 curve was scaled down by a factor of 30% to fit on the chart.

The Effect of Sulfur Dioxide on Sulfur/Chlorate Initiation

The effect of evolved sulfur dioxide on the reactivity of sulfur/chlorate mixtures was examined by passing sulfur dioxide through heated samples. All compositions were ignited at considerably lower temperatures than had occurred without the addition of sulfur dioxide. Table 9 summarises the effects observed.

Table 9. Effect of Passing Sulfur Dioxide through Potassium Chlorate and Mixtures Containing Sulfur/Chlorate.

Composition	Temperature (°C)	Observation
100% AnalaR KClO₃	80	immediate exotherm, decomposition after 290 s
	70	immediate exotherm, decomposition after 140 s
	60	immediate exotherm, no decomposition up to 900 s
30% Flowers of Sulfur 70% AnalaR KClO₃	80	immediate exotherm, ignition after 115 s
	70	immediate exotherm, ignition after 160 s
	60	immediate exotherm, ignition after 155 s
	50	immediate exotherm, ignition after 300 s
	40	immediate exotherm, ignition after 960 s
Rocket composition * (20% KClO₃)	80	immediate exotherm, ignition after 74 s
	70	immediate exotherm, ignition after 150 s
	60	immediate exotherm, ignition after 180 s
	50	immediate exotherm, ignition after 240 s
Gerb Composition* (20% KClO₃)	70	immediate exotherm, sample exploded violently, cardboard tube destroyed, time not recorded

* See Table 1 for basic composition.

Discussion

Thermal Stability of Fireworks Compositions Modified To Contain Sulfur/Chlorate

In recent years, a number of fireworks compositions in the UK have been found to contain sulfur/chlorate mixtures. To investigate the effect of the presence of this mixture in fireworks, a series of compositions was modified to produce the sulfur/chlorate mixture. No ignitions were observed below 200 °C in compositions that did not contain a sulfur/chlorate mixture. (This was the highest temperature attainable in the heater blocks used.) Several of the compositions were based on Black Powder, which is reported to have an ignition temperature of approximately 350 °C, while the ignition temperature of flash and star compositions may be considerably higher.[7] The addition of potassium chlorate to a sulfur-containing composition produced a significant reduction in the ignition temperature. When 20% of the normal oxidizer had been replaced by potassium chlorate, the ignition temperatures were similar to those of sulfur/chlorate mixtures alone. Those compositions with the largest amount of charcoal (rocket 21%, pinwheel 20%, and tourbillion 9% plus 32 % meal powder, Table 1) required larger amounts of potassium chlorate to achieve similar low ignition temperatures. Conversely, the flash-cracker composition, with no charcoal, was the most affected by the addition of chlorate. The added stability of charcoal-containing mixtures has been previously identified[2] and is probably due to the ability of charcoal to absorb gaseous material.

Sensitiveness of Fireworks Compositions Modified To Contain Sulfur/Chlorate

A similar trend was observed in sensitiveness testing. The addition of potassium chlorate reduced the values of the limiting impact energies and limiting loads, indicating that the materials were more sensitive. Impact energies equivalent to a mixture that is too sensitive to transport (≤ 2 J)[8] were found when iron was present as a component in a composition containing sulfur/chlorate. Similar sensitisation of

fireworks compositions by hard metallic particles has been reported.[9]

Thermal Stability of Wet Processed Compositions and Compositions Prepared from Co-Precipitated Potassium Chlorate

Wet processed materials (Table 7) had similar ignition temperatures to those previously reported for dry processed samples.[2] However, when co-precipitation of potassium chlorate was carried out with salts likely to form less stable chlorates, significant lowering of the ignition temperatures was observed. Group II chlorates such as barium and strontium were cited by Amiel[4,6] as being much less stable than potassium chlorate when in the presence of sulfur (and other Group VI elements). Copper salts doped into the potassium chlorate lattice are identified by McLain[10a] as causing room temperature detonations of sulfur/chlorate mixtures.

Mass Spectrometry Study of the Sulfur/Chlorate Initiation Reaction

When small samples of sulfur/chlorate were heated in an inert atmosphere, a gas with m/e 64 was generated at temperatures above 100 °C. This corresponds to the m/e ratio for sulfur dioxide or the S_2 fragment. The main sulfur isotopes are 32 (95.0%) and 34 (4.2%) atomic mass units, and an S_2 molecule would be expected to show peaks at 64, 66 and 68 atomic mass units (M, M+2, and M+4). As there are M+2 but no M+4 peaks, the species with m/e 64 is sulfur dioxide. Additionally, at temperatures below the sulfur melting point (119 °C),[11] it is unlikely that S_2 fragments would be generated. Above the melting point there would be an increased possibility of S_2 fragments contributing to the m/e 64 signal. However, it is not until temperatures well above those investigated (ca 2200 °C)[11] that the S_2 fragment is the predominant sulfur species. Additionally, a gas with m/e ratio of 80 is generated slightly later. This corresponds to sulfur trioxide rather than to any sulfur fragment m/e ratio. Other major peaks can be attributed to breakdown products of sulfur dioxide and sulfur trioxide: m/e 48 SO, m/e 32 S, both of which show M+2 peaks, and m/e 16 O. Other species, which were con-

sidered as possibilities, [ClO_2 (m/e 67 and 69), Cl_2O (m/e 102, 104 and 106) and $SOCl_2$ (m/e 134, 136 and 138)] were not observed during the course of thermolysis.

The Effect of Sulfur Dioxide on Sulfur/Chlorate Initiation

Mechanisms for the initiation of sulfur/chlorate mixtures, as reported by Tanner,[12] suggest that it is the production of sulfur dioxide from some source that initiates the reaction:

$$SO_2 + 2\,KClO_3 + 4\,S \rightarrow$$
$$2\,SO_2 + S_2Cl_2 + K_2SO_4$$
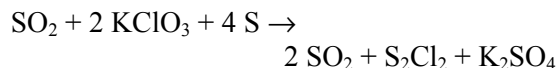
A mechanism was proposed by Rudloff[13] in which sulfur vapour reacts with potassium chlorate to generate sulfur dioxide:

$$2\,KClO_3 + S \rightarrow KClO_4 + KCl + SO_2$$

The only gaseous product of this reaction is the sulfur dioxide and therefore no chlorine-containing species would be detected in the mass spectrum as was observed in the test results. Much of the low temperature (i.e., solid state) reactivity of potassium chlorate is attributed to the low (42 °C) Tammann temperature.[14] At this temperature there is significant lattice diffusion,[10b] which would allow sulfur to migrate into the lattice and be oxidised. At low temperatures this will be a slow process and, if sufficient heat were lost, would not generate an ignition. As the temperature rises and approaches the 119 °C sulfur melting temperature, this diffusion process would accelerate and lead to an ignition. The presence of extraneous sulfur dioxide would short-circuit the initiation and produce a very low temperature, almost instantaneous, ignition. Probably the worst case would be a slow initiation with sufficient material to insulate and retain heat. This could in time lead to an ignition as the processes accelerates through self-heating.

Once sulfur dioxide has been formed, there is an exothermic reaction with potassium chlorate. Decomposition of the material was recorded at temperatures as low as 70 °C. When sulfur was also present, this was reduced to 40 °C with ignition of the mixture occurring. Similar reactions were reported for sulfur/chlorate mixtures by Storey.[15] When a rocket composition—modified to contain sulfur/chlorate—was similarly treated, a low ignition temperature was observed. However, when the composition additionally contained iron, a much more vigorous and rapid reaction resulted. We have not investigated the processes involved in causing the greater violence of the reaction but report it here as a safety warning to others who may wish to investigate these reactions further.

Conclusions

Sulfur/chlorate-containing mixtures are more likely to be initiated by accidental stimulus (friction and impact) than similar mixtures that do not contain both components. Similarly, they have considerably lower ignition temperatures than other compositions commonly found in fireworks. As such, sulfur/chlorate-containing compositions pose a greater hazard than other fireworks compositions that do not contain both components. As there are suitable compositions that do not pose these added hazards,[16] it is suggested that they are best avoided.

Acknowledgements

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Practical Applications of Capillary Extrusion Rheometry to Problems in the Processing of Energetic Materials

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ABSTRACT

Energetic materials are manufactured by processes involving flow, often under conditions of elevated temperature and pressure. Such processes include extrusion, casting and pressing. If the manner in which the material flows under these conditions is not well understood, production and quality problems may result.

A capillary extrusion rheometer is essentially a laboratory-scale extrusion press that is highly instrumented and accurately controlled. As such, it provides an ideal tool for studying and quantifying the properties of the materials as they flow under conditions likely to be encountered in practice. Additionally, the extruded output from the instrument may be subjected to further testing such as for mechanical and ballistic properties to relate changes in processing conditions to product properties.

Keywords: processing, extrusion, filling, analysis, rheology, rheometry, flow, viscosity

Introduction

Working at the United Kingdom's Propellants, Explosives and Rocket Motor Establishment in the 1970's and 1980's, Carter and Baker[1,2] designed and built a laboratory to study the flow properties, or rheology, of filled nitrocellulose/nitroglycerine (Cordite) gun propellants. Attempts to modify the solvent-wet production process by changing solvent types resulted in instabilities ("Twiglets") during extrusion of the solvent-wet doughs. Detailed and systematic studies of the effects of changes in process parameters and formulation on the rheology and the mechanical and ballistic properties allowed short-term manufacturing difficulties to be resolved. In the longer term, this permitted new processing technology to be designed with a high degree of confidence around the materials' processing requirements.

In the fullness of time, the facility was used to study many types of energetic material, including solventless double-base propellants, plastic explosives and propellants, and pyrotechnic binders.

In this paper, some of the many parameters that may be deduced with the aid of a capillary extrusion rheometer will be defined, and the relevance of these parameters to practical processing issues discussed.

Equipment

A capillary extrusion rheometer is, in essence, a laboratory-scale, ram-operated, vertically oriented extruder; see Figure 1. It has a barrel with an accurately honed bore in which the temperature can be accurately controlled, typically to better than ±0.5 °C. An orifice or extrusion die of precisely known geometry is fastened at the lower end of the barrel, and the barrel is filled with the test specimen. A closely fitting piston is driven down the barrel at a series of constant speeds. The equilibrium pressure required to extrude the material through the die at that speed is recorded via a pressure transducer. Various dies with different diameters, bore lengths, and entrance angles are used to investigate the flow properties of the sample to eliminate geometrical effects. Several ranges of pressure transducers are usually used to optimise the precision of
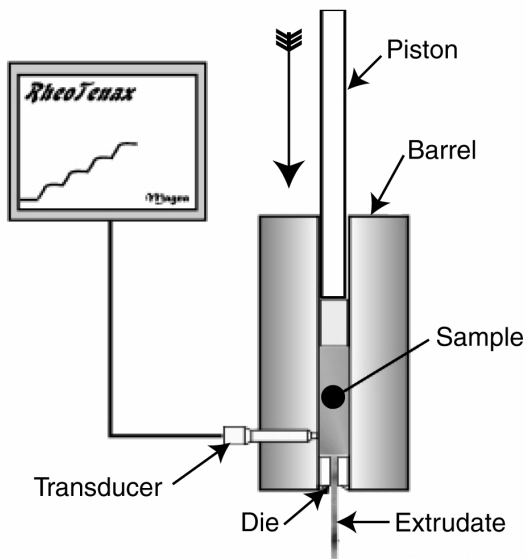
Figure 1. Diagram of a capillary extrusion rheometer.

measurement under a particular set of operating conditions.

Other Devices That Enable Additional Analyses

A slit die is a die of rectangular profile fitted along its length with three or four flush-mounted pressure transducers. It may be used directly to obtain corrected flow data and allow the investigation of some viscoelastic parameters. The pressure coefficient of viscosity,[3] is an important, yet much-overlooked, parameter describing how the viscosity of a material changes with hydrostatic pressure. This parameter may be measured using a tandem-die technique as shown in Figure 2. With this instrument, the pressure drop across the upper die is measured with the two-melt pressure transducers. Several runs are carried out with different geometries of the lower die to develop a range of hydrostatic pressures in the intervening chamber.

Several devices exist for examining the condition of the extruded material immediately after it leaves the die. Optical equipment can measure the diameter and detect any expansion due to elastic effects ("die swell"). Other optical devices can measure the surface temperature of the extrudate to detect an increase in temperature caused by frictional heating during passage through the die.

The specimen, extruded under a range of controlled conditions, may then be examined by other techniques to establish the relationships between raw material, formulation, process parameters and the properties of the final product. Such techniques include dynamic mechanical analysis and dynamic thermomechanical analysis (DMA/DMTA), thermomechanical analysis
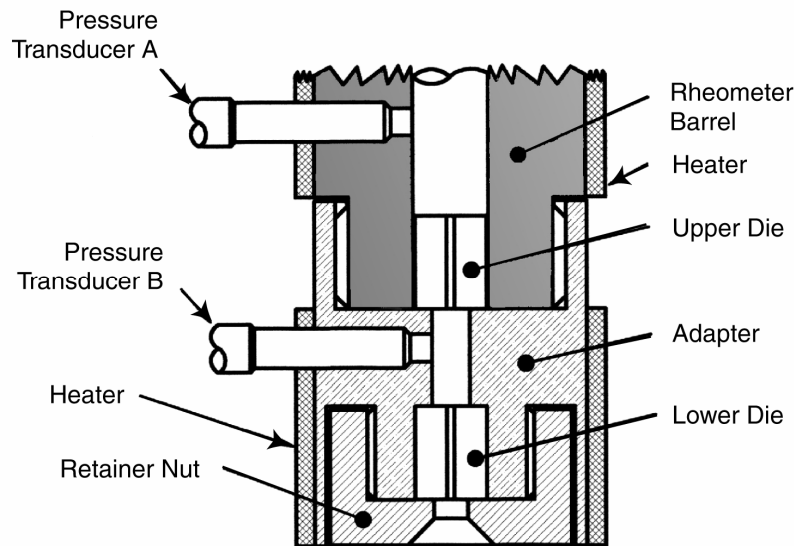

Figure 2. Diagram of a rheometer with tandem dies showing an adaptor for measuring the pressure coefficient of viscosity.
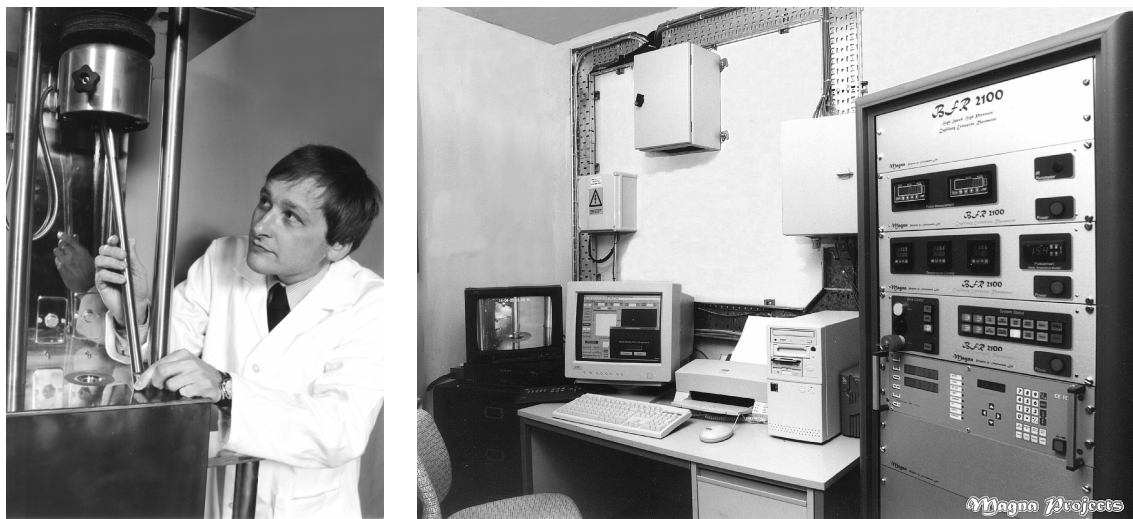
Figure 3. BFR 2100 capillary extrusion rheometer for energetic materials: (left) extrusion head; (right) remote control console.

(TMA), differential scanning calorimetry (DSC), optical and electron microscopy, tensile testing, and many others.

To use the technique safely with energetic materials, the design of the capillary extrusion rheometer must be modified to minimise the risk of danger to the operator and to the equipment: Blind holes and cracks should be removed. Materials that are likely to react with the energetic materials must be replaced. Electrics and electronics should be sealed or the signals routed through intrinsic-safety barriers. Preferably, the instrument should be fully remote controlled, with observation of the extrusion head on closed-circuit television (CCTV). Such an instrument, the BFR 2100, shown in Figure 3, has recently been installed by Magna Projects at a major UK defence R & D laboratory.

Interpretation of Data

In shear flow, materials tend to flow in one of several different ways. See Figure 4. An ideal or Newtonian material shows a linear relationship between shear rate (proportional to piston speed) and shear stress (proportional to pressure). The slope of the line is by definition the viscosity. However, apart from water, very few materials exhibit such ideal behaviour. Many common industrial materials, such as polymer melts, show *pseudoplastic* or *shear-*

thinning behaviour. Here, as the shear rate is increased, proportionately less pressure is required to maintain extrusion at that rate. This can be beneficial in industrial processes. On the other hand, some materials—especially those such as pastes containing high filler levels—can exhibit *dilatant* or *shear thickening* behaviour. With such materials, die and tool design is crucial and process monitoring and control is vital as sudden increases in pressure can occur. Some normally pseudoplastic materials can switch to dilatant behaviour at high pressures. Polypropylene and polycarbonate, for example, can stress-crystallize, and some filled materials "bridge". With energetic materials, such a sud-
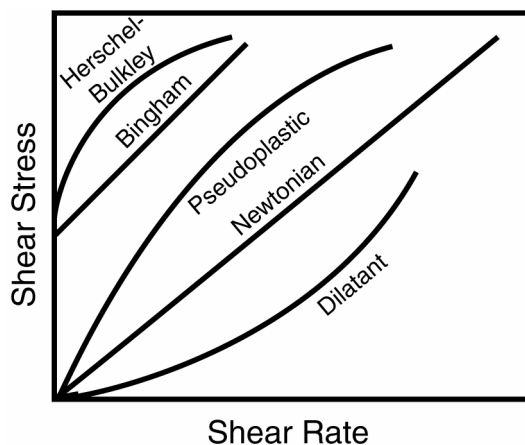

Figure 4. Types of shear flow behaviour.

den increase in pressure can be extremely dangerous.

Some materials will not start to flow (within the experimental timescale) until a *yield stress* has been exceeded. Those that flow in a linear manner after yielding are termed *Bingham Fluids*, an example of which is wet cement paste. Some fluids, such as doughs, flow in a pseudo-plastic manner after yielding, and these are termed Herschel-Bulkley Fluids. Carter, Baker and Warren[1,2,4] found that, for solvent-processed Cordite doughs, yield stresses of significant magnitude were present and were necessary for the extruded profile to maintain its shape until the process solvent was removed. In one case, the yield stress was found to be high enough to exceed the tensile strength of the central pin of a small tubular profile die causing it to snap, with subsequent product being produced without the hole; the problem was resolved by redesigning the die with a shorter pin. Indeed, in those studies, it was found that the logarithmic flow curve, Figure 5, was S-shaped. After much work, it was discovered that the non-linearity at lower shear rates was due to the presence of a yield stress, and that the non-

linearity at higher shear rates was due to frictional heating as the material passed through the die. In some cases, the magnitude of the temperature increase was sufficient to boil the processing solvent. This discovery solved a manufacturing problem that had been thought to be due to air inclusion but was shown by rheological studies to be due to the solvent boiling at high pressure. The problem was overcome by redesigning the extrusion die.

The temperature dependence of the various flow parameters may be measured easily with the capillary extrusion rheometer system. In one study, it was found that a change of filler from a needle-shaped crystal to a spherical crystal resulted in a profound increase in the temperature sensitivity of viscosity, necessitating a major increase in process control at the factory. In another study, it was found that the yield stress of a formulation went through a minimum as the temperature increased and then it increased again as the temperature continued to rise. This explained why processing problems with this material were experienced at the higher temperatures.
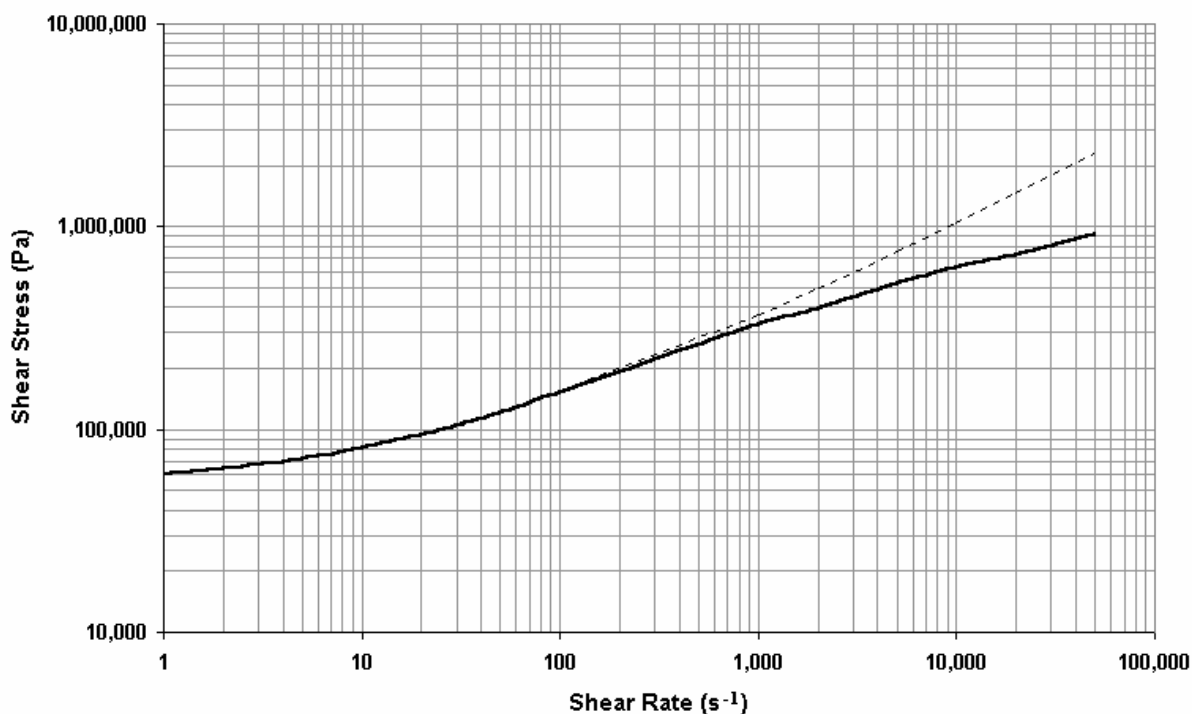

Figure 5. *Typical flow curve for nitrocellulose/nitroglycerine (Cordite) gun propellant dough.*

Another rheological phenomenon that may be detected and quantified with capillary extrusion rheometry is *wall slip*. This is caused by the extruding material ceasing to adhere to the die wall, giving a discontinuity in the flow curve at a critical shear stress. This can be caused by a low-molecular weight component such as a solvent or plasticizer layer acting as a lubricant, or by a pressure-induced filler-enriched layer appearing close to the die wall. The mere presence of this effect is sufficient to rule out the use of processing techniques such as single-screw extrusion that relies upon the adhesion of the material to the screw and to the extruder barrel, and to explain the inefficiency of the batch-mixing machines, which had hitherto been used. Based on their rheological research in the 1980's, the team at Waltham Abbey selected the co-rotating twin-screw extruder for processing energetic materials. The twin-screw extruder acts as a positive pump to move material through the barrel rather than relying on surface adhesion. Much work has been carried out since on such machines for processing propellants, plastic explosives and other energetic compositions.

Over the past decade or two, the mathematical understanding of capillary extrusion rheometry has developed such that the extensional properties may be separated from the shear flow properties.[5,6] These properties are important in processes where stretching flows dominate, such as extrusion. Often, materials with similar shear flow behaviour but markedly different extensional properties process in different ways.

Conclusions

Capillary extrusion rheometry provides a powerful and versatile technique for studying the flow behaviour of energetic materials under conditions that are similar to those encountered during processing. Potential hazards may be identified in the safety of the laboratory. Additionally, the method is invaluable for trouble-shooting processing problems and for routine quality assurance work.

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Fixed and Scanning Infrared Radiometers for Combustion Studies

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ABSTRACT

The feasibility of using lead selenide (PbSe) detectors and simple electronic circuitry, including a 600 Hz chopper and chopper frequency/phase reference circuit, to detect infrared emissions from flames and rocket motor plumes was demonstrated. A fixed wavelength radiometer, employing one-inch interference filters and mechanical phase adjustment, was constructed to monitor the 4.4-µm carbon dioxide band and the 2.7-µm water vapor band. The fixed wavelength radiometer was used in flame studies and in several rocket motor tests. The design of the fixed wavelength radiometer was modified to produce a spectroradiometer. The spectroradiometer system included a circular variable filter (CVF) having a wavelength range of 2.1 to 4.7-µm, which allowed wavelength scanning. The circuitry for the spectroradiometer was improved to include a time constant, which could be adjusted electronically, and an electronic phase adjustment. The spectroradiometer was used to monitor numerous rocket motor firings.

The infrared emissions detected by the spectroradiometer included: the water vapor band at 2.7 µm, the hydrogen chloride band at 3.5 µm, and the carbon dioxide band at 4.4 µm.

Keywords: IR radiometer, rocket plume monitoring, PbSe detector, engine health, combustion diagnostics, infrared spectroscopy, IR emission

Introduction

Since World War II, the scientific study of emissions from hot gases has been an increasing area of interest. The earliest research used model systems to simulate jet exhaust.[1] Later investigations dealt mostly with infrared emissions from rocket plumes.[2] A large percentage of infrared rocket plume emission data was collected in the spectral region from one to five micrometers (µm). Two distinct bands occur between these two wavelengths. The first band is centered at 2.7 µm and is attributed to water vapor and an overtone band of carbon dioxide. The other band, centered at 4.4 µm, is much more intense and corresponds to carbon dioxide. Figure 1 shows an infrared spectrum obtained from a Bunsen burner. Both the water vapor and carbon dioxide bands are present.

Equipment currently available for collecting data from rocket plumes is sophisticated, and often includes Fourier Transform Infrared (FTIR) instrumentation or imaging systems. Rapid scanning instrumentation for both spatial and spectral measurements in rocket plumes has been described by various research groups.[3–5] Many of the experiments conducted were primarily spatial in nature, and required the use of liquid nitrogen cooled indium antimonide detectors. These studies provided little, if any, spectral information.

Existing systems are not an economical means for obtaining infrared emission data from rocket ground testing. The expense is especially important when the detection system is used in conjunction with experimental rocket propel-
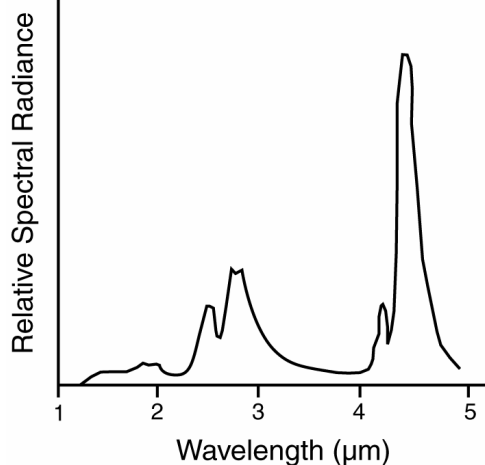
Figure 1. Infrared emission spectrum of a Bunsen burner flame. Peaks in the 2–3 μm region are attributed to water vapor and an overtone band of carbon dioxide. Peaks in the 4–5 μm range are attributed to carbon dioxide.

lants or new rocket motor configurations, which may be prone to catastrophic failure. Typically, these systems are also not portable. Portability is crucial if instrumentation is to be used in the field. The instrumentation described in this paper is very simple and inexpensive. While primarily meant to monitor emissions at a specified wavelength as a function of time, the instrument can also scan the spectrum in the 1–5 μm region. The data obtained from the instrumentation can be used for characterization of rocket propellants, and for signature studies. It can be correlated with other data such as chamber pressure.

Experimental

Fixed Wavelength Radiometer

To ascertain the feasibility of using a lead selenide (PbSe) detector in conjunction with flame and plume studies, a prototype infrared radiometer system was constructed. This prototype was based on previous designs by Hudson et al.[6–8] In this prior work, a room temperature PbSe detector was used in a laboratory unit for gas chromatographic experimentation and em-

ployed fairly simple electronic circuitry combined with a commercial lock-in-amplifier for signal processing.

The fixed wavelength radiometer used a Hamamatsu P791-01 PbSe photoconductive cell as the sensing element. The sensitive area was arranged in a 1×3 mm slit shape. The radiometer employed a 600 Hz chopper motor and chopper frequency/phase reference circuit, mechanical phase adjustment, one-inch diameter Optical Coatings Laboratories narrow bandpass filters (with the bandpass centered for either 2.7 or 4.45 μm), an aperture for field-of-view limitation, a preamplifier circuit, and a dedicated synchronous detector.[9] The radiometer was mounted on a rigid metal base, which served as an optical rail. This allowed for accurate aiming of the system.

Feasibility testing of the radiometer was accomplished by using a Perkin-Elmer atomic absorption (AA) burner, modified to allow the introduction of liquid compounds, via its nebulizer, into an acetylene/air flame. Flame fuel and oxidant gases were controlled using Cole-Parmer flow meters with integral flow valves. The burner system was used to ascertain the response of the radiometer to specific organic functional groups and solutions of inorganic compounds.

Instrument testing, involving rocket motor plumes, took place at Hercules Aerospace, McGregor, Texas. The building where the rocket test motors were fired was approximately 100 feet (30.5 m) from the control bunker. The motors were mounted in a steel cradle, parallel to the ground, and connected to ignition cables stretched from the bunker for computer controlled firing. A pulse from a rocket ignition control system logic board was used to trigger a Metrabyte DAS-20 analog-to-digital (a/d) converter board, installed in a Compaq 80286 portable computer, to initiate data collection. The data were stored in voltage/time pairs. Data were also obtained simultaneously from a pressure transducer on the rocket motor. Data were collected for several rocket propellants including: a low-smoke formula, an aluminized formula, and an experimental formula. The experimental formulation was subjected to fifteen trials.
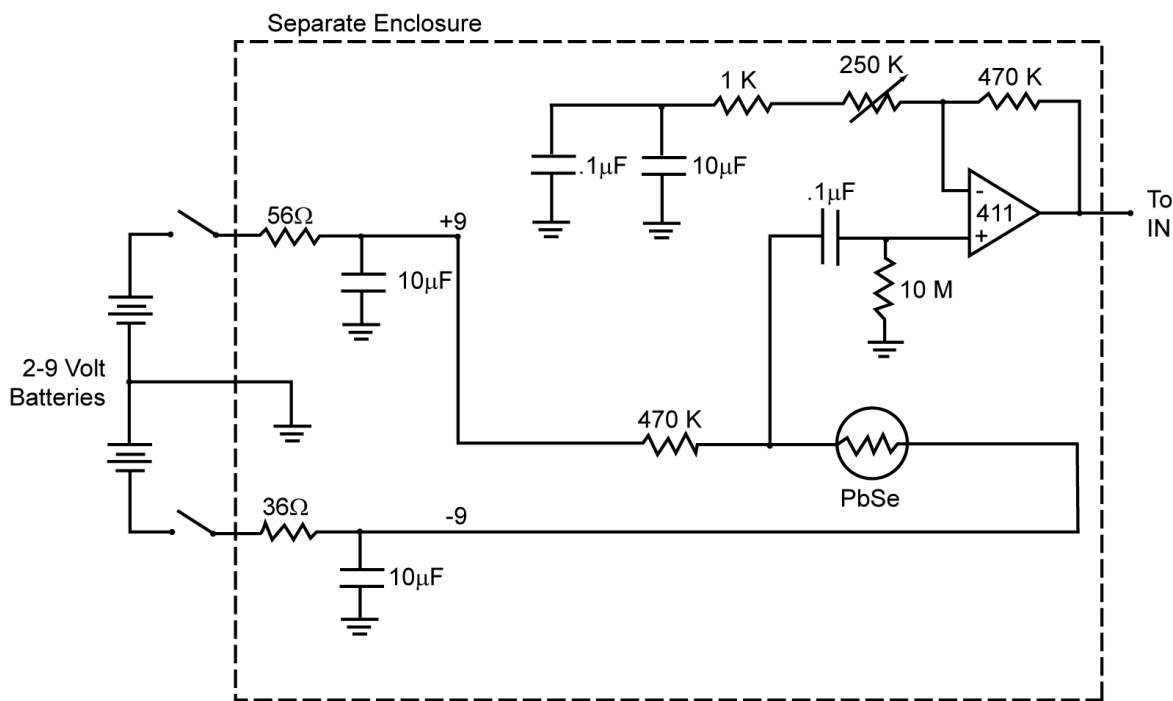
Figure 2. Detector and pre-amp circuitry.

Spectroradiometer

Modifications were made to the fixed wavelength radiometer design to produce a spectroradiometer. The electronic circuitry was improved. The original preamplifier and synchronous detector circuits were combined with a reference circuit designed to allow offset adjustments for electronically locking to the chopper phase angle. The new circuitry also provided RC time constant adjustment using a potentiometer. Schematics of the electronic circuits are shown in Figures 2–4.

Once again, the sensing element for the spectroradiometer was a 1×3 mm PbSe detector. To decrease noise, the detector circuitry was housed in a brass enclosure, and the detector was powered by two 9-volt batteries. The batteries were center tapped to ground to provide bipolar outputs. The system was mounted on a rigid metal base similar to the fixed wavelength radiometer. The bandpass filters were replaced by an Optical Coatings Laboratories circular
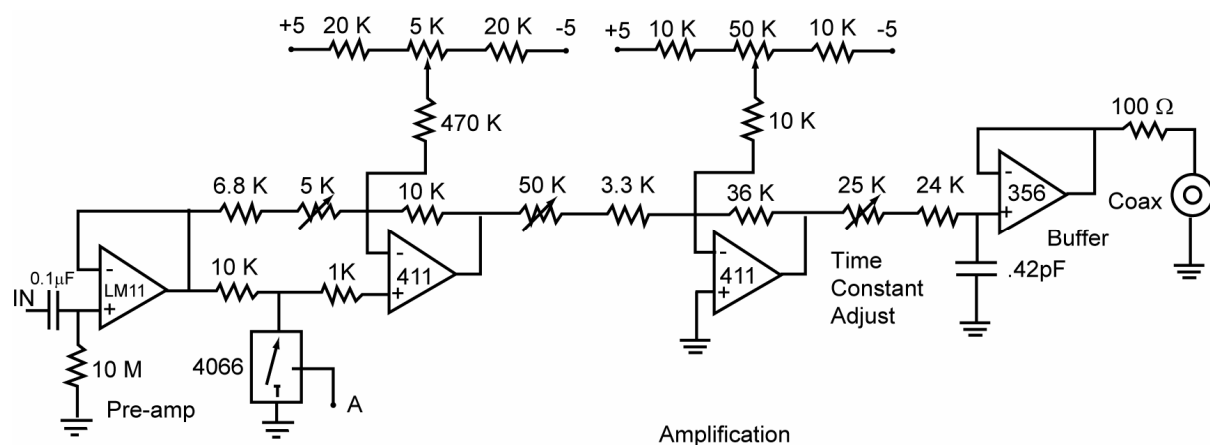
Figure 3. Synchronous detector circuit.
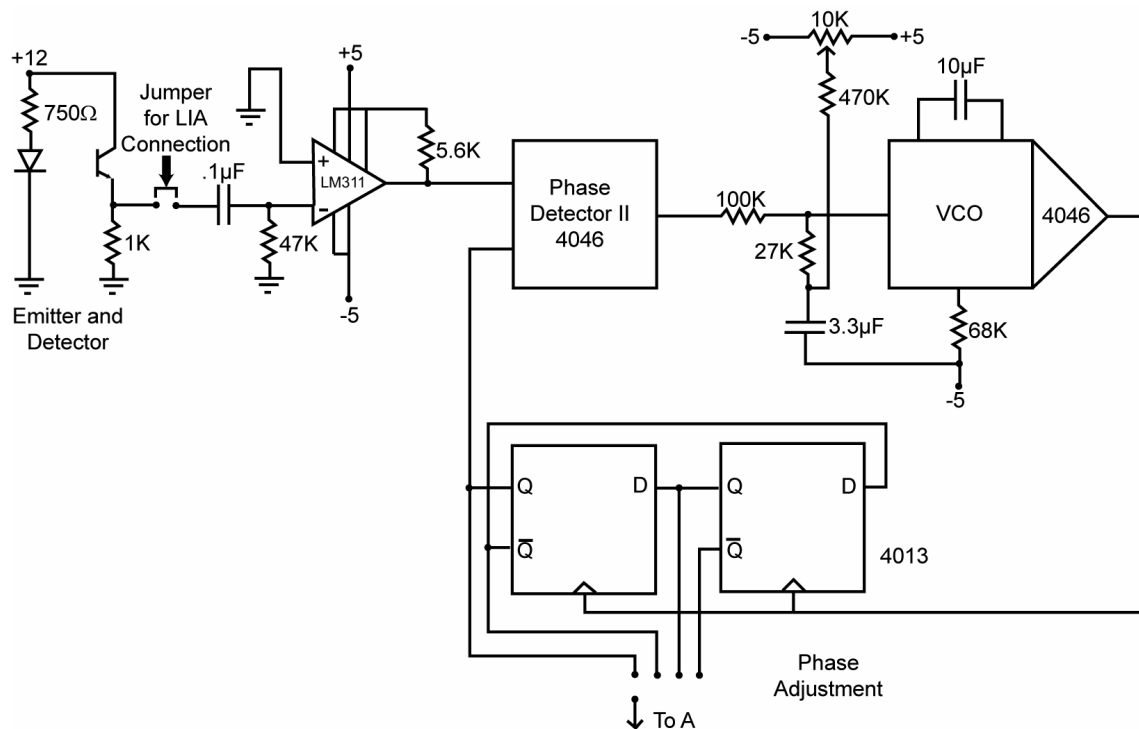
Figure 4. Reference circuit.

variable filter (CVF). The wavelength range for the CVF was 2.1 to 4.7 μm. The CVF was placed in a wheel mounted to a Superior Electric Slo-Syn MO61 stepper motor. The stepper motor was powered by a 12-volt B&K Precision model PR-3A power supply and controlled by a Metrabyte MSTEP-5 stepper motor controller board, installed in a BEST 16 MHz 80386-SX portable computer.

Data were obtained from rocket motor tests. Twenty-eight tests were completed. The three classes of rocket propellants tested were fuel-rich, aluminized, and low-smoke. The stepper motor was computer controlled from the bunker via a Metrabyte CACC-2000 ribbon cable plugged into a Metrabyte STA-STEP screw terminal box. The screw terminal box provided terminals for the connection of wires from a 100-foot (30.5-m) eight-conductor cable. The cable was then attached to the spectroradiometer. The data were collected using a Computerboards CIOAD-16F a/d converter board using a 100-foot (30.5 m) RG58 coaxial cable. All data acquisition and stepper motor control functions were performed by software written in Borland Turbo C version 2.01 language. The software

allowed the user to enter an approximate burn time of the flame/plume of the rocket motor, a file number for saving the data file, and to choose whether the entire wavelength range should be scanned, or the CVF should be parked at a specific wavelength. The software initiated when the a/d converter board was triggered by a falling edge 5-volt pulse from the rocket ignition control system logic board.

During a scan, the entire CVF was stepped through by the motor two steps at a time. Two steps are equivalent to 3.6°, or a displacement of 0.104 μm on the filter. The number of scans possible was calculated from the burn time entered by the user. After the motor moved two steps, ten data points were taken and then averaged. This average number was assigned to a wavelength. The average and wavelength data pair was then saved to a two-dimensional array. Once the filter had been stepped the calculated number of times, the data pairs were saved in an ASCII file to the hard disk, and then to a 3.5-inch floppy disk. If more than one scan was performed, the average of each scan at each wavelength was calculated. These averages and their

corresponding wavelengths were also saved to disk.

For ease in file naming, an extension was automatically added to the file number entered by the user. Graphics commands were also saved into each file. After all of the data were saved to disk, a DOS system call ran a graphics program named DPLOT that has no user interface. The program opens the last data file saved, and using graphics commands in the file, displays a spectrum on the monitor screen.

If the user chose to monitor single band emissions (i.e., carbon dioxide at 4.4 µm) the program first instructed the stepper motor to move to the desired wavelength position. The position on the filter was known by using a roller microswitch and a groove cut into the wheel as a base for measurement. When the program instructed the stepper motor to proceed to the base point, the motor rotated the wheel until the microswitch was released into the normally "on" position. A change of five to zero volts signaled the stepper motor controller board that the base point had been located.

Once the movement had ceased, the program then calculated a value corresponding to the entered burn time. This number was entered into the counter. The counter counted down as the data were acquired. The data were only taken at intervals equivalent to four times the RC [RC = resistance × capacitance] time constant; this ensured proper electronic settling time. At each interval, ten data points were taken and averaged, and the data were assigned a time (in seconds). The data pairs were then stored in a two-dimensional array. After all the data had been collected, the data were saved in an ASCII file to the hard disk and a 3.5-inch disk. DPLOT was called and the specific wavelength spectrum versus time was displayed on the screen.

Results and Discussion

Fixed Wavelength Radiometer Design and Performance

The fixed wavelength radiometer was constructed primarily to show the feasibility of using a PbSe detector, operating with relatively simple and inexpensive electronic circuits, to detect spectral emissions from flames and rocket exhaust plumes. The PbSe detector has several advantages for detection in the one to five micrometer region when compared to other infrared detectors. The detector can be used at room temperature with high sensitivity. This eliminates the need for expensive and bulky cooling methods. The detector is also housed in a standard TO-5 transistor case; therefore, it is very small.

The radiation was chopped by a mechanical chopper at 600 Hz. This enabled the system to employ AC circuits, but with a dedicated synchronous detector substituted for the usual lock-in-amplifier. The chopping rate was chosen to be above the flicker noise threshold of the PbSe detector. Operation of the system in DC mode was possible, but stability and sensitivity would have been compromised.

One-inch narrow bandpass filters were used because of availability and ease of placement. Center frequencies were selected to closely match the gas emission band maximums for carbon dioxide and water vapor at plume temperatures. The filter for water vapor was centered at 2.7 µm with a bandwidth of 0.2 µm, and the filter used for carbon dioxide was centered at 4.45 µm with a bandwidth of 0.5 µm. To achieve maximum blackbody rejection, the bandwidths chosen were as narrow as were available. This was very important because the PbSe detector integrates the total incident signal on its active surface. If the bandpass was too large, any blackbody radiation emitted from propellant condensed phase particles would be detected.

Problems were encountered with employing these types of bandpass filters. To change wavelengths, the radiometer had to be disassembled. Once the filter had been changed, the radiometer system had to be realigned with the source of infrared radiation. This proved rather difficult and time consuming. Data could only be collected at one wavelength at a time; therefore, a spectrum analysis of one rocket motor burn was impossible. Multiple firings were required to obtain data at just two wavelengths. This was quite expensive and not very spectrally informative.

Circular apertures to limit the field-of-view were used at the entrance to the radiometer and directly in front of the PbSe detector. Due to the slit shape of the PbSe active area, and because of the placement of the rear aperture, it was expected that this aperture would change the shape of the viewed solid angle of the plume or flame. The smallest aperture opening was 1.2 mm in diameter. Considering the 1×3 mm detector area, this allowed a 1×1.2 semicircular field to be viewed. Opening the aperture to 5 mm produced an oval shaped image due to the entire 1×3 mm detector area viewing the plume or flame. This gave nearly a 3-fold increase in signal level. For all other experimental trials, the rear aperture was left in the full open position.

The front aperture modified the size of the image (i.e., viewed area). This aperture varied in opening diameter between 1.2 and 5.0 mm, allowing a large effect on the viewed solid angle and the available radiation. During experimental trials it was found that the front aperture had a great effect, seen as apparent changes in orders of magnitude of signal level. With the high intensities from the rocket plumes, the front aperture was set at about 2.0 mm. This allowed the use of most of the electronic circuit's dynamic range. Opening the front aperture to 2.0 mm and the rear aperture to 5.0 mm, the detector had an oval viewed field. The oval had a major axis of 11 mm and a minor axis of 7.4 mm.

The electronic circuits used in the radiometer were designed to be rugged, small, and to offer reliable performance as an overall package. The circuit board was mounted to the side of the optical bench near the PbSe detector. This enabled short leads to be used in connections to the detector, minimizing noise pick-up. The circuit included a preamplifier, chopper reference comparator, and a synchronous detector. This circuit replaced a lock-in-amplifier, giving a radiometer package that was portable. All of the experimental trials were run with a 250 ms time constant. A shorter time constant would have revealed more temporal detail. This fact was not apparent until the rocket data were taken in conjunction with an existing chamber pressure measurement system. An analysis of the pressure data, using a Fast Fourier Trans-

form, indicated changes occurring on a time scale closer to 10 ms.

Flame Combustion Studies — The AA burner was initially used to test the radiometer and to assess its performance. Burner studies were done with a front aperture diameter of 5.0 mm. The acetylene/air flame was adjusted to give fuel-rich, stoichiometric, and lean flames. The emission from the burner was monitored using a filter centered at 2.7 μm for the water band and a filter centered at 4.45 μm for the carbon dioxide band. This allowed a comparison of the two bands. Also, organic compounds containing various functional groups were aspirated into the flame for combustion. The relative contribution of organic structure functionality to the emission seen at each band was noted. It was found that introduction of compounds containing an alcohol functional group gave larger infrared signals. This was due to the alcohol fueling the flame. In addition, several aqueous solutions of metals were aspirated, at levels from 250 to 1000 ppm. These metals had no effect on the infrared signal. The radiometer response to metals was very important because metals, such as potassium, aluminum, zirconium, and iron, are often added to rocket propellants to modify plume signatures and propellant ballistic properties such as burn rates.

Rocket Plume Studies—The radiometer was positioned with the entrance aperture located 18 inches (457 mm) from the plume. For this preliminary set of experiments, the radiometer was mounted on a wooden box under the plume and looked up into the plume. Concerns that particles might fall into the radiometer were unfounded. The high exhaust velocities insured that any condensed phase particles would be ejected well beyond the radiometer. The radiometer location was varied from two to approximately thirty inches (50 to 760 mm) from the exit plane of the rocket nozzle to view different axial portions of the plume. As the radiometer position was varied, the curves generated were very similar, and the infrared intensity decreased as the unit was moved further from the nozzle. It was expected that the 4.4 μm carbon dioxide signal would go through a maximum as the distance from the nozzle was increased, due to afterburning with atmospheric oxygen. The actual plotted data did not indicate
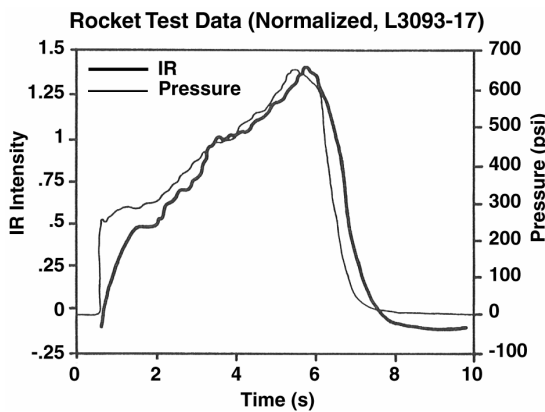
Figure 5. Carbon dioxide band infrared emission intensity and pressure data from a solid propellant taken using the fixed wavelength radiometer.
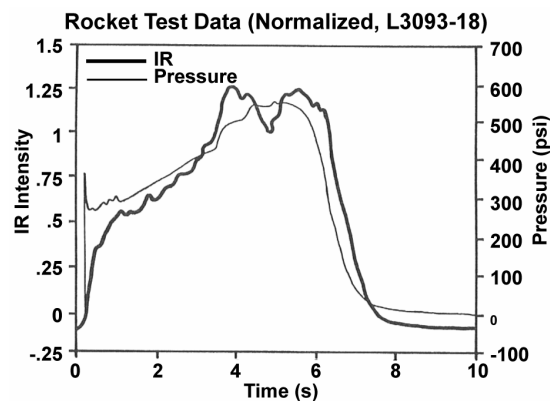
Figure 6. Carbon dioxide band infrared emission intensity and pressure data from a solid propellant taken using the fixed wavelength radiometer.

a maximum for carbon dioxide. However, the hypothesis was confirmed when the areas under the infrared intensity curves, for rocket motor tests at various distances from the nozzle, were integrated. A maximum was found for the overall IR intensity at a point 10 inches from the rocket motor nozzle.

Several plots showing infrared intensity as a function of pressure were made and analyzed. These plots illustrated that the curve produced from the infrared emissions at 4.4 μm generally followed the curve of the internal pressure data. Figures 5 and 6 show this behavior. Note that the pressure rose rapidly at rocket ignition, while the infrared data rose more gradually. Much of this effect was due to the 250 ms time constant, which effectively averaged the data with respect to time. This was also seen at burnout. However, the infrared data indicated greater magnitude changes, especially in Figure 7. The infrared data in Figure 7 showed a sharp rise in emission just before burnout. This was noted by the operators as an audible change in rocket exhaust noise pitch, which was somewhat indicative of thrust. It was thought that this anomaly might be due to the final portion of the propellant casting tearing loose from the front of the rocket motor inner casing, causing an increase in propellant surface area. It was interesting that this effect was exhibited in the infrared data, but not in the internal pressure data.

Two trial runs each of a smoky and a clean burning propellant formulation were compared. While not entirely conclusive, these runs indicated that a visible difference in particle emissions or smoke does not allow the prediction of infrared emissions. Therefore, the industry practice of watching a videotape of trial runs cannot be used to predict the infrared signature of a rocket motor. It certainly cannot quantify the emissions.

Figure 7. Carbon dioxide band infrared emission intensity and pressure data from a solid propellant taken using the fixed wavelength radiometer.
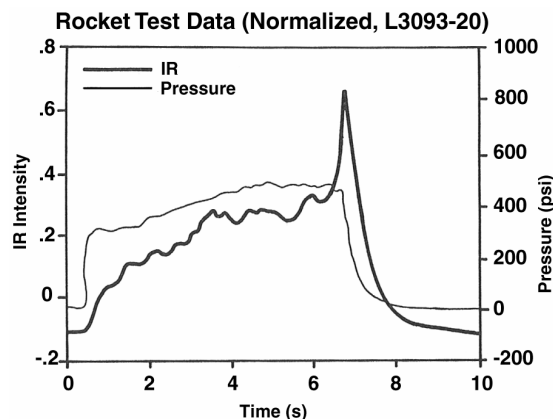
Spectroradiometer Design and Performance

After the feasibility of using a PbSe detector and simple electronics in flame/plume studies was proven, modifications were made to the fixed wavelength radiometer design. The first modification addressed the problem of changing bandpass filters. A circular variable filter was chosen to replace the bandpass filters. The CVF was ideal for the modified system since it functions like an interference filter. The spectral characteristics depend on the refractive indices of the individual films, the substrate, and the incident medium. The wavelengths passed by the filter vary according to the thickness of the coatings. In the CVF, the thicknesses are varied linearly with angular position on the substrate. All filters are designed to have a deviation of less than three percent from a straight line.

The CVF used in the spectroradiometer had a wavelength range from 2.1 to 4.7 µm. The filter covered a 90° angle and had a quartz substrate. The bandwidth for the filter, with an aperture of 1.0 mm, was approximately 0.04 µm. A four-inch (102 mm) diameter aluminum wheel was designed to house the filter. A slot was cut for the filter, with a narrow lip used for support of the filter. The filter was then affixed using silicone rubber. This type of mounting was employed because of the relatively fragile nature of the CVF.

A stepper motor was used to move the filter for scanning. The filter wheel was attached to the hub of the stepper motor for ease of rotation. To operate the motor, computer control was required, which used a stepper motor controller board installed in a computer. A software program was written to achieve motor control. At first, the motor was single-stepped, where one step was equivalent to 1.8°. However, rocket motor burn time constraints dictated that the motor had to be moved in sets of two steps or 3.6° per set.

The next step was the design of the mechanism for finding a base point on the wheel. A notch was filed in the edge of the filter wheel approximately equal to one step. The notch was used to turn a roller microswitch to the on position when it was released, as the wheel rotated. When the switch turned on, a signal was sent to the stepper motor controller board, which lo-cated the base point. Once the base point was known, the number of steps to specific wavelengths on the filter was calculated.

Electronic circuit design was the next concern. The electronics used in the fixed wavelength radiometer were sufficient for feasibility studies; however, they did not allow for easy adjustment of parameters. In the radiometer, the time constant was hardwired on the circuit board. The electronics in the spectroradiometer were redesigned to provide time constant adjustment from 100 down to 10 ms using a potentiometer. The electronics in the fixed wavelength radiometer also did not allow phase adjustment since the phase was adjusted mechanically. This caused repeatability problems in phase settings. The electronics for the spectroradiometer were designed for electronically locking to the phase of the reference.

After the circuits were built, the line driver output randomly oscillated. This oscillation was stopped when the PbSe detector circuitry was enclosed in a brass box. To avoid noise problems, the detector was powered by two 9-volt batteries, and various capacitor values were optimized.

It was decided that the data should be collected at intervals of four times the time constant to ensure electronic settling. Data were obtained from Bunsen burner flames using the a/d converter board. The purpose of these first experiments was to ascertain the response of the spectroradiometer with the CVF in place. The flame tests were also used to ensure that the position on the filter corresponded to the correct wavelength assigned by the software. During the original experiments, short lengths of coaxial cable and eight-conductor cable were employed for data acquisition and stepper motor control. After successful experimentation, the cable lengths were changed to 100 feet (30.5m). This was necessary to ensure proper functioning of the instrument when it was used at Hercules Aerospace.

Rocket Plume Studies—Twenty-eight rocket motor tests were performed. During these tests, it was determined that the aperture on the front of the spectroradiometer needed to be fully opened to 5.0 mm since the CVF transmittance was less than the bandpass filters. This allowed

for an oval viewed area on the plume. The oval had a major axis of 19.40 mm along the axis of the plume, and a minor axis of 15.81 mm.

Various propellants were used to determine the spectroradiometer's response. The propellants were classified as: low-smoke, aluminized, and fuel-rich. Figures 8 to 11 show examples of spectra obtained during the testing. Figures 8 and 9 are motor tests using two different low-smoke propellants. Both low-smoke propellants have the same elements present, but the elements are at varied concentrations. The emissions in these two spectra look like typical rocket and flame emissions found in the two to five micrometer region. The bands centered at 2.7 and 4.4 µm are due to water vapor and carbon dioxide, respectively. The carbon dioxide peak does not exhibit the two lobes seen in the Bunsen burner spectrum. This is because spec-

tra taken with the spectroradiometer have very little spectral detail due to the speed of the scan and the resolution used in obtaining data. Due to the short duration of rocket motor burns, less than two seconds, it was necessary to step the filter two steps at a time. This allowed a full scan to be performed in 0.6 seconds. Stepping two steps at a time decreased the maximum resolution of the system approximately three times, from 0.04 to 0.104 µm. However, this operation allowed scan averaging, while permitting dynamic plume monitoring. Although the resolution had dropped, information could be discerned from the spectra. One detectable feature was the hydrogen chloride band centered at 3.5 µm.

The rocket propellant used to produce Figure 11 was fuel-rich. When the spectrum was viewed, it appeared that the instrument was

Figure 8. Infrared spectrum of a low-smoke propellant taken using the spectroradiometer.
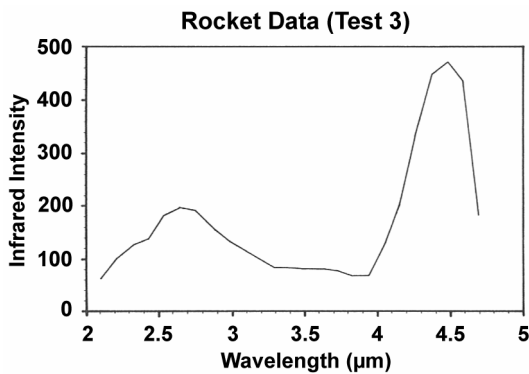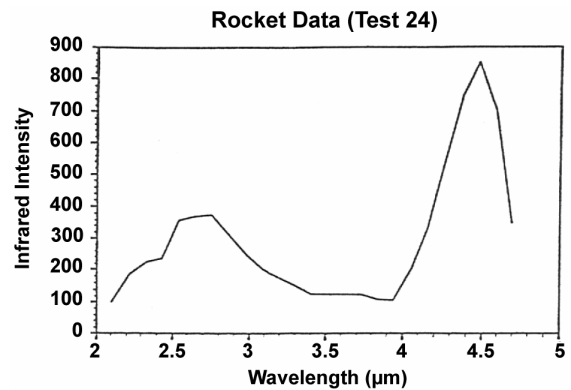

Figure 9. Infrared spectrum of a low-smoke propellant taken using the spectroradiometer.
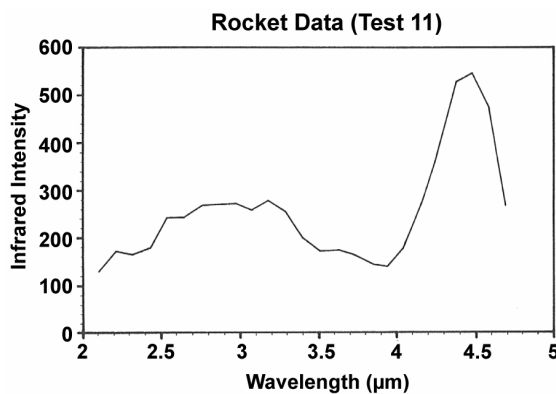

Figure 10. Infrared spectrum of an aluminized propellant taken using the spectroradiometer.
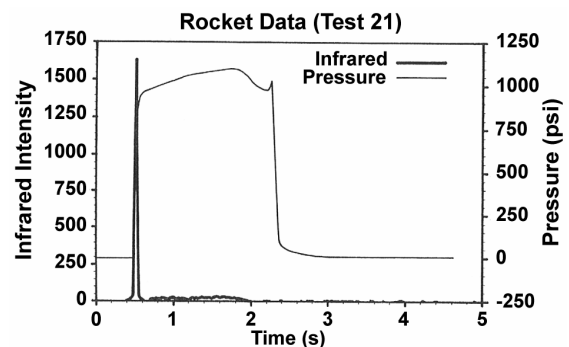

Figure 11. Carbon dioxide band infrared emission intensity and pressure data from a fuel-rich propellant taken using the spectroradiometer.

malfunctioning. All that was present in the spectrum was the igniter spike. The instrument was tested using a hot soldering iron. Once the instrument was shown to be functioning, further fuel-rich tests were run. All of the tests produced the same results: detection of the igniter spike and negligible infrared intensity afterwards. The fuel-rich motors may not have had sufficient oxygen content to give complete oxidation to final combustion products. This would result in a predominantly particulate and/or hydrocarbon output, which may not give significant infrared emissions in the two to five micrometer region. The fuel-rich tests proved that even though a smoky plume may be present, the detected infrared energy, in the two to five micrometer region, could be negligible.

Figure 12 shows infrared intensity and pressure data taken with the spectroradiometer. The CVF was parked at 4.4 µm, which corresponds to carbon dioxide. The infrared intensity and pressure curves are very similar. The 10 ms time constant allows the infrared intensity curve to follow the pressure curve directly. The 250 ms time constant used in the fixed wavelength radiometer caused the infrared intensity to slope up more slowly. A large amount of temporal detail was revealed with the shorter time constant. Further testing of the spectroradiometer stationed at 2.7 and 3.5 µm produced similar results.

Conclusions

The fixed wavelength radiometer and the spectroradiometer both proved the feasibility of using PbSe detectors, in conjunction with simple electronics, to monitor emissions from flames and rocket motor plumes in the two to five micrometer region. Both of these systems were inexpensive, rugged, and portable which made field monitoring possible. The problems associated with the fixed wavelength radiometer included filter changing, difficulties found using a mechanical phase adjustment, and the length of the time constant. These were eliminated in the design of the spectroradiometer. The spectroradiometer had enough sensitivity to detect specific bands that corresponded to water vapor, carbon dioxide, and hydrogen chloride. It should also be noted that the sensitivity of the
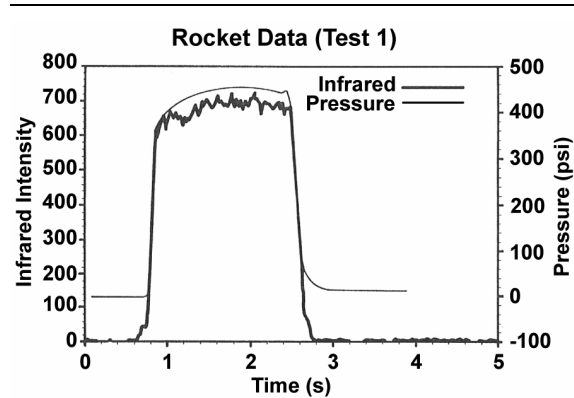
Figure 12. Carbon dioxide band infrared emission intensity and pressure data from a low-smoke propellant taken using the spectroradiometer.

spectroradiometer could be improved by scanning the CVF at a much slower rate.

The spectroradiometer enabled Hercules Aerospace to develop a spectral database based on infrared intensities produced by various propellant mixtures and motor architectures. This database was constructed by obtaining infrared data at specific wavelengths (2.7 µm for water vapor, 3.5 µm for hydrogen chloride, and 4.4 µm for carbon dioxide) and by scanning the entire CVF from 2.1 to 4.7 µm. A direct correlation between specific wavelength data and pressure data was found. As the pressure increased, the infrared intensity grew larger. Large differences between visible data, that is the amount of smoke and particulates in the plume, and the infrared intensity data were also discovered. In the future the spectroradiometer may be modified to detect emissions in other portions of the infrared spectrum. This may give more insight into the performance of rocket motors and flame-based systems.

Acknowledgments

Sciences, Fayetteville, AR, USA. This is an updated version of a paper presented at the 30th AIAA/ASME/SAR/ASEE Joint Propulsion Conference, June 27–29, 1994, Indianapolis, IN USA.

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Comment on:
"Shell Altitude vs. Mortar Length" by Ron Dixon, Issue 11, p 70 (Summer 2000)

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Ron Dixon has presented results on the correlation between the altitude achieved by a 3-inch (76-mm) shell and the length of the mortar from which it was fired. Provided that the mortar length was at least 18 inches (457 mm), there was no further gain in shell altitude with increasing mortar length. My own anecdotal observations are entirely in accord with Ron Dixon's measurements, provided that a commercial Black Powder lift is used. However there may be more to the old pyrotechnists' wives' tale of increasing shell altitude with increasing mortar length than these measurements suggest.

My first shell building efforts were solely with 3-inch (76-mm) shells, one of the initial problems being with the attainment of sufficient altitude. It turns out that access to commercial Black Powder, such as Fg, would have made the solution trivially simple. A rather poor quality hand made powder, such as I had at the time, is quite a different story. Using 100 grams of this powder (granular, sieved to 5–10 mesh) as lift, the following mortar lengths were tried: 15, 18, 24, 30, 37, 40, and 42 inches (381, 457, 610, 762, 940, 1016, and 1067 mm). No measurements of shell altitude were made. However, the crude observations were that a mortar length of 15 or 18 inches (381 or 457 mm) resulted in the shell burst being on the ground after descent; 24 or 30 inches (610 or 762 mm) resulted in the shell burst being dangerously low during descent; and 37, 40, or 42-inch (940, 1016, or 1067-mm) mortar lengths were all satisfactory with no obvious difference between them.

The acquisition of commercial Black Powder radically changed the situation. Not only was the amount required greatly reduced, but also the mortar length could be reduced to 18 inches (457 mm) without any noticeable altitude diminution.

In summary, anecdotal observations of the relationship between mortar length and altitude achieved by 3-inch (76-mm) shells using commercial Black Powder lift were entirely consistent with the measurements of Ron Dixon, suggesting no further altitude gain beyond a mortar length of 18 inches (457 mm). However, when a larger quantity of an inferior hand made lift powder was used, there appeared to be a more gradual gain of shell altitude with mortar length at least until the latter was three feet (1 m). It would be of interest to subject this observation to quantitative measurement.

Review of

Experimental Composite Propellant

An Introduction to Properties and Preparation of Composite Propellant Design, Construction, Testing and Characteristics of Small Rocket Motors

Terry W. McCreary
Self Published, 2000
[No ISBN]

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There are many references available to address design, construction, and evaluation of chemical propulsion devices. Terry McCreary has provided a fresh look at the science and specific processes associated with development of ammonium perchlorate composite propellant (APCP) solid rocket motors in his recently self-published book, *Experimental Composite Propellant*. There is little content in this book that

has not already been explored in other publications, but presentation of the material has never been more kind to the reader.

Experimental Composite Propellant delivers a variety of topics that the beginner and journeyman solid rocket motor technician will find useful, from simple step-by-step instructions for formulating and casting high energy polybutadiene acrylic acid acrylonitrile prepolymer (PBAN) bound APCP, to the complete discussion and explanation of the combustion processes of a solid rocket motor. Information for use of hydroxyl-terminated polybutadiene (HTPB) to bind APCP is also well detailed, though largely relegated to the Appendix.

This book is more of an associate than a text, with discussions moving along as if a friend were close at hand providing guidance, slowing down when operations get complex or dangerous. Each step of PBAN-APCP rocket motor construction is detailed with the safety and success of the beginner in mind, as well as providing new insights to the veteran.

Many of the digested topics are expanded in the 107-page Appendix, including details of propellant and polymer chemistry, optimization of nozzle design, construction of a thrust measuring test stand, as well as scores of other topics.

Experimental Composite Propellant, with a pleasant, almost entertaining demeanor, explores great depths of safety, the applicable mathematics, and discussion paramount to successful solid rocket motor development. This 243-page reference sets a new standard for publishers of experimental motor "How-To" books.

For procurement information, contact the author by email at: prfesser@hotmail.com or write to him at: Experimental Rocketry Group, PO Box 1414, Murray, KY 42071, USA. Additionally, a web site will soon be available at:

www.experimentalrocketry.com

Review of

The Chemistry of Fireworks

Michael S. Russell
Royal Society of Chemistry, 2000
ISBN 0-85404-598-8

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Michael S. Russell's treatise on the chemistry involved in the composition of display fireworks is a welcome primer on the chemistry of pyrotechnics. While this book was written for the student with 'A' level qualification or equivalent, it has potential for use in a college level general chemistry course. (The British 'A' level equates to Advanced Placement (A.P.) coursework at the high school level in the United States.)

Russell's 12 chapters cover the basic devices used in fireworks and conclude with pyrotechnic safety, and British regulations and standards. Chapter 1 includes a seven-page glossary of pyrotechnic terms designed to help the person reading pyrotechnic literature for the first time. Some of the definitions are quite brief and do not completely explain some key terms. *Stars* are defined simply as "a compressed pellet of explosive composition designed to be projected as a pyrotechnic unit". This definition excludes two major forms of stars—rolled and cut. This reviewer found the glossary helpful in translating some of the British terms for fireworks; terminology is not always the same. For example, the U.S. pyrotechnician would know the *burster* as the burst charge or composition, the British term for lift charge is *propellant,* and U.S. terms Quick match and Black Match are called *piped match* and *quick match*, respectively in Britain.

Chapter 1—Historical Introduction is a nine-page condensation of the history of Black Powder. While this survey focuses on the development of Black Powder in Britain, Russell also covers key international history and gives

the reader a chronological time frame to see how this compound has progressed. Starting with the Chinese and Arabs as the discoverers of Black Powder he continues through Roger Bacon's work ending with modern day knowledge.

Chapter 2—The Characteristics of Black Powder gives the reader a very concise yet sufficient account for understanding some of the basic dynamics of Black Powder. Russell includes the influences of composition density, moisture and the stoichiometry. This chapter could be used in practical application for teaching such basic tenets of chemistry as: heat of reactions, enthalpy change, stoichiometry, and activation energy as applied to ignition temperature.

Chapter 3—Rockets invokes the science of physics and chemistry in describing the basics of rocketry. This ten-page chapter provides an introductory view of the key principles including propellants, ballistics (internal and external), and influences of rocket design.

Chapter 4—Mines and Shells deals with the two major devices used in modern display fireworks. Once again internal and external ballistics are discussed. Russell uses the European system to describe shell diameter in millimeters in contrast to the U.S. practice of describing shell and mortar dimensions in inches. He describes the current trend toward using plastic hemispheres to construct ball type shells. While plastic has grown in popularity, he refers to a type of plastic shell with lift included that is rather outdated and not currently seen in the U.S. The author introduces mines but gives little description of how they are constructed as compared to aerial shells.

Chapter 5—Fountains not only describes how fountains are constructed, but also introduces the reader to atomic and quantum theory. This information prerequisites a cursory understanding of how different colors are produced in fountains and other fireworks. His descriptions are adequate for this level of book, but he fails to complete the discussion in this chapter.

He writes about **Sparklers** in **Chapter 6** and **Bangers** in **Chapter 7**. Then in **Chapter 8—Roman Candles** he finishes explaining how the main colors of fireworks are produced. As an introductory text this separation does not help the newcomer to pyrotechnics to apply the theory with current applications. I would recommend this subject be discussed consecutively rather than dispersed among different chapters. These chapters, however, do provide the novice a clear initiation point as to how these items perform.

He divides the discussion of color by giving the standard information for green and red stars in Chapter 8; blue stars are completely omitted. Blue producing compositions are the most challenging to understand and consistently make, and they are not discussed until two chapters later in **Chapter 10—Special Effects,** which describes how different color lance materials, including blue, are formulated. The author does an ample job of handling the current understanding of how blue flames are produced during the combustion of the pyrotechnic material. Unfortunately, this discussion occurs some five chapters after this subject was introduced. Consolidating the discussion of color would have strengthen this text and afforded a more systematic and cohesive understanding of this key topic. **Chapter 9—Gerbs and Wheels** provides a good description of these interesting and entertaining historic fireworks devices.

Chapter 11—Fireworks Safety and **Chapter 12—Fireworks Legislation** help the reader to begin to grasp how important safety and following the regulations are to properly and legally displaying fireworks.

This book would make good reading material as a supplemental text to a high school A. P. Chemistry or General Chemistry college course. Fundamental principles of chemistry can be illustrated through their applied uses in pyrotechnics, and this text provides some of that correlation. The author has some errors such as in Chapter 2 equations 2.9 and 2.10, where k, the rate constant for a reaction, is equal to t the time to ignition. The rate constant (k) will increase with a temperature increase, whereas the time to ignition (t) must decrease. Perhaps this was a transposed equation that could be easily corrected in a second printing of this text. While this volume can be improved, it does offer a starting point for the beginning student of pyrotechnics and chemistry.

Review of

The Chemistry of Fireworks

Michael S. Russell

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At first glance, this 117-page paperback book[1] looks very promising. According to the publisher's description, the book "is aimed at students with 'A' level qualifications or equivalent. The style is concise and easy to understand, and the theory of fireworks is discussed in terms of well-known scientific concepts wherever possible. It will also be a useful source of reference for anyone studying pyrotechnics as applied to fireworks."[1a]

The author of the work, Michael S. Russell, is a research chemist with a background in military and marine pyrotechnics, and he has worked as a firework display operator. He should be well qualified to write on this subject.

A quick look at the organization of the book is encouraging. The scientific material is presented in discussions of the various types of fireworks, and this seems a good way to achieve a balance between theory and practice. The initial enthusiasm and high expectations, however, soon turns to disappointment. Although the book is titled *The Chemistry of Fireworks*, there is not much chemistry, and there are far too many errors and misleading statements. In a book of this type, there should be none. There is quite a bit of physics, but this too is often either misleading or wrong, and the discussion of fireworks is rather superficial. Few formulations are given, and some of those are out-dated and downright dangerous.

The book has 12 chapters plus a glossary, the latter being located right after the Table of Contents. Some of the entries in the Glossary do not correspond to this reviewer's understanding of the current usage of the terms. For example, "bombette" is defined as "a combination of candles and/or shells packed in a box and fired by interconnecting fuse".[1b] Perhaps this definition comes from what Weingart[2a] calls "bombette fountains:"—"an effective combination of candles and floral shells packed in a box." The glossary in the third edition of Lancaster's *Fireworks Principles and Practice*, however, says that "bombette" is "in essence a mini shell, usually found as a component of a roman candle, and less often as a component of a mine or even as a sub-component of a shell."[3a] Another entry defines a mine as a "firework that is fired from a mortar and which contains a single propellant charge and pyrotechnic units".[1c] This excludes those mines in which the case of the firework serves as the mortar. The statement that meal powder is "used for priming and making matches"[1c] could be misleading. Presumably Russell was thinking about quick match, but it is likely that a reader would think of safety matches. A rocket is defined as a "self-propelled firework with stick for stabilization of flight".[1d] Are rockets with fins,[2b] or rockets stabilized by spinning,[4] any the less rockets for being without sticks? A notable aspect of the glossary is the number of entries associated with the British explosives regulations. The legislative control of fireworks is an important issue for those in the trade, but is it an appropriate subject for a book that is supposed to be about the *chemistry* of fireworks?

The first chapter, "Historical Introduction", is almost completely focussed on Black Powder. There are speculations about possible ways in which ancient Chinese alchemists might have discovered the fire-enhancing properties of saltpetre. Reading Russell's description of the alchemists' experiences with "their brew of honey, sulfur and saltpetre",[1d] one cannot help but wonder "How could he know *that*?" Presumably Russell's assertions are based on some work of historical research, but what, and by whom? This is an example of a very great shortcoming of this book: there are no references. There is a bibliography, but that is no substitute for references. It is most surprising, and regrettable, that the publishers did not insist that references be provided, particularly as they claim that the book will be "a useful source of reference for

anyone studying pyrotechnics as applied to fire-works."[1a]

The first chapter also includes a discussion of the pyrotechnic contributions of Roger Bacon, whose recipe for Black Powder is given as six parts by weight of saltpetre, five of "young willow (charcoal)" and five of sulfur. This recipe, along with the picture of Bacon on the same page,[1e] appears to have been taken from T. L. Davis' book *The Chemistry of Powder and Explosives*.[5a] Bacon's supposed recipe for gunpowder has been discussed in detail by Michael Swisher.[6] The recipe evidently originated in H. W. L. Hime's solution of an anagram, LVRV VOPO VIR CAN VTRIET attributed to Bacon, but for which "no manuscript authority now exists, nor do we know what ever did".[6a] According to Swisher, Hime gives Bacon's formula as *seven* parts of saltpetre, five of young hazlewood (charcoal) and five of sulfur. Swisher mentions that Davis "corrects" the formula to 6:5:5—a correction that does nothing to improve a formula already deficient in potassium nitrate. Davis' translation of the passage that includes the anagram[5b] is repeated word for word in this book,[1e] complete with the mistranslation of "corvli" as "willow" instead of "hazel". In his introductory remarks on the details of Black Powder manufacture, Russell states that a "loose" mixture of the three ingredients of Black Powder is "almost impossible to light", and "if ignition does occur, the burning is fitful and prone to extinguishment."[1f] Many a schoolboy knows better.

Another section in this chapter deals with "Further Uses of Black Powder". Here again the lack of references is frustrating. It would have been interesting to read more about the use of smoke from a potassium nitrate charcoal mix as a fire-extinguishing agent, an application that derives, we are told, from "the way in which the potassium salt in the smoke interferes with the combustion chemistry of a fire".[1g] Although it is supposed to provide a historical introduction to the chemistry of fireworks, this chapter offers instead a rather poor discussion of the development of Black Powder. Davis' outline[5c] of the development of pyrotechnic mixtures is vastly superior, despite having been written over half a century earlier.

The second chapter deals with the characteristics of Black Powder. There are brief discussions on the influence of pellet density and moisture content on burn time. The following sections, discussing the thermal decomposition of Black Powder and its ignition, introduce the Arrhenius equation,

$$k = Ae^{-E/RT}$$

where k is the rate constant of the reaction, A the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

This equation is almost immediately confused with one of similar form that deals with the time to ignition, rather than the reaction rate constant. This equation is presented in the book as equation (2.10):

$$t = Ae^{-E/RT}$$

"where t is the time to ignition (i.e., ignition delay) at a temperature T in degrees absolute, and the other parameters are as described for equation (2.9)". Equation (2.9) is the Arrhenius equation. An increase in the rate constant k is associated with a decrease in the time to ignition, so the negative sign of the exponent in the Arrhenius equation must be changed to positive if the equation is to describe the time to ignition. Additionally, the constant of proportionality will be different in each equation. Neither of these changes has been made. One might perhaps attribute this to a printer's error, had not the incorrect sign been used in both the exponential and logarithmic versions of the equation, and had not the author stated that the "other parameters" were the same in both equations.[1h] The associated graphs (Figures 2.5 and 2.6) are correct and inconsistent with the equation.

A section on the thermal analysis of Black Powder includes exceedingly terse descriptions of thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).[1i] The definitions of the latter two techniques appear to have suffered from the omission of some words. It seems as if the definition of DTA should have read "(a method) 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 program". The italicised words appear in

Russell's definition of TG but have been omitted in the definitions of DTA and DSC.

A discussion on the heat of reaction[1j] introduces the enthalpy change, but without any discussion of the sign convention that makes the enthalpy change *negative* when a reaction produces heat. This convention can be confusing to those new to the subject and would have been worth mentioning. The discussion of the calculation of the heat of reaction at a particular temperature is incorrect. The effect of the change in enthalpy of the products is discussed, but that of the change in enthalpy of the reactants is not. Both have to be taken into account. In the example given, a straight line is plotted between two calculated points. This assumes that the relationship is linear—an assumption that requires at least some justification.

The chapter on rockets is particularly bad. The statement that Black Powder is classed as a composite propellant is followed immediately by a definition of a composite propellant as one "where the fuel and oxidiser are intimately mixed". This is all very well, but the term "composite propellant" is usually used to mean one in which particles of solid oxidiser and powdered fuel are held together by a polymeric binder.[7a] Black Powder would not normally be classed as a composite propellant, though it would be according to Russell's definition. A book intended to introduce students to a subject should not introduce new definitions of terms that already have a specific technical usage.

The discussion of the science of rockets is hopelessly confusing. Equations are defined with some parameters specified in metric units (e.g., millimeters per second) and others in the same equation use non-metric units (e.g., pounds per square inch).[1k] An impressive-looking equation[1l] turns out to be nothing more than an attempt to show the calculation of the slope of a straight line—and it is wrong. Perhaps it is a misprint, but it is wrong all the same.

Having indicated an intention to show how to estimate the pressure inside an operating rocket motor, Russell digresses to make some remarks about the operation of a firework rocket. He writes, "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 nozzle. As the propellant is consumed, its area diminishes and the gas flow or 'thrust' reduces".[1m] The statement that the area of the burning surface decreases as the propellant is consumed is exactly the opposite of what happens in the early stages of the combustion of rockets having a long conical cavity. After this confusing digression, Russell returns to his treatment of the pressure in a rocket motor, and he produces equations

$$K = A_p/A_N$$
$$= C \cdot p^{1-n}$$

that relate the chamber pressure p to the propellant area A_p and the nozzle area A_N, with C and n being constants. He writes that the equation

$$K = A_p/A_N$$

"can be compared with the burning rate equation (i.e., his equation (3.2): $R_B = 3.38p^{0.325}$ where R_B is the burning rate) by taking note of the fact that 'n' [or 0.325 in equation (3.2)] … becomes '$1-n$' [or 0.625] in the area ratio equation". This is an unsatisfactory explanation, to say the least. Inclusion of a proper derivation of the relationship[8a] would have taken little space and would have been well worthwhile. An example is then given of how the equations can be used to work out the pressure-time profile for a rocket, after the required constants have been determined by empirical measurement. The results are set out in Table 3.1.[1n] After an increment of 2 mm of propellant has been consumed, the area of the propellant is shown to have decreased from 50 to 40 cm^2. This is obviously impossible for a rocket burning from a central cavity.

A section on rocket design and manufacture gives some rather questionable pieces of information. For example, the reader is given the impression that the choke is formed after the propellant has been loaded and is told that a "pressing of clay" is applied on top of a flashpowder charge to close the head of the case of a thunderflash rocket.[1o]

The section headed "RECENT DEVELOPMENTS"[1p] could well have been omitted. Russell follows the bad example of Weingart[2c] by discussing V2 rockets, a topic that really has no place in a book on fireworks. We are told that

the Russians use military-type propellants in "rockets to reach astonishing heights in firework displays above the tall buildings in Moscow". It would have been interesting to know the source of this information, if only to find out how the Russians handle the problem of spent rockets falling into the city. Examples are given[1q] of "ingredients used for composite propellants". Some of the materials listed are not so used, having been found to be unsuitable. For example, Sutton[7b] writes "Nitronium perchlorate is objectionably hygroscopic, is relatively incompatible with available binders, and detonates easily. A decade of effort was made to overcome these problems… but it was to no avail". Furthermore, writes Sutton,[7c] "boron… has not proven to be a practical fuel". Russell, despite being a professional chemist, evidently believes boron to be a metal.[1q] It is regrettable that space has been given to this irrelevant and inaccurate material when there is no mention of some of the propellants based on whistle (see references 9 and 10) and strobe (see references 11 and 12) compositions that have been used in firework rockets in recent decades.

The next chapter covers mines and shells. Russell should have found no shortage of detailed information on the construction of shells. (See references 2d, 3b, 12, and 13.) Despite this, the information he gives is vague, misleading or inaccurate. For example, "the shell case can be made from paper, wood or similar material reinforced, with string". Then, a multi-break shell is said to break first at the maximum altitude, with successive breaks "afterwards while the shell is falling back to earth". Also, what are we to make of the statement that "Plastic…offers the advantage of unit construction whereby the lifting charge may also be contained inside the plastic case"?[1r] The introductory remarks give little confidence in the more technical sections that follow.

It is questionable whether a discussion of shell ballistics is really appropriate in a book on the chemistry of fireworks. The equation[1s] for the linear burn rate of Black Powder is different from that presented in the previous chapter.[1k] Much of the material presented in this chapter (even the numerical examples) have evidently been taken, without acknowledgement, from Dr. Shimizu.[15] The equation for the time of

flight of a shell[1t] has been copied incorrectly[15a] and has been worked through to give a different answer (5.2 s) from that presented by Dr. Shimizu (6.4 s). It is odd that Russell did not notice this discrepancy. It is odd, too, that he indicates[1t] that the units of the acceleration due to gravity are dm s^{-2}, and then uses its value in m s^{-2}

A section on the efficiency of the transfer of energy between the burning powder[1u] and the shell reveals that Russell is under the impression that kinetic energy is not $\frac{1}{2}\,mV^2$, (where m is the mass and V the velocity), but rather $\frac{1}{2}\,mV^2/g$, where g is the acceleration due to gravity. Incidentally, he calls the acceleration due to gravity "the gravitational constant", a term that normally refers to the constant G in Newton's equation $F = Gm_1m_2/d^2$ where F is the gravitational force between two bodies of masses (m_1 and m_2) and d is the distance between them. Naturally enough, the use of an incorrect equation for the kinetic energy yields a wrong answer for the efficiency. Its small value (4.5%) is explained away by the observations that "the shell is never a good fit in the bore of the mortar, there are no gas-tight seals around the shell, and that the shell is never perfectly spherical (or cylindrical)".[1v] It is a pity that instead of trying to rationalize the answer, Russell did not check his original equation. A simple dimensional analysis, as taught in high school physics, would have alerted him that something was wrong.

The next chapter deals with fountains. Here again, Russell's idiosyncratic terminology is evident. He seems to think that "fountains" and "waterfalls" are equivalent. While waterfall effects can be achieved with fountains (see reference 2e), more usually waterfalls are made with fireworks having quite a different construction from that of a fountain.[3c16] The typical waterfall unit has a thin case designed to burn away as the composition is consumed— the opposite of what is required for a fountain. This chapter also is used to introduce atomic theory and quantum theory. Russell makes the interesting point that the colors of sparks are dependent on the type (i.e., chemical nature) of the material as well as on the temperature.[1x] Once again it is frustrating to be presented with

snippets of interesting information without any references to the original work.

A diagram of a 38 mm fountain [1y] shows a composition that contains only potassium nitrate, sulfur, charcoal, meal gunpowder and coated iron. However, the discussion of the same diagram refers to antimony trisulfide, fine aluminium, barium nitrate and dextrin. In the following paragraph, we are told "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." Furthermore, "at STP, for every gram of KNO_3 that decomposes, 0.39 litres of gaseous products are produced, whereas for every gram of charcoal that decomposes, 1.3 litres of gaseous products are produced (at STP)". What possible sense can be made of all this?

The next chapter begins with a very odd statement: "There are two main types of firework: wire sparklers…and tubed sparklers."[1z] Presumably Russell did not intend to write this—on the other hand, perhaps he really is exceptionally keen on sparklers. He discusses the production of a "silver sparkler" but gives as its composition one that he correctly indicates would produce only orange-red and gold sparks.[1aa] In describing the manufacture of tubed sparklers, he refers twice to the process of putting the powder into the tubes as the powder being "sifted in".[1aa] To "sift" means "to pass through a sieve". If the powder is "sifted in", that presumably means that a sieve is held over the top of the case and the powder passed through the sieve into the case. Is that really how these fireworks are filled?

The chapter on "bangers" begins with the incorrect statement that the terms "banger" and "squib" are equivalent.[1ab] The traditional British "squib"[17] was a different firework from the "banger" described in this chapter, though it, too, concluded its performance with a bang. Russell tells us that bangers were filled by the explosive charge being "sifted in".[1ab] Lancaster[3d] devotes a whole chapter to mixing and charging, but fails to mention this method of getting powder into cases.

The chapter on Roman Candles includes a remark about "the projectiles reaching greater heights with every shot".[1ac] Candle makers take care to avoid this happening, but it seems that what was once seen as a shortcoming is now regarded as an interesting effect. The manufacture of Roman Candles is outlined, and here again we are told that the delay composition is "sifted in". Once again, Russell presents one composition in a diagram and discusses another in the text.[1ad] The diagram shows a rather old-fashioned composition for a green star: barium chlorate, potassium chlorate, acaroid resin, charcoal and dextrin. Such a star would be regarded these days as too sensitive to shock and friction, as Russell himself explains in the next section.[1ae] In the text, however, we are told about a different composition: "a green star could contain barium nitrate, potassium chlorate and aluminium together with binders", and an analogous composition, with strontium nitrate and strontium carbonate replacing the barium nitrate, is suggested for a red star. Compositions combining a nitrate, a chlorate and aluminium have been called "death mixes"[18,19] because of the possibility of their spontaneous ignition in the presence of moisture. Given the large range of published compositions for red and green stars, it is most unfortunate that Russell has chosen to present these out-dated and potentially dangerous examples.

The section on the chemistry of the green star[1ae] starts off with a muddle. Chemical equations are presented showing the formation of singly ionised barium monochloride, $BaCl^+$. Yet, as Russell correctly indicates, the main species responsible for the green colour of barium flames is $BaCl$, the neutral barium monochloride molecule. The formation of $BaCl^+$ would not favour the production of green light.

The discussion of the chemistry of the red star[1af] makes the interesting point that the presence of chlorine promotes the volatilisation of $SrCl_2$, which subsequently dissociates to form $SrCl$. Oddly enough, Russell lists $SrOH$ as the main species responsible for the red colour in Sr flames. This is true for laboratory flames coloured with strontium salts,[20] but is unlikely to be so for chlorine-rich pyrotechnic flames.

Rather crudely drawn diagrams are presented to illustrate the spectra of green[1af] and red[1ag] stars. These spectra could be confusing, because

the wavelength range extends well into the invisible near-infrared region of the spectrum. As a consequence, the main feature in the spectrum of the green star is a huge peak in the near infrared.

The next chapter discusses gerbs and wheels. One would have expected to find gerbs included in the chapter on fountains. According to Lancaster's glossary, the distinguishing feature of a gerb is its having a choke, whereas fountains may or may not be choked. In this book, the gerb is evidently distinguished from a fountain on the basis of a gerb having propulsive properties.[1ah]

The discussion of wheels introduces the term "Catherine Wheel", which Russell uses for any firework wheel.[1ai] This is consistent with the definition in Lancaster's glossary.[3e] It is noteworthy that in Alan St. Hill Brock's day the use of "Catherine Wheel" was evidently restricted to the firework that consists of a long, thin case coiled in a spiral around a central disc.[21a] This firework has very little in common with wheels that are driven by gerbs or drivers, and it deserves a name of its own. According to Brock, the French call it *Pastille*. Brock wrote "at one time, the latter name (i.e., Catherine Wheel) was also applied to the larger, compound wheels seen in displays".[21a] It seems that the once-specific English term has reverted to its former non-specific usage, and naturally this leads to confusion. The section in Russell's book on the construction of wheels[1ai] begins with a description of the manufacture of "Catherine wheels (pin wheels)", which are clearly "pastilles". We are then told, "Catherine wheels with diameters up to 50 cm are readily available". In this reviewer's experience wheels of this size are not constructed in the way Russell describes but are built with a number of drivers fixed to the wheel's rim.

Chapter 10, titled "Special Effects", does not deal as one might perhaps expect with fireworks in the motion picture industry but with a collection of topics including quick match, plastic fuse, lances, set pieces, flash and noise effects, whistles, smoke puffs, coloured smokes and electrical firing. It would be tedious to go through all these in detail, but a few remarks should be made. In the discussion of quick

match we are presented with a third version[1aj] of the equation for the burn rate of Black Powder. The constants are different again from those in the previous two,[1k,1s] but we still find the units of one parameter being taken from the metric system and those of the other from the British.

In this book the term "quickmatch" refers to what the Americans call "black match"[2f] and what the British[21c] used to call "raw match:" cotton wick impregnated with gunpowder, prepared by treating the cotton wick with a paste of gunpowder and starch, gum or dextrin. This burns relatively slowly unless it is enclosed by a loosely fitting paper tube or "pipe". Raw match so enclosed was once called "quickmatch"[21b,2g] or "piped match",[3f] terms that were consistent with both the performance and the construction. According to Lancaster's glossary,[3g] however, "quickmatch" and "raw match" are now synonymous. This is another example of British firework terminology having lost some of its precision since the time of Brock.

In the discussion of piped match it is assumed that the increase in burn rate happens because "the paper pipe serves to trap some of the evolved gases and so increases the ambient pressure, thereby significantly increasing the rate of burning." A calculation of the expected increase, with the very generous assumption of an ambient pressure of 100 psi, produces a "theoretical burning time" of 28 seconds per metre. Russell admits that the actual burn rate is at least 100 times greater than this, and states "secondary effects play an important role".[1ak] The primary reason for the increased burn rate of piped match is that the "pipe" confines the flame, providing a "fire path" that forces hot gases and sparks along the surface of the enclosed match.[22,23]

The section on lances returns to the subject of coloured flames with a short discussion of the production of blue. The green colour of copper-containing flames in the absence of chlorine is erroneously attributed to "free copper atoms",[1al] when it is actually produced by $CuOH$.[24] Curiously, the green bands of $CuOH$ are mentioned in passing later in this section.

A section on flash and noise effects contains a discussion of inorganic oxidizers. Some of the statements made are rather strange: "In practice, copper salts are not commonly used because of the difficulty involved in their ignition".[1am] It could be argued that this is a very economical way of summarizing the shortcomings of the copper salts of oxidizing anions. The statement could, less charitably, be described as vague and confusing. A table of inorganic oxidants[1an] includes ammonium dichromate, despite its available oxygen content being correctly given as zero.

The brief chapter on safety includes the statement "in any free country the inhabitants have the choice between purchasing and lighting their own fireworks, or leaving it to the professionals".[1ao] One can only agree. By this standard many citizens of the USA, and most citizens of Australia, do not live in a free country. In the final chapter on British fireworks legislation Russell notes the banning of the sale to the general public of bangers, fireworks containing bangers, aerial shells and maroons, and shells or maroons preloaded into mortars. Britain, too, seems well on the way to losing its status as "a free country" in this regard.

The bibliography at the end of the book is remarkable for its omission of the two works most relevant to the book's subject: Conkling's *Chemistry of Pyrotechnics*[25] and the Kosankes' and Jennings-White's *Lecture Notes for Pyrotechnic Chemistry*.[26] It would be interesting to know why these, and Shidlovskiy's classic textbook,[27] were left out while Brauer's book,[28] which is of very little relevance, was included.

In summary, this book fails to meet the expectations raised by the publisher's description. A book intended for the guidance of students should be accurate and consistent, and it should provide references to the literature. This book does not meet these very basic requirements. It would be disappointing enough to find so many shortcomings in a self-published work; one certainly does not expect to find them in a book published by the Royal Society of Chemistry. In publishing the book in its present state the RSC has grossly neglected its obligations to its readers and to the book's author.

With careful revision and the inclusion of appropriate references, this book could become a useful introduction to the chemistry of fireworks. Meanwhile, readers seeking instruction in this subject should look elsewhere.[25, 26]

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Events Calendar

Pyrotechnics and Fireworks

Pyrotechnic Chemistry Course

April or May 2001, Fort Halstead, UK

Contact: Ken Kosanke
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    Phone/FAX: +970-245-0692
    email: ken@jpyro.com
    web: www.jpyro.com

Pyrotechnics Guild Int'l Convention

Aug. 4–10 2001, Appleton, WI, USA

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    web: www.pgi.org

4th Int'l Autumn Seminar on Propellants, Explosives and Pyrotechnics

Oct. 25–28 2001, Shaoxing, China

Contact: Dr. Chen Lang
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    email: webmaster@iaspep.com.cn
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28th Int'l Pyrotechnics Seminar

Nov. 4–9 2001, Adelaide, Australia

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    web: www.intlpyro.org/IPS28/

6th Int'l Symposium on Fireworks

Dec. 3–7 2001, Orlando, FL, USA

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2nd Int'l Disposal Conference

Nov. 9–10 2000, Linköping, Sweden

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Non-Lethal Weapons and Applications (Nicht-lethale Waffen und Wirkmittel) [Note the course language is German.]

Nov. 14–15 2000, Oberpfaffenhofen, Germany

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Röhthenbach, Germany
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                 wb/wb0807.html

5th Int'l Symp. & Exhib. on Sophisticated Car Occupant Safety Systems "Airbag 2000+"

Dec. 4–6 2000, Karlsruhe, Germany

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27th ISEE Conference on Explosives and Blasting Technique

Jan. 28–31 2001, Orlando, FL, USA

Contact: Lynn Mangol
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Univ. Pardubice – 4th Seminar "New Trends in Research of Energetic Materials"

Apr. 11–12 2001, Pardubice, Czech Republic

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12th Int'l Symp. on Chemical Problems Connected with the Stability of Explosives

May 14–18 2001, Sweden

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32nd Int'l Annual Conf. ICT "Energetic Materials – Ignition, Combustion and Detonation"

July 3–6 2001, Karlsruhe, Germany

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3rd Int'l Symposium on Heat Flow Calorimetry for Energetic Materials

Sep. 18–20 2001, Frenck Lick, IN, USA

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Name of Event

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