Journal of Pyrotechnics

Issue 21, Summer 2005

Policy Board Members:

Ettore Contestabile Canadian Explosive Research Lab 555 Booth Street Ottawa, Ontario K1A 0G1, Canada	Keith Hudson, Director Dept. of Applied Science University of Arkansas at Little Rock Little Rock, AR 72204, USA	Gerald Laib, Code 4440C Sr. Expl. Appl. Scientist, NSWC Indian Head Div., 101 Strauss Ave. Indian Head, MD 20640, USA
Wesley Smith Department of Chemistry Brigham Young Univ. – Idaho Rexburg, ID 83460, USA	Barry Sturman 6 Corowa Court Mt. Waverley, VIC 3149 Australia	Roland Wharton Health and Safety Laboratory Harpur Hill, Buxton, Derbyshire SK17 9JN, United Kingdom

Managing Editor: Ken Kosanke, PyroLabs, Inc., 1775 Blair Road, Whitewater, CO 81527, USA

Technical Editors for this issue:

Arthur H. Barber, III Springfield, VA, USA	Frank Eisenträger, Clariant Germany	Patrick Miller, Hardin-Simmons Univ., Abilene, TX, USA
David Chapman, Health & Safety Lab., Harpur Hill, Buxton, UK	Ron Hancox, Keilor East, Vic, Australia	Michael Podlesak, WSD-SSL – DSTO Edinburgh, SA, Australia
Paul Cooper Albuquerque, NM, USA	Keith Hudson, UALR, Little Rock, AR, USA	Warfield Teague, Dept. Chem., Hendrix College, Conway, AR, USA
Joseph Domanico, Edgewood CB Ctr (Pyro. Team) Aberdeen PG, MD, USA	Will Meyerriecks Tampa, FL, USA	Michael Wilson. North Eltham, Vic, Australia

Direct Editorial Concerns and Subscription Requests to:

Journal of Pyrotechnics, Inc.
Bonnie Kosanke, Publisher
1775 Blair Road
Whitewater, CO 81527, USA
(970) 245-0692 (Voice and FAX)
email: bonnie@jpyro.com

CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is felt to be important for the reader to be duly cautioned. Without the required training and experience no one should ever experiment with or use pyrotechnic materials. Also, the amount of information presented in this Journal is not a substitute for necessary training and experience.

A major effort has been undertaken to review all articles for correctness. However, it is possible that errors remain. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

Table of Contents

Issue 21 Summer 2005

A Review of the Chemistry and Dynamics of Pyrotechnic Whistles
Matthew L. Davies 1

Air Blast TNT Equivalency for Rolls of Paper Toy Caps
K. R. Mniszewski and K. L. Kosanke 13

Optical Studies of Combustion Chamber Flame in a Hybrid Rocket Motor
Andrew B. Wright, Jason E. Elsasser, M. Keith Hudson, and Ann M. Wright 21

Choked Flow, a Frequently Misunderstood Term Lawrence Weinman 31

Special Materials in Pyrotechnics: IV.[1] The Chemistry of Phosphorus and its Compounds
Ernst-Christian Koch 39

Impact Sensitiveness Analysis of Pyrotechnic Flash Compositions
S. P. Sivapirakasam, M. Surianarayanan, P. Nagaraj, G. S. Venkataratnam 51

Spectral Study of Metallic Molecular Bands in Hybrid Rocket Plumes
K. L. Maxwell and M. K. Hudson 59

Communications:

Note on "Metal Monochloride Emitters in Pyrotechnic Flames –
Ions or Neutrals?" by Barry Sturman 71
Review by F. J. Feher of: *The Chemistry of Explosives* by Jacqueline Akhavan 72
Review by K. Kosanke of: *Color, An Introduction to Practice and Principles*
by Rolf G. Kuehni 74
Review by John R. Steinberg of: *Pyrotechnic Chemistry* by Journal of Pyrotechnics 75
Review by Bernard E. Douda of: *Pyrotechnic Chemistry* by Journal of Pyrotechnics 78
Review by Tony Cardell of: *Pyrotechnic Chemistry* by Journal of Pyrotechnics 79

Author Instructions 70

Editorial Policy 30

Errata 38

Events Calendar 36

Sponsors for Current Issue 80

If you want to receive titles and/or abstracts for future issues by email, send a note to bonnie@jpyro.com. You will then receive this information about two weeks before the next issue is ready to mail.

Publication Frequency

The *Journal of Pyrotechnics* appears approximately twice annually, typically in mid-summer and mid-winter.

Subscriptions

Anyone purchasing a copy of the Journal will be given the opportunity to receive future issues on an approval basis. Any issue not desired may be returned in good condition and nothing will be owed. So long as issues are paid for, future issues will automatically be sent. In the event that no future issues are desired, this arrangement can be terminated at any time by informing the publisher. Additional discounts are available for payment in advance for issues of the *Journal of Pyrotechnics*. Contact the publisher for more information.

Back issues of the Journal will be kept in print permanently as reference material.

A Review of the Chemistry and Dynamics of Pyrotechnic Whistles

Matthew L. Davies
Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, UK

ABSTRACT

Although the first efforts in understanding pyrotechnic whistles began over fifty years ago, there is still no firmly established mechanism that accurately describes their operation. This review describes the progress made and the current state of knowledge of combustion phenomena in whistle devices. In addition, investigations into identifying alternative safer fuels and additives to increase the striking audio-visual features of these devices are also reported. Finally, it is concluded that despite these great advances in understanding pyrotechnic whistles, there is still some doubt as to their true operating mechanism.

Keywords: pyrotechnic whistle, combustion mechanism, oscillatory combustion, acoustics

Introduction

Although most pyrotechnic items produce some audible effect, for whistles, sound is the primary effect. The first published description of pyrotechnic whistles is that of Amédée Denisse;[1] one British Authority[2] says they were first used at the Crystal Palace displays in London. Whilst no specific date is given, it is likely to be in the early 1850s. In any case, it seems safe to say that whistles are a development of the late nineteenth century and were very popular by the beginning of the twentieth century. The original compositions were based on potassium picrate mixed with an oxidiser, usually potassium nitrate, to control the burning rate and reduce the likelihood of explosion. Picrate whistles are still made in some countries.[3]

Many authors[4,5] have described the use of picrate whistles (and coloured stars made with picric acid) as too shock-sensitive to be used in fireworks mortar shells. However, for many years, the Italo-American manufacturers used enormous numbers of picrate whistles as shell garnitures.[3] Nowadays, picric acid (a close relative of TNT) and its salts are rarely found in any kind of commercial product in Europe or the US as they have a reputation for being very hazardous. One of the earliest "shock-safe" alternatives, potassium chlorate–gallic acid, is more sensitive to friction than potassium picrate.[3] Whistle compositions are almost as explosive as flash powder in the loose powder form; the original "whistling chasers" used a loosely loaded whistle composition for the report and a pressed composition for the acoustic effect.

The use of picric acid has many drawbacks. Firstly, heavy metal picrates are sensitive primary explosives comparable to the materials found in blasting caps. For this reason, picric acid should not come into contact with the brass sieves, lead ramming blocks and similar tools commonly used in firework factories. Iron and steel are also to be avoided because of the spark hazard. Instead, a dedicated set of aluminium tools is the only practical option for working with picrates.[3] Secondly, the price of picric acid has risen sharply in recent years due to the decline in its use, and a technical grade is usually not available. Finally, picric acid and soluble picrates are powerful yellow dyes, which are messy to handle, and they have a bitter taste (the name picric is derived from Greek and means bitterness). As stated by Lancaster, "*Picric whistles are not popular with firework makers mainly because no-one cares to work with them.*"

Contemporary whistle compositions are made of a benzoate or similar fuel and a perchlorate oxidiser, usually the potassium salt in both cases. Current whistle compositions are still sensitive to shock and friction and must be handled with care.

Serious incidents involving whistle composition and whistle devices are known.[6] The first was an explosion of approximately 3 kg of a loose charge (composition unknown), which destroyed processing equipment at a government explosives manufacturing facility in New South Wales, Australia. The second incident occurred when a consolidated column of whistle composition (about 20 g) in a metal cylinder exploded in a soldier's hand, fragmenting the cylinder and severing a number of his fingers. There is also a recorded case of a fireworks demonstrator being killed when a pyrotechnic whistle that was being deliberately operated in a vest he was wearing (and located over his heart) exploded.

Fortunately, many different aromatic compounds have been found that will burn in a suitably oscillatory manner when combined with a chlorate or perchlorate oxidiser. Cost and availability are of paramount importance for commercial firework production. Gallic acid is still in use and the Chinese reportedly use phthalate salts but today the most common whistle fuels are sodium salicylate and the benzoates of sodium and potassium. The potassium perchlorate–potassium benzoate mixture is probably as safe as any composition in this class.[7] Sometimes, catalysts, such as iron oxide or other transition metal compounds are added to these whistle compositions to alter the pitch or increase performance.[8] It has become popular in the last 10 years to add titanium to whistles, which produces a "silver tail" without much change in the sound. Degn[9] was the first to introduce this effect in 1973.

Whistle tubes are not pressed completely full; an empty space about half an inch long (13 mm) is customary at the open end to produce the sound. The sound will vary somewhat with the length and diameter of the tube, but only a limited amount of tuning can be achieved, about 0.5 to 5.0 kHz,[10] depending on chimney length. Tubes of larger diameter produce a louder noise but a point of diminishing returns is reached very quickly. Large whistles are more likely to explode and are much more destructive when they do so. Therefore, whistling components, both in consumer and in display fireworks, rarely exceed half inch inside diameter. Whistles may be combined with practically any other type of firework and are especially popular in fountains, wheels and aerial shells. Benzoate and salicylate whistle compositions are characterised by low cost, high-energy output, and (except when they contain metal powders) low light output. These properties have made them increasingly popular as propellants in some tube items and as bursting charges in aerial shells.

Few investigators have contributed to the current state of knowledge of the mechanisms involved in pyrotechnic whistle chemistry but three authors have made significant progress in the area. A review of their work is set out below.

Early studies

Maxwell[11] studied pyrotechnic whistles extensively and has written an authoritative treatise on their behaviour and the possible mechanism of sound production. Maxwell made most of his measurements with a 70:30 potassium perchlorate–potassium benzoate mix, but also investigated mixes of 60:40 potassium picrate–potassium nitrate, 25:75 gallic acid–potassium perchlorate and 70:30 potassium dinitrophene–potassium nitrate. His most important findings are summarised in Figures 1 to 5.

Figure 1 shows that the frequency of the main component of the sound falls continuously as the length of the tube above the burning surface increases. Maxwell constructed a constant-frequency whistle by applying the coachman's lamp principle. He used a telescoping case with the upper portion resting on a shoulder of the burning mix. As the mix was consumed, the upper case descended, maintaining a constant throat. Figure 2 shows that the mix burns faster at higher whistle frequencies and burns fastest if not constrained to whistle at all.

Acoustic output, shown in Figure 3, increases somewhat faster than the cube of the diameter. Maximum acoustic output for the potassium perchlorate–benzoate system, as indicated in Figure 4, occurs at critical proportions of the ingredients. The proportions do not produce the maximum burning rate but correspond closely to stoichiometry for the reaction:

$$4\,C_6H_5COOK{\cdot}3H_2O + 15\,KClO_4 \rightarrow 26\,CO_2 + 22\,H_2O + 15\,KCl + 2\,K_2CO_3$$

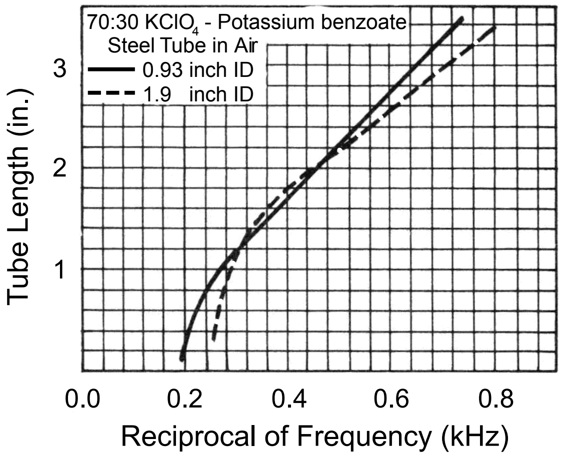


Figure 1. Effect of open tube length on whistle frequency.[11]

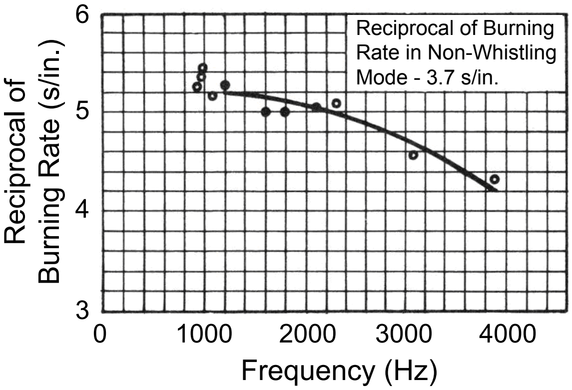


Figure 2. Effect of whistle frequency on burning rate.[11]

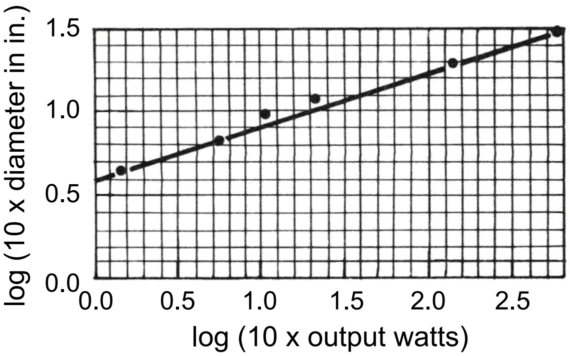


Figure 3. Effect of whistle diameter on acoustic output.[11]

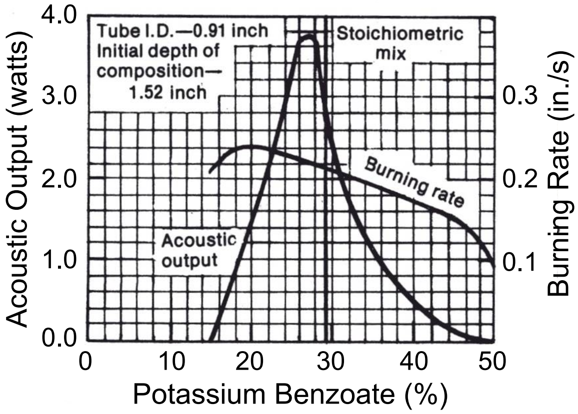


Figure 4. Effect of whistle composition on acoustic output and burning rate.[11]

A stoichiometric mixture is comprised of 70.8% potassium perchlorate and 29.2% potassium benzoate. Figure 5 shows that the burning rate of the whistle mix decreases as the surrounding pressure falls.

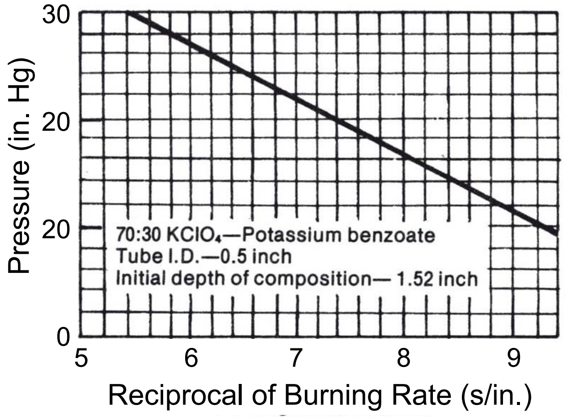


Figure 5. Effect of pressure on whistle burning rate.[11]

A Mechanism for Pyrotechnic Whistle Operation

Maxwell completed his work with an hypothesis for a possible mechanism of burning of pyrotechnic whistles. From the work described above, Maxwell proved that a whistling composition burns intermittently. Each time the composition surface is ignited, a pressure wave rises in the tube. When the pressure wave reaches the end of the tube, part of it passes out of the tube and part is reflected back into the tube as a rarefaction wave. When the reflected wave reaches the burning surface, the increased pressure causes the whistle composition to burn faster. This produces a pressure wave, which rises in the tube, beginning the process over again. Maxwell recognised that these waves of compression and rarefaction are what cause the composition to burn intermittently, but he stated that the exact mechanism is not clear.

This open organ pipe model appears to cause some confusion in later literature. The open organ pipe model represents a half-wave resonator with two low impedance boundaries[12] where the ratio of the upper harmonic to the fundamental frequency is termed the modal ratio, which follows a simple arithmetic progression. While the experimental data show such a relationship between the mode frequencies, they do not fit the half-wave resonator model, which yields unrealistically low acoustic propagation velocities when calculated as the product of wavelength and frequency, with the wavelength equal to twice the effective chimney length. This problem was addressed later by Wilson.[13]

A Mechanism for Pyrotechnic Whistle Combustion

A further point made by Maxwell in his article is that the variation in pressure on the burning surface is small (typically less than 7 to 14 kPa, i.e., 1 to 2 psi). This fluctuation cannot possibly account for the intense fluctuations in burning rate for a composition that is not abnormally sensitive to pressure when compared with propellants and other compositions.

Maxwell ascertained that spin had no effect on the burning rate, which suggests that whistles burn with a solid surface. In addition, he pointed out that whistling compositions are porous since they consist of consolidated crystals; this is confirmed by the fact that there is a complete lack of solid residue left in the burnt-out tube of a whistle. It is thus suggested that there is a connection between whistling power and the presence of a solid porous burning surface composed of fine crystals. Maxwell pointed out that the small crystals of chlorate, perchlorate or the salts of organic acids will decrepitate in a flame; this latter fact is also mentioned by Lancaster.[5]

On the basis of these observations, Maxwell suggested the following "mechanism" for the combustion of pyrotechnic whistles:[11]

"*The combustion of a whistling composition, whether in a tube or in the form of a pellet, involves the explosion of crystals as an essential part of the process. If the composition is not contained in a suitable tube, these crystals will explode in a random fashion and the products of combustion will flow from the surface at a uniform rate and no definite note or indeed any sound of appreciable intensity will result. If however, the composition is contained in a suitable resonating tube, the flame will be forced in and out of the surface by alternate waves of compression and rarefaction and every time it is forced into the surface a fresh mass of crystals will explode.*"

Significant Advances

The results of this literature survey suggest that until Wilson[14] published his findings in 1998, little work had been conducted in the area of pyrotechnic whistle chemistry since Maxwell presented his comprehensive findings in 1952. Wilson's paper details experiments carried out at the Aeronautical and Maritime Research Laboratory, DSTO, Australia, where a working theory was developed to describe the combustion mechanism of pyrotechnic whistles. Also, in the interests of safety, an investigation was undertaken to determine the reasons why pyrotechnic whistles can explode during combustion.

Wilson and co-workers experimentally investigated a number of the possible causes of explosion of whistle compositions. These included: shock propagation, mechanical disintegration, pressure-induced deflagration through the voids and the "flash-down-the-side" phenomenon. Their findings are included here for completeness and to give an understanding of some of the properties of pyrotechnic whistles.

Shock Propagation

An exploding bridgewire detonator was initiated on the surface of a column of whistle composition that had been compressed in a brass tube. The entire mass was consumed in the resulting explosion but no indentation of the witness plate occurred, and the brass cylinder fragmented into large longitudinal shards, typical of a pressure burst. From this it was concluded that although the whistle could be initiated by shock and that it would release a large amount of energy, propagation by shock in the whistle composition (detonation) did not occur.

Mechanical Disintegration

Mechanical crush tests of whistling composition revealed that it exhibits similar physical integrity to gunpowder and is apparently physically stronger than many other pressed pyrotechnic formulations. The burning fronts of a number of whistles were each subjected to a single dynamic peak pressure pulse ten times the estimated peak sound pressure within the tube by firing flash composition (1 g) at a distance of 2 cm from the tube mouths of functioning whistles. If these articles were susceptible to explosion by this mechanism, a pressure pulse of this magnitude should have been sufficient to cause disintegration and explosion of the columns. Of the articles tested, none performed abnormally.

Pressure-Induced Deflagration

The rate of burning of many gas-producing pyrotechnic formulations increases as the pressure at the combustion front is increased. This is mainly due to preheating of the reactants ahead of the combustion front by product species flowing through the voids present in the consolidated composition. If the magnitude of the environmental pressure becomes sufficiently great, the burning rate may increase and result in explosion of the column. However, a series of tests showed that although a five-fold increase in the mass burning rate can be observed between 20 and 200 kPa(a) (3 to 30 psia), the gradient of the curve increases only marginally thereafter up to 700 kPa(a) (100 psia). This is consistent with $\alpha < 1$ in Vieille's burning rate equation[15] and shows that the composition tested is not abnormally affected by pressure applied statically to the combustion front[15]. Although this series of tests was not comprehensive (the authors concede that the results could be very different if the environmental pressure could be increased rapidly) they go on to show that the assumption of the existence of void space in whistle compositions is not necessarily valid.

Flash-Down-the-Side

The propensity for pyrotechnic whistles to explode can partly be explained by the observation that both whistle fuels, potassium benzoate and sodium benzoate, exhibit self-lubricating properties; the compounds consist of flat platelets, which exhibit a slippery feel. It has been well documented[16] that many consolidated pyrotechnic compositions, including flares, tracers and smokes, will explode if steps are not taken to ensure that combustion cannot take place between the outer surface of the composition and the wall of the container into which the composition is pressed. With whistle compositions containing about 30% by mass of the fuels described above, it is to be expected that their wall bonding properties might be considered poor when compared to other pressed pyrotechnic compositions.

Wilson carried out a series of experiments that involved thermally cycling a whistle tube and then applying a drift load until displacement of the composition occurred. He showed that the mean displacement load required was halved when the tube had undergone thermal cycling. Thermal cycling easily breaks the already weak bond, and this introduces a slight gap between the composition and its tube. At any stage during the combustion process, hot combustion products could be forced down this gap and combustion could occur on a greatly increased surface area resulting in explosion. That explosion would inevitably result due to failure of the wall-to-composition bond was experimentally demonstrated.[13]

Combustion Mechanism of Pyrotechnic Whistles

To investigate intermittent combustion phenomena, Wilson and co-workers, undertook a series of experiments whereby static pressure was applied to a burning whistle. The results indicated that the environmental pressure did not affect the combustion frequency over the range from 20 to 200 kPa(a) (3 to 30 psia). Additional observations from this work were that at sub-atmospheric pressures the whistles were observed to produce increased amounts of excess particulate carbon during the reaction. They also found that combustion was not reliably sustained at pressures below 20 kPa(a) (3 psig).

To investigate the effect of incident pressure waves on burning pyrotechnic whistle composition, Wilson[14] performed a second series of experiments whereby two whistles—designed to produce different frequencies—where placed in opposition to each other. He found that the incoming sound pressure waves of the high frequency article increased the combustion cycle rate at the burning front of the low frequency article, confirming Maxwell's assertion[11] that cyclic incident pressure waves are probably an important part of the combustion mechanism.

It was clear from the two sets of experiments that pressure waves (but not static pressure) could control the combustion frequency of pyrotechnic whistles, but still one factor—the total energy output—could not be explained by pressure alone. It was calculated that during each pressure pulse, created during whistle operation, 3.6×10^{-4} g of whistle composition was consumed. To understand how such a small mass of consolidated pyrotechnic powder, consisting of discrete particles of fuel and oxidiser, could react at a rate fast enough to produce the observed acoustic output, Wilson[14] examined the reaction chemistry.

From his experiments on the effect of spin, Maxwell[11] proposed that whistle compositions burn in the solid phase. If this is correct, it is highly unlikely that a reaction rate that produces pressure pulses of the observed frequency and magnitude could be established. Both potassium perchlorate and potassium benzoate decompose at similar temperatures, which means that once this critical temperature (about 450 °C) is reached in either cycle of the whistle system, the potassium perchlorate will release oxygen and the potassium benzoate will produce hydrogen and free carbon at the same time resulting in an explosive mixture being compressed at the combustion front by the incoming pressure wave. Clearly ignition and explosion of the mixture would follow, and the outgoing pressure wave would cause rarefaction and a temperature decrease at the combustion front with a consequent suppression of the burning rate. The cycle would then be repeated. Some experimental confirmation of this proposed mechanism is given by Wilson; principally he showed that the decomposition temperatures of the fuel and oxidiser must be closely matched for the composition to both burn and whistle. He has shown that carbon plays an important role in the acoustic and thermal efficiency of whistle systems by identifying that the gradual substitution of carbon by nitrogen in the aromatic ring of the fuel has the effect of reducing the acoustic output. As a final point, the ability of whistle compositions to form the proposed explosive fuel-to-oxygen mix under specific conditions of temperature and pressure could also contribute to their tendency to explode by the flash-down-the-side phenomenon, where the configuration of the burning surface is relatively uncontrolled.

Refining the Model

In a later article, Podlesak and Wilson[13] extended the previous work and proposed an hypothesis that attempts to account for the observed high levels of explosive and acoustic power of pyrotechnic whistles.

Quarter-Wave Resonator

The acoustic model proposed by Maxwell[11] is not exactly clear. At first, he likened the pyrotechnic whistle to an open organ pipe, which under commonly understood terminology would represent a pipe with an open-open boundary and therefore a half-wave resonator, but later he describes the acoustic pulse generation process as in an open-closed pipe, which is a quarter-wave resonator. The half-wave resonator would infer unrealistically low sound propagation velocities. To overcome this problem, Podlesak and Wilson[13] model the acoustic behaviour of the device using a quarter-wave resonator, where the reaction front of the burning pyrotechnic composition provides both a high acoustic impedance boundary and an acoustic energy source, and the open end, or mouth, of the whistle chimney provides a low impedance boundary. A half-wave resonator with a low impedance boundary at both ends yields a 1, 2, 3, 4 … modal ratio as in the observed harmonic frequencies. The modal ratio for a quarter wave resonator, however, normally follows a 1, 3, 5, 7 … relationship, but it can be shown[17] that nonlinear distortions in the acoustic wave output are capable of producing the observed 1, 2, 3, 4 … modal ratios.

Thermo-Acoustic Feedback Mechanism

Podlesak and Wilson[12] proposed a "thermo-acoustic feedback" mechanism for pyrotechnic whistle operation. This is based on previous evidence that the acoustic pressure wave trapped in the chimney controls the combustion process and that the energy of the combustion feeds back positively into the trapped acoustic wave.

Energetics

By comparison with flash composition, Wilson[13] showed that a pyrotechnic whistle device is a very efficient converter of chemical to acoustic energy. They also concluded that the mechanism of sound production from the consolidated burning front within an open tube is evidently different (producing a greater acoustic impulse) from that when the composition deflagrates in the normal sound-producing mode (i.e., when filled as a loose powder and ignited under confinement).

Having considered the consumption of mass and the fuel–oxidiser decomposition temperatures, Wilson[13] turned to looking at the decomposition products of selected pyrotechnic whistle fuels.

Thermal decomposition analyses in a reducing atmosphere were carried out experimentally by Wilson.[13] It was found that highly energetic fuel species were formed during the dehydration reactions. This is thought to be a key factor in the oscillatory burning environment in whistle compositions even though it has not been directly observed at the combustion front of a whistle device. The observation that the whistle fuels exhibit a lower onset decomposition temperature than the ignition threshold temperatures of their pyrotechnic compositions, suggests that the physico-chemical properties of the fuels might be altered within the reaction zone immediately before ignition of the fuel-oxidant mixture occurs. This is not an uncommon observation in pyrotechnics technology. It is normally an ongoing process occurring just ahead of the combustion front. The reactants are preheated as a result of the permeability of the consolidated whistle composition, particularly when combustion occurs under pressure. However, as mentioned earlier, whistle compositions have been shown to have low permeability due to the physical properties of the aromatic fuels.[14] This has the effect of restricting the mass of reactants to a very thin layer at the burning front.

Wilson's thermal decomposition analysis yielded the results shown in Table 1.

Table 1. Thermal Decomposition Analysis Results of Wilson.[14]

Reactant	Combustible Volatiles Present
Potassium benzoate	CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO
Sodium salicylate	CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO, C_6H_5OH

Complete details are given in Wilson's article,[14] which shows that the relative abundance of the species in Table 1 varied with decomposition temperature. An important result of this study was the finding that about 40% by mass of elemental carbon and carbon compounds was present in the condensed residue. When examined under a Scanning Electron Microscope (SEM), it was found that the residue was mostly in the form of carbon spheroids with a diameter of approximately 1 µm (Figure 6). The discovery that these carbon spheres were, in the most part, hollow led to speculation about the dynamics of the formation process. Although no direct evidence is given, Wilson[13] speculated that at the moment of destruction of the aromatic ring (when temperatures at the combustion front are high) the carbon thus released is probably in the finely divided form. This would result in a hot and highly reactive form of carbon and combustible gases. The carbon forms the hollow spheres and the hot hydrocarbon gases likely fill the sphere's voids. This new and relatively energetic mixture, when burning during the compression cycle in the oxygen gas (evolved from the decomposing oxidiser) might account for the observed acoustic efficiency and explosive power of pyrotechnic whistles.

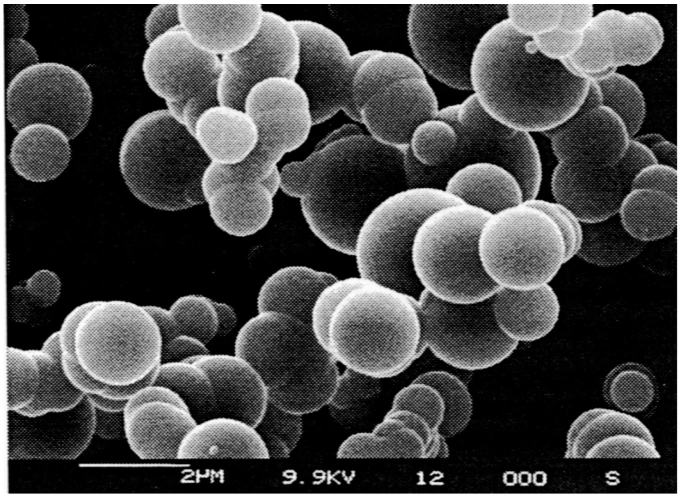


Figure 6. SEM electron micrograph of carbon spheres resulting from the thermal decomposition of whistle fuel in a reducing atmosphere.[13]

Some Other Aspects of Pyrotechnic Whistle Chemistry

Contributions from several other authors will now be considered. Their work has not been left until the end because it is considered to be less valuable; rather it is less critical, chronologically, in describing the advances made in understanding the chemistry and dynamics of pyrotechnic whistles.

Variations in the Performance of Pyrotechnic Whistles

All of the work described so far in this review has considered binary mixtures of pyrotechnic fuel and an oxidiser to produce the whistle effect. Hardt[3] reports that it has become common practice to add titanium to whistles, producing a silver tail without much change in the acoustic properties. Titanium does not cause a significant increase in the sensitiveness of finished benzoate or salicylate whistles, although it is especially important to be careful about friction when charging loose powders containing this metal.

The transition from a binary to a tertiary mixture demands a focus on safety concerns. As reported previously, the amount of energy stored in a pyrotechnic whistle composition is large, and under the correct conditions it is possible to increase the burn rate such that a transition from normal burning to a rapid deflagration occurs. Therefore, in *practical* applications, only large diameter powders (such as the reported titanium additive) are added to whistle compositions. Domanico *et al.*[8] investigated the effects of adding a third component to a binary whistle composition using very finely ground materials. They emphasise that this is done for scientific purposes only and that many of the compositions used were "very sensitive to ignition", although they fail to explain whether this enhanced sensitivity is demonstrated through a friction or impact mechanism. They are so sensitive that they are not suitable for commercial purposes. Additional work would need to be performed to take these formulations to a level where they could be used in a practical way.

Domanico and co-workers performed four sets of experiments. The first considered the effect of replacing a proportion (5%) of the potassium benzoate of the control mixture with an alternative organic fuel. The burn rate and the peak noise level were recorded (see Table 2). In all cases, the control had the highest noise level recording but did not exhibit the fastest burn rate. One organic fuel, stearic acid, gave a slower burn rate and a significantly smaller acoustic output, whilst the remainder of those tested burned faster and also gave lower acoustic output than the control composition.

Table 2. Organic Fuel Results from Reference 8.

Additive	Burn Rate		Peak All Band Pass Level
	(in./s)	(mm/s)	dB
Stearic acid	0.181	4.60	113.0
Control	0.207	5.26	120.7
Terphthalic acid	0.210	5.33	117.5
Red gum	0.227	5.77	118.7
Sucrose	0.250	6.35	119.2
Charcoal	0.270	6.86	119.2

The second set of tests carried out by the group showed the effect of replacing some of the potassium benzoate with inorganic fuels (Table 3). Again, nearly all of the additives increased the burn rate with the exception of manganese, whilst none had the effect of increasing the acoustic output.

Table 3. Inorganic Fuel Results from Ref. 8.

Additive	Burn Rate		Peak All Band Pass Level
	(in./s)	(mm/s)	(dB)
Manganese	0.207	5.26	119.5
Control	0.207	5.26	120.7
Magnesium (–50 mesh)	0.213	5.41	120.1
Iron powder (–20 mesh)	0.214	5.44	119.8
Cadmium	0.217	5.51	103.3
Antimony	0.222	5.64	119.3
Nickel	0.224	5.69	119.2
Zinc	0.227	5.77	120.7
Copper	0.230	5.84	119.1
Titanium	0.232	5.89	120.5
Aluminium (–60 mesh)	0.232	5.89	119.9
Iron-silicon (50/50)	0.247	6.27	120.3
Silicon	0.261	6.63	120.6
Iron (–325 mesh)	0.261	6.63	121.2
Boron	0.262	6.65	119.2

A third series of tests used different oxidisers as the additive. In a similar fashion to the previous results, nearly all had the effect of increasing the burn rate (see Table 4). An insignificant increase in acoustic output was observed in two cases where the burn rate was also increased. These were for the oxides of copper and iron (in a later section it will be shown that the oxides of copper and iron can act as catalysts in these compositions).

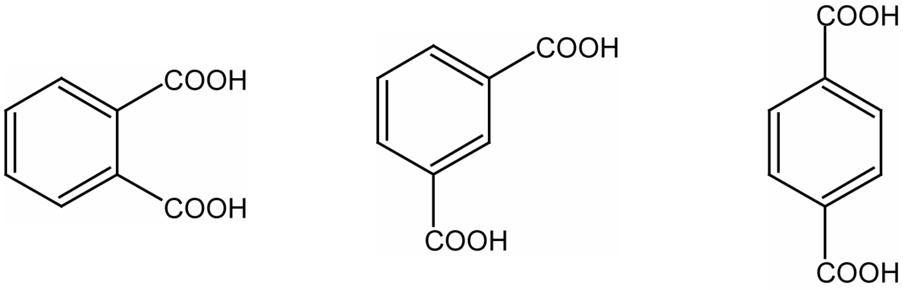
Table 4. Oxidiser Results from Reference 8.

Additive	Burn Rate		Peak All Band Pass Level
	(in./s)	(mm/s)	(dB)
Zinc oxide	0.199	5.05	119.7
Control	0.207	5.26	120.7
Cobalt oxide	0.242	6.15	119.8
Black Iron oxide	0.264	6.71	121.1
Titanium dioxide	0.272	6.91	119.1
Red iron oxide	0.274	6.96	120.9
Red copper oxide	0.275	6.99	120.8
Manganese dioxide	0.285	7.24	119.3
Lead dioxide	0.286	7.26	120.8
Lead trioxide	0.294	7.47	120.0
Black iron oxide	0.295	7.49	121.4
Black copper oxide	0.303	7.70	120.1

Domanico and co-workers also reported on the visual observations of tertiary mixtures. Each additive appeared to have a unique signature within the exhaust plume of the whistle. Colour additives were successfully used in combination with some of the tertiary mixtures to produce unique whistling devices. They showed that with the right proportions a whistle device can be manufactured that produces both noise and a colourful display of light.

Alternative Whistle Fuels

Amons[18] gives a basic account of the use of phthalic acid salts in whistle compositions. The author begins with a discussion on the basic properties of the materials and moves on to de-



a) Phthalic acid *b) iso-phthalic acid* *c) terephthalic acid*

Figure 7. The(a) ortho-, (b) meta-, and (c) para-isomers of phthalic acid.

scribe a series of experiments that use these alternative fuels. He then points out a few requirements for the successful use of phthalic acid salts in whistle compositions.

Whilst modern pyrotechnic whistles contain an aromatic carboxylic acid salt as a fuel with a suitable oxidiser such as potassium chlorate or potassium perchlorate, some reference works[5,20] have mentioned the salts of phthalic acids (alternatively benzene dicarboxylic acids). These are polybasic benzene carboxylic acids, which make them somewhat more complicated than their monobasic counterparts. The polybasic form has 3 isomers (Figure 7), each with different properties. The ortho isomer is phthalic acid, the meta form is iso-phthalic acid and the para isomer is terephthalic acid. The meta form was not investigated by Amons[18] because cost would prohibit its use as a pyrotechnic whistle fuel. When compared, terephthalic acid has the lowest solubility, which must be reckoned with when manufacturing the salt.

Potassium hydrogen terephthalate, which is only sparingly soluble in hot water, is used extensively by Chinese[20,21] manufacturers. As a consequence, it is less likely to absorb atmospheric moisture. Potassium hydrogen phthalate is another candidate for whistle fuel. It is readily soluble in water, which makes it easier to manufacture than the terephthalate salt.

The two salts described previously are formed by a partial neutralisation of the acid. A different salt is formed by complete neutralisation of the acid. In this instance, the ortho isomer is unusable as it absorbs moisture strongly. Even with the salt of the para isomer, neutralisation in excess acid is recommended to reduce moisture absorption problems. These salts make good whistle fuels but they have more affinity to absorb moisture than the hydrogen phthalates formed by partial neutralisation. This is critical since even a small amount of absorbed moisture can have a significant effect on performance.[19]

When the performances of phthalic acid salts as whistle fuels were compared to conventional compositions, Amons found that the particle size specified for traditional mixes was not appropriate when used in 8- and 10-mm inside diameter whistles tubes. The composition did not burn with a whistle; rather, a sputtering sound with intermittent whistling was observed. This observation seems to be more significant with mixtures containing stoichiometric quantities of ingredients; it was less significant with excess oxidiser. The irregular burning was overcome to a certain extent by the addition of a suitable catalyst such as iron(III) oxide or copper(II) oxychloride. Performance was also shown to improve by further refining the particle size of the fuel, but a catalyst may still help to improve performance further.

Phthalic acid salts, though more costly to manufacture, have significant advantages over their benzoic acid cousins. Potassium hydrogen terephthalate has a low hygroscopicity, which reduces the chances of poor performance if it is stored in damp conditions. It is also much easier to reduce potassium hydrogen terephthalate to a fine powder (the ortho form is more difficult in this respect). But, perhaps the most significant finding of Amons' report is that the alternative whistle composition potassium perchlorate–potassium hydrogen terephthalate is much less sensitive to friction (by about half) than the traditional potassium perchlorate–potassium benzoate mixture.

Curious Observations

In a communication to this journal Weinman,[21] described a "screeching" sound heard during the burning of bulk whistle composition (such practice is common at facilities that use pyrotechnics and require destruction of excess inventory). This observation was also made by Öztap [23] and Wilson.[6]

The disposal was carried out following a standard procedure. A trail of the excess composition was laid out on the ground? 3 m long, 50 mm wide and 7 mm thick and ignited from one end. The expected "whoosh" sound was not observed but was instead replaced by a sound, which was said to mimic that of a high-pitched whistle but with lower intensity. This observation strongly suggests that this technique should not be used to destroy unwanted whistle compositions.

A further "curious observation" was that made by Webb,[24] who noted that a whistle can be heard even when a thin layer of composition is coated on the inside of a tube and initiated.

These observations seem to contradict the proposed mechanisms that have been described in previous sections. However, the incidents have not been investigated beyond these first initial tests, and it is quite likely that there is some unrelated explanation for the observed phenomena. Nonetheless, these are curious observations worthy of further investigation.

Concluding Remarks

Preliminary investigations to ascertain the functioning properties of pyrotechnic whistles were carried out by Maxwell over 50 years ago. From his studies, Maxwell determined relationships between:

- Frequency and tube length
- Frequency and composition
- Acoustic output and tube diameter
- Acoustic output and ingredient ratios
- Sound quality and tube diameter

He also established the effect of frequency and the effect of lowering the ambient pressure on burning rate. In completing his authoritative elucidation on pyrotechnic whistles, Maxwell proposed a mechanism by which pyrotechnic whistles might be expected to burn. Although Maxwell made some attempt to explain the combustion mechanism of pyrotechnic whistles in terms of "the explosion of crystals," it is not a satisfactory explanation of either the reaction dynamics or the reaction chemistry.

The work was taken up by Wilson some years later and shortly thereafter Podlesak developed an acoustic model which showed that acoustic pressure doubling at the reaction front may be critical to the coupling between acoustic waves trapped in the whistle chimney and the combustion process. Temperature and pressure switching is currently believed to control the decomposition rates of the whistle fuel and oxidant. This results in a two-stage combustion cycle. The first quiescent stage involves the decomposition of fuel to form highly reactive species in an oxygen-poor atmosphere through acoustically-lowered pressure and temperature. These highly reactive species might take the form of hollow carbon spheres and hydrocarbon gases, which fill the voids of the spheres during this quiet phase of the combustion cycle. The second active stage involves the rapid combustion of the new fuel species in an oxygen-rich atmosphere through acoustically-elevated temperature and pressure. The energy released in the active cycle feeds back positively into the acoustic wave trapped in the chimney, but its final amplitude will be governed by the balance of energy injected by the combustion and the radiation and visco-thermal losses. A further limiting factor in the acoustic output is that the amplitude of the internal wave cannot exceed vacuum conditions during the pressure doubling of the rarefaction phase. Further investigations are required to confirm the mechanism proposed by Podlesak and Wilson.

In addition to the mechanisms of combustion, other aspects of pyrotechnic whistle operation have also been reviewed here. Domanico et al. showed that tertiary mixtures of whistle composition could be made that produce colourful displays of light without adversely affecting the acoustic output. Amons investigated alternative fuels that could help to improve the safety of these devices. Finally a review of a communication from Weinman showed that despite all of the intense research by the aforementioned investigators, the various theories of the dynamics and chemistry of pyrotechnic whistles is still widely open for debate.

Acknowledgments

I would like to thank Mike Wilson, of Pains Wessex Australia, and Rutger Webb of TNO Prins Maurits Laboratory, The Netherlands, for helpful discussions during the preparation of this review. I would also like to thank The Combustion Institute for allowing me to reproduce Figures 1 to 5 of this paper from Maxwell's 1952 article and DSTO, Australia for allowing me to reproduce Figure 6.

References

1) A. Denisse, *Feux d'artifice sifflants*, Poulenc frères, Paris, 1888.
2) A. Brock, *A History of Fireworks*, Harrap, London, 1949.
3) A. P. Hardt, *Pyrotechnics*, Pyrotechnica Publications, Post Falls, ID, USA, 2001.
4) G. W. Weingart, *Pyrotechnics*, 2nd ed., Chemical Publishing, NY, USA, 1947, p 14.
5) R. Lancaster, *Fireworks, Principles & Practice*, 3rd ed., Chemical Publishing Co., New York, 1998.
6) M. A. Wilson, Private communication, 2004.
7) T. Shimizu, *Fireworks: The Art, Science and Technique*, Pyrotechnica Publications, Austin, TX, USA, 1981.
8) J. A. Domanico, G. V. Tracy, M. N. Gerber, "Pyrotechnic Whistle Performance Variations", *Proc. 22nd Int'l Pyrotechnics Seminars*, CO, USA, 1996, pp 489–495.
9) R. Degn, "Pyrotechnic Whistle and Method of Making", US Pat 3,712,223, Jan 23 1973.
10) F. Ryan, "The Production of Music with Pyrotechnic Whistles", *Journal of Pyrotechnics*, No. 7, 1998, pp 1–10.
11) W. R. Maxwell, "Pyrotechnic Whistles", *4th Symposium on Combustion* at MIT Cambridge, MA, USA, 1952. Reprinted in *J. Pyro*., No. 4, 1996, pp 37–46.
12) N. H. Fletcher and T. D. Rossing, *The Physics of Musical Instruments*, Springer Verlag, NY, 1991.
13) M. Podlesak and M. A. Wilson, "A Study of the Combustion Behaviour of Pyrotechnic Whistle Devices (Acoustic and Chemical Factors)", *J. Pyro*., No. 17, 2003, pp 19–34.
14) M. A. Wilson, *The Combustion and Explosion of Pyrotechnic Whistling Composition*, Report DSTO-TR-0717, Aeronautical and Maritime Research Laboratory, Defence Science and Technology Organisation, Melbourne, Australia, 1998.
15) A. Bailey and S. G. Murray, *Explosives, Propellants & Pyrotechnics*, Brassey's New Battlefield Weapons Systems & Technology Series, Vol. 2, Brassey's (UK), 1989.
16) M. Podlesak and M. A. Wilson, "Study of Explosive and Combustion Behaviour of Pyrotechnic Whistle Devices – Acoustic Factors*", Proc. Symposium on Explosives and Pyrotechnics*, April, 1999, Philadelphia, PA, USA.
17) J. W. S. Rayleigh, *The Theory of Sound*, Vol. 2, Dover, NY, 1945.
18) R. Amons, "Consideration of Alternate Whistle Fuels", *J. Pyro*., No. 6, 1997, pp 65–67.
19) J. A. Conkling, *Chemistry of Pyrotechnics Basic Principles and Theory*, Marcel Dekker, NY, 1985.
20) R. Dilg, "Whistle While You Work*" American Fireworks News*, No. 74, 1987, p 4.
21) Private communication between R. Amons and A. Hahma, reported in reference 15.
22) L. Weinman, "A Curious Observation during the Burning of Bulk Whistle Composition", *J. Pyro.*, No. 17, 2003, p 79.
23) S. Öztap, "The Pyrotechnic Whistle and its Applications", *Pyrotechnica XI*, June, 1987.
24) R. Webb, TNO Prins Maurits Laboratory, Private communication, 2004.

Air Blast TNT Equivalency for Rolls of Paper Toy Caps

K. R. Mniszewski, FX Engineering, Inc., Hinsdale, IL, USA
and
K. L. Kosanke, PyroLabs, Inc. Whitewater, CO, USA

ABSTRACT

A study of the explosive output of rolls of paper toy caps, in variously sized assemblages, was conducted. The testing has shown that toy cap rolls are clearly capable of producing a powerful explosive effect if initiated with a sufficiently energetic event. TNT equivalencies based on toy cap composition mass ranged from approximately 10 to 80% for different sized configurations, with the largest equivalences being produced by the largest assemblages of toy caps tested. The results of this study are disturbing, considering that the toy caps (even in bulk packaging) have a UN classification of 1.4S, which by definition should not produce significant blast or fireball effects when initiated. Thus perhaps it is appropriate to consider whether the UN test protocol is adequate for this product.

Keywords: air blast, TNT equivalence, toy caps, Armstrong's mixture, UN test

Introduction

A few years ago, an accident occurred in a toy factory in California. Several workers were killed and others were injured when a number of bulk cases of rolls of paper toy caps exploded with great violence, sufficient to produce traumatic amputations of limbs. The workers involved were repacking the bulk cases of toy caps at a workstation using a blister pack machine. A number of enforcement and regulatory agencies were involved in the accident investigation and reconstruction. However, while it seemed quite clear that the toy caps were the cause of the accident, this was hard to reconcile with the fact that the bulk cases of toy caps were classed as Explosive 1.4 S.

No quantitative information had been produced by the primary investigating agencies regarding the expected explosive output of bulk quantities of toy caps, and a literature search was unsuccessful in locating such data. As part of the continuing accident reconstruction effort, an estimate of the effective amount of energetic material involved in the explosion was sought. The technique used was to determine the TNT equivalence of various quantities of the toy paper cap rolls. As with any condensed phase explosion, a number of effects are produced, including the production of an air blast wave, fireball, ground shock and projectiles. To estimate the explosion yield, the most useful effect is the air blast wave. This paper reports on that study.

Paper Toy Cap Materials

Toy cap composition is typically composed of Armstrong's mixture, generally consisting of approximately 67% potassium chlorate, 27% red phosphorus, 3% sulfur and 3% calcium carbonate by weight.[1] To form the toy caps, the composition is prepared wet and extruded onto a strip of paper as a series of tiny dots, which are then laminated over with another layer of paper and wound into rolls. The dry mixture is extremely sensitive to accidental ignition[1–2] and, even in small quantities (1 gram), is reported to have significant explosive strength (approximately 23% TNT air blast equivalent when initiated using a electric match).[3]

Careful weight audits of sample cap materials in this case were conducted to determine the average mass of toy cap composition per cap. This was determined through a comparison of: 1) the mass of a collection of paper dots, taken from the rolls of caps from the areas between the individual caps using a paper punch; and 2) the mass of a collection of individual toy caps harvested using the same paper punch that was used to produce the paper dots. The result was an average energetic material content of approximately 1.85 milligrams per cap.

The bulk quantities of this particular brand of cap were packaged 100 caps per roll, 12 rolls per thin-walled plastic tube, 12 tubes per paper package, and 100 packages per corrugated cardboard case. Thus a case contained 1.44 million individual toy caps, estimated to contain a total mass of 2.66 kg (5.86 lb) of energetic material.

TNT Equivalence Concept

A blast wave from an explosion can damage structures and injure personnel in the area. From an analysis of this damage an estimate of the charge size involved in an explosion can be calculated. While complicating factors must be considered, such as reflections off structures in the area, the geometry of the charge, etc., the technique is viable and quite useful.[4] However, when practical, the direct measurement of explosive output is preferred. Since in this case there was a sufficient (but not abundant) supply of the paper toy caps, the direct measurement approach was taken.

The information to follow is based on reference 5; however, much the same information can be found in other standard reference texts.[6,7] The ability of explosives to cause damage is often stated in terms of its TNT equivalence (*E),* which can be defined as the ratio of the mass of TNT (trinitrotoluene) to the mass of a test explosive that produces the same explosive output under the same conditions, specifically

$$E_{Test} = \frac{M_{TNT}}{M_{Test}} \tag{1}$$

where M is charge mass, E is usually expressed in terms of percent, and a common measure of explosive output is peak air blast overpressure.

Using this technique typically begins with measuring the peak overpressure, p^o, produced at a measured distance from a test explosive charge of known mass. Then the amount of TNT that would be needed to produce the same peak overpressure is determined using accepted "standard" data for a charge of TNT under similar test geometry.

The comparison between the measured output of a test explosive charge and that from TNT is accomplished using a so-called mass-scaled distance, Z, defined as

$$Z = f_d \cdot \frac{R}{M^{1/3}} \tag{2}$$

where R is the distance between the center of the explosive charge and the point of measurement of its output, and f_d (called the atmospheric transmission factor for distance) corrects for the effect of differing air densities. This atmospheric transmission factor is

$$f_d = \left(\frac{P_a \cdot T_o}{P_o \cdot T_a} \right)^{1/3} \tag{3}$$

where P and T are the absolute atmospheric pressure and temperature. The subscript a denotes ambient conditions at the time of the measurement, and o denotes the standard conditions of the TNT blast data, specifically 1.013 bars and 288 K (15 ºC).

Procedurally, after one determines the peak air blast overpressure for the test explosive charge, it is converted to a relative peak overpressure, p^o/P_a. Then using the data and method of reference 5, the scaled distance, Z, is determined for which a standard charge of TNT (i.e., a spherical 1 kg charge of TNT exploded at 1.013 bars pressure and a temperature of 15 ºC) is known to produce the same relative overpressure as did the test explosive charge. Then, using the value of Z just determined, and the values of R, T and P that existed for the overpressure measurement of the test explosive charge, equation 2 can be rearranged to solve for the mass of TNT, M_{TNT}, which would produce the same peak overpressure under the same conditions as did the test charge. At that point, knowing both the masses in equation 1, the TNT equivalence can be calculated for the test explosive.

In cases where a booster (or initiating charge) is used, the output from that charge may contribute a significant portion of the overall explosive output. When that is the case, it is necessary to account for the booster's contribution. This can be done by measuring the explosive output of the booster exploding alone and calculating its TNT equivalence, Z_B. Knowing the explosive mass of the booster, M_B, equation 1 can be used to calculate the booster's equivalent mass of TNT, $M_{(TNT)B}$.

$$M_{(TNT)B} = Z_B \cdot M_B \tag{4}$$

Then in calculating the TNT equivalence for the test charge (less the contribution of the booster), the booster's equivalent TNT mass, $M_{(TNT)B}$, must be subtracted, and equation 1 becomes

$$E_{Test} = \frac{M_{TNT} - M_{(TNT)B}}{M_{Test}} \quad (5)$$

Paper Toy Cap Testing Program

First, a relatively soft initiator was devised for testing the cap materials. The intent was to provide a relatively strong shock without producing much in the way of high density fragments that could act as flyer plates. The first configuration tried was simply to insert an electric match (Daveyfire A/N 28 B) inside one of the tubes of toy cap rolls. This initiator would have been preferred because the explosive charge would be a single electric match with virtually zero explosive output; however, in three tests this initiator was unsuccessful in initiating a reaction of the toy caps.

The next igniter tried was a small acrylic tube filled to capacity with a large number of individual toy caps (obtained from a roll of caps using a paper punch) and carefully stacked on top of one another. After installing an electric match (Daveyfire A/N 28 B) in the tube, which rested against the bottom of the stack of toy caps, the tube was sealed on both ends with a small amount of hot-melt glue. The tube's dimensions (75 mm long, 6 mm ID and 9 mm OD) were chosen because it would fit snugly into the central hole in the rolls of paper toy caps. This initiator had the desirable characteristic of being solely composed toy caps; however, this initiator also failed to function.

A third initiator configuration was tried, in which the stack of toy caps mentioned above was replaced with a 1 gram charge of fireworks flash powder (70% potassium perchlorate and 30% pyro aluminum). The flash powder configuration performed quite nicely and was chosen as the initiator for subsequent testing. The construction of the initiator is shown in Figure 1.

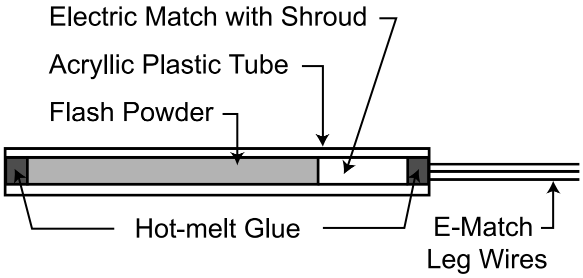


Figure 1. Sketch of the initiator chosen for use in the testing.

This initiator and a number of toy cap configurations were tested in a steel blast chamber (2.5 m in diameter and 5 m long). In each case the test explosive charge was suspended in the chamber approximately on its center axis. Two free-field piezoelectric pressure gauges (PCB model 137A12) were used to measure the side-on pressure from the test devices. The distances to the gauges were chosen to be commensurate with the size of the charges being tested; however, in each case the far gauge was at twice the distance of the near gauge, see Table 1. Digital oscilloscope records were made of the pressure-time history of each explosion.

A series of tests were conducted using increasingly larger assemblages of tubes of toy cap rolls. These configurations were constructed to approximate a right circular cylinder (actually having a hexagonal cross-section) with a height to diameter ratio reasonably close to one. The initiator was always inserted into the middle of one of the tubes of 12 rolls of paper toy caps, and that tube of toy caps was placed at the approximate geometric center of the test charge. Tests were conducted using 7, 28.5, 74, 183, and 676 tubes of toy cap rolls. Figure 2 is a photo of two of the configurations tested, those with 28.5 and 74 tubes. Because there were a limited number of toy caps available, only the test configuration with 7 tubes of toy caps was conducted more than once. Most of the explosion testing was conducted inside the blast chamber described above. The blast chamber tests were conducted at an air temperature of approximately 5 ºC and at a pressure of 0.87 bar (at an elevation of 4600 feet, in western Colorado). Testing of the configuration using 676 tubes of toy cap rolls had to be moved outdoors because, based on the previous

Table 1. Raw Data from the Paper Toy Cap Testing Program.

Number of Tubes of Toy Caps (a)	Composition Mass (b) (kg)	Total Charge Mass (c) (kg)	Near Blast Gauge		Far Blast Gauge	
			Distance (ft) (d)	Pressure (psi) (e)	Distance (ft) (d)	Pressure (psi) (e)
0	0.001 (f)	n/a	2	1.71	4	0.71
				1.52		0.79
				1.82		0.87
0 (g)	0.001 (f)	n/a	2	1.57	4	0.72
7	0.016	0.10	2	4.84	4	1.81
				4.15		1.59
				4.22		1.86
7 (h)	0.016	0.10	2	3.07	4	1.38
28.5	0.063	0.41	3	3.19	6	1.38
74	0.164	1.06	3	6.53	6	2.76
183	0.406	2.16	3	10.2	6	4.11
676	1.50	9.67	6	17.3	12	8.84
1200 (i)	2.66	17.2	10	15.9	20	5.26

a) Each tube of caps had 12 rolls of 100 toy caps for a total of 1200 individual toy caps.

b) This is only the mass of toy cap composition, exclusive of their inert components and initiator. The amount of composition per cap averaged approximately 1.85 milligrams.

c) Total mass of toy caps, including paper and packaging, but exclusive of the initiator. The total mass of a tube of toy caps averaged approximately 14.3 grams.

d) To convert feet to meters, divide by 3.28.

e) This is peak air blast pressure to three significant figures. To convert psi to kPa, multiply by 6.89.

f) No toy caps were used; this was an initiator only, and it used 1.0 gram of a flash powder.

g) No toy caps were used; this was an initiator only, but it was wrapped with paper approximating the confinement provided by the rolls of toy caps

h) This was the same as the other 7 tube tests, but used an initiator with only 0.5 gram of flash powder.

i) This was one case of toy caps in an unaltered condition, with the exception of placing an initiator in a tube of toy caps in the approximate center of the case. The case consisted of 100 packages of 12 tubes of toy caps.

testing, it was thought it might exceed the safe capacity of the blast chamber. In addition, one final test was performed that used a full case of the bulk toy caps, which consisted of 1200 tubes of toy caps, for a total of 1.44 million individual caps (100 packages of 12 tubes of 12 rolls of 100 toy caps). This test also needed to be conducted outdoors because of the large size of the test charge. The outdoor testing was conducted with the test charges and free field blast gauges at approximately 3 feet above the ground, and at an air temperature of approximately 27 °C and a pressure of 0.86 bar.

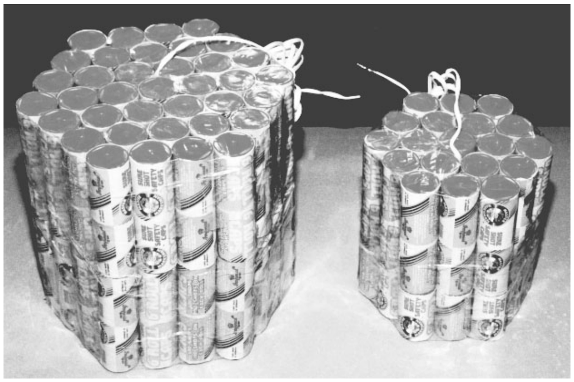


Figure 2. A photograph showing two of the toy cap test configurations, those containing 74 (left) and 28.5 (right) tubes.

Results

The three tests conducted using the chosen initiator in the absence of any toy caps produced an average overpressure TNT equivalency of 47%, see Tables 1 and 2. Given the construction of the initiator, the result is reasonable. With a mass of 1.0 gram of flash powder, the booster weight contribution ($M_{(TNT)B}$ in equation 5) used in subsequent testing was 0.47 grams TNT equivalent. One test was performed to determine whether the stronger confinements produced by insertion of the initiator into a roll of paper toy caps would result in a significant difference in its performance (see Table 1). While the peak air blast overpressures were less than the average from the three previous tests of the initiator, the overpressures were within the range of the three previous measurements. Thus it was concluded that the effect of wrapping the initiator with paper (or rolls of toy caps) was negligible.

The results of testing the assemblages of toy caps are presented in Tables 1 and 2, including the calculated TNT equivalencies—based on the mass of toy cap composition alone and on the total mass of the rolls of caps—for the variously sized configurations. After three tests of the smallest test charge (7 tubes of toy cap rolls), an additional test again using 7 tubes of caps was conducted; however, in this case the flash powder charge in the initiator was reduced to only 0.5 gram. The result was a significant drop in the explosive output of the toy caps. This suggests that the 1.0 gram initiator, at best, may only be marginally sufficient for the purpose. However, there was not enough space inside the rolls of toy caps to have used an initiator with a larger charge of flash powder, and the use of a non-pyrotechnic (high explosive) initiator was thought to be excessive for the purposes of these output tests.

Table 2. TNT Equivalence Results for Paper Toy Caps.

Number of Tubes of Toy Caps [j]	Equivalent TNT Mass (kg) [k]	TNT Equivalence (%) [l]	
		Composition Only [m]	Total Toy Cap Mass [n]
0 [o]	0.00047	47	n/a
7	0.0024	15	2.4
7 [p]	0.0012	9	1.4
28.5	0.0057	9	1.4
74	0.020	12	1.9
183	0.056	14	2.6
676	0.81	54	8.4
1200 [q]	1.9	81	12.5

j) Each tube of caps had 12 rolls of 100 toy caps for a total of 1200 individual toy caps.

k) Based on peak air blast overpressure and correcting for the contribution of the initiator. This is the average of the results from the near and far blast gauges. When multiple tests were performed, this is the overall average of the results. The results are reported to two significant figures.

l) Calculated using the average of the near and far equivalent TNT masses.

m) Calculated based only on the mass of toy cap composition, but correcting for the initiator. The results are reported to the nearest 1%.

n) Calculated based on the total mass of toy caps, including paper and packaging, but correcting for the initiator. The results are reported to the nearest 0.1%.

o) No toy caps were used; this was an initiator only.

p) This was the same as the other 7 tube tests, but used an initiator with only 0.5 g of flash powder.

q) This was one case of toy caps in an unaltered condition, with the exception of placing an initiator in a tube of toy caps in the approximate center of the case. The case consisted of 100 packages of 12 tubes of toy caps.

The output from the smaller assemblages of paper toy caps (those comprised of 7 to 183 tubes and using the 1.0 gram initiator) ranged from 9 to 15% TNT equivalence based on composition mass, and there was no obvious trend in the data. This is in significant contrast with the results from the two larger assemblages (those comprised of 676 and 1200 tubes), which produced TNT equivalences of 54 and 82%, respectively, based on composition mass.

The physical debris produced in the tests of the smaller assemblages of paper toy caps consisted of a moderate amount of cap paper and unexpended caps, indicating the non-homogeneous nature of the rolls of toy caps and the incomplete propagation throughout the test charges. However, the amount of visible paper and unexpended caps present after the largest two test configurations (676 and 1200 tubes) was substantially less than in the smaller test configurations. This is consistent with a more complete propagation of the explosive reaction through the assemblages and accounts for the significantly higher TNT equivalencies obtained for these larger assemblages of toy caps.

The propagation mechanism involving the rolls of paper toy caps is not fully understood but is assumed to be one of sympathetic explosion, where the initiation of one cap may on average initiate one or more caps as a result. Given the construction of the cap rolls, the transfer mechanism may be one of impact through the thin paper separating the individual caps. Tube-to-tube transfer may be similar, through the plastic tube separations which are much thicker. To some extent, the efficiency of propagation was evidenced by the amount and nature of the debris left after each test. Larger charges were shown to be more efficient in their ability to propagate, as described above.

Differences in the shape of the overpressure decay curve (the portion of the air blast positive phase after reaching peak overpressure) change the efficiency with which the blast wave propagates in air. Thus the air blast TNT equivalences found at various distances from a non-TNT test charge depend on details of the shape of the blast wave produced by that explosive, as compared with a blast wave from TNT.[8] This is certainly true for this study, due to the non-ideal explosive involved and the non-spherical geometries to a lesser extent. A comparison of the air blast results in this toy cap study reveals that the far gauge consistently resulted in significantly higher TNT equivalences. (It was verified that this was not a calibration or other problem with the instrumentation.) Accordingly, in Table 2, the TNT equivalences reported are the average of the near and far gauge results. While this is a reasonable approach, it must be realized that had the gauges been placed at other distances than those in this study, the TNT equivalences would be somewhat different as well.

Both high and low speed video cameras were setup to record the two test explosions produced outdoors. However, in the first test (that using 676 tubes of caps) the unexpectedly large air blast shock cause a circuit breaker to trip-off, which caused the high speed video record to be lost. Other than that, the recorded results of both tests were quite similar although somewhat different in scale. Figure 3 is a series of 1/60 second video fields, with a shutter speed of 1/60 second, recorded using the low speed video camera. (The low speed video images are reproduced here because they were captured with a more appropriate *f*-stop setting and the images are more distinct.) The numbers on these images are the number of video fields elapsing after the first image, which was the last image recorded prior to the explosion. The field of view in the images, at the location of the explosion, is approximately 18 feet high by 26 feet wide (5.5 by 8 m). In image number zero, the full carton of paper toy caps and the near blast gauge have been highlighted with circles.

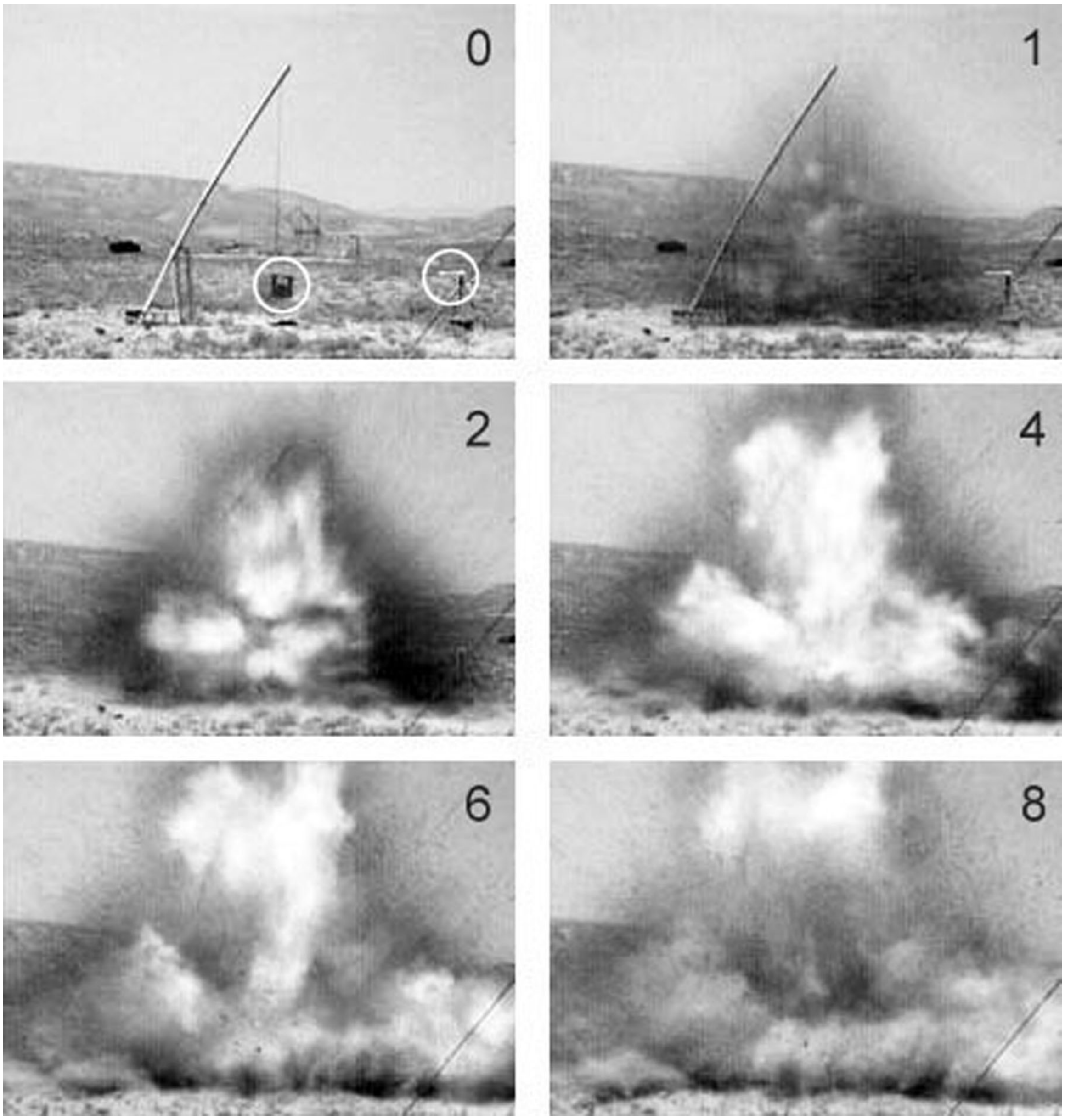


Figure 3. Video images just before and during the test involving a full case of paper toy caps. The field of view at the approximate distance of the explosion is 18 by 26 feet (5.5 by 8 m), and the numbers on the images are the number of 1/60 second video fields elapsing after the first image.

It is of interest to note that in the first image of the explosion (#1) that, while some of the debris from the explosion (appearing dark in the image) has been propelled to a diameter of approximately 16 feet (4.9 m), essentially no flash of light is discernable. In the next image (#2) the debris has expanded to approximately 21 feet (6.4 m), and a fireball has started to develop. In the next image (#4) the fireball has developed fully and thereafter decays. It is thought that the fireball is not part of the explosive reaction, but rather the burning in air of the finely shredded paper debris from the toy caps. This is consistent with the observation of a near total lack of paper debris after the explosion, including remnants of the heavy cardboard carton. The lack of a significant flash during the initial stages of the explosion and the subsequent development of a fireball was confirmed in the high frame rate video record.

Conclusion

Had greater quantities of toy caps been available for study, more tests could have been performed. This would have produced greater certainty in the results and other aspects of the case could have been investigated, such as identifying possible causes for the initiation of the caps in the accident. Nonetheless, the testing has shown that bulk quantities of paper toy cap rolls are clearly capable of producing a powerful explosive effect if initiated with a sufficiently energetic event. TNT equivalencies, based on toy cap composition mass, ranged from approximately 10 to 80% in different sized configurations, with the largest equivalences being produced by the largest assemblages of toy caps tested. This was unexpected, as the authors had thought that the opposite would likely have been the case, with very large assemblages tending to fail to efficiently propagate the explosion.

The results of this study are disturbing, considering that paper toy caps (even in bulk packaging) have a UN classification of Explosive 1.4S, which by definition should not produce significant blast or fireball effects when initiated. In the UN test protocol it is only required to initiate one item near the center of one case used in the testing. As part of this study of TNT equivalence, some very limited testing was performed in an attempt to learn how the accident might possibly have come to occur. During that testing, it seemed clear that a single toy cap functioning, or even a significant fraction of a single roll of caps functioning, was unlikely to have been sufficient to propagate well enough to produce the massive explosion that caused the fatalities or those explosions observed in the TNT equivalencies tests. Thus, it is understandable that the current UN test would conclude that the proper classification for the toy caps was Explosive 1.4S. Nonetheless, massive explosions certainly are possible (and have accidentally occurred at least once) for bulk cases of paper toy caps. This would generally not have been thought to be possible for items with a Explosive 1.4S classification. Accordingly, perhaps some consideration should be given to changes in the UN test protocol or the classification of paper toy caps.

Acknowledgments

The authors gratefully acknowledge P. Cooper and D. Chapman for providing comments on an earlier daft of this paper.

References

1) T. L. Davis, *The Chemistry of Powder and Explosives*, Angriff Press, 1970 [reprint of 1941 book published by J Wiley], p 105.

2) R. R. Rollins, *Potassium Chlorate / Red Phosphorus Mixtures*, Contract number DAAA-21-67-C-0682 for Picatinny Arsenal, available from Franklin Research Laboratories, (date unknown).

3) K. L. and B. J. Kosanke, "Explosive Limit of Armstrong's Mixture", *American Fireworks News*, No. 177, 1996.

4) R. Merrifield, J. Mackenzie, "Methodology for Estimating the Explosion Yield of Incidents Involving Conventional or Improvised Explosives", *Proceedings of the 8th International Symposium on the Effects of Interactions of Munitions with Structures*, Washington, D.C., 1997.

5) G. F. Kinney and K. J. Graham, *Explosion Shocks in Air*, Springer-Verlag, 1985.

6) W. E. Baker, *Explosions in Air*, Univ. of Texas Press, 1973.

7) P. W. Cooper, *Explosives Engineering*, VCH Publishers, 1996.

8) P. W. Cooper, "Comments on TNT Equivalence", *Proceedings of the 20th International Pyrotechnic Society Seminar*, 1994.

Optical Studies of Combustion Chamber Flame in a Hybrid Rocket Motor

Andrew B. Wright*, Jason E. Elsasser*, M. Keith Hudson*, and Ann M. Wright†

*Department of Applied Science, University of Arkansas at Little Rock (UALR), Little Rock, AR 72204 USA

†Department of Physics, Hendrix College, 1600 Washington Ave, Conway, AR 72032 USA

ABSTRACT

The oxygen injector head in UALR's labscale hybrid rocket motor has been redesigned to include a coaxially located optical port. This port permits viewing directly into the space in front of the fuel grain where combustion is initiated. It is designed to allow a visible-imaging fiber optic, a UV-Vis fiber optic, or an infrared fiber optic to be aligned coaxially with the motor. The imaging fiber optic shows swirling and pulsating flow fields, which indicate that one-dimensional flow model assumptions are not valid. The quartz fiber optic is used with a UV-Vis spectrometer to perform spectral studies using fuels doped with metals. It is demonstrated that the same species that are seen in the plume can be detected in the combustion zone, which permits comparison of species at the two end points of the combustion process.

Keywords: hybrid rocket motor, spectroscopy, flow patterns, metal emission spectra, combustion diagnostics

Introduction

A chemical hybrid rocket motor contains a solid, stationary fuel element and a fluid oxidant that is pumped into contact with the fuel. This is distinct from a liquid rocket motor where both the fuel (hydrogen) and the oxidant (oxygen) are mixed or a solid rocket motor where the fuel and oxidant are combined in the propellant grain.

In 1993, a labscale hybrid rocket motor facility, complete with computer control and data acquisition system, was designed and constructed at the University of Arkansas at Little Rock (UALR) (see Figure 1). This facility has aided the aerospace community in numerous studies on hybrid rocket motors including their possible future use

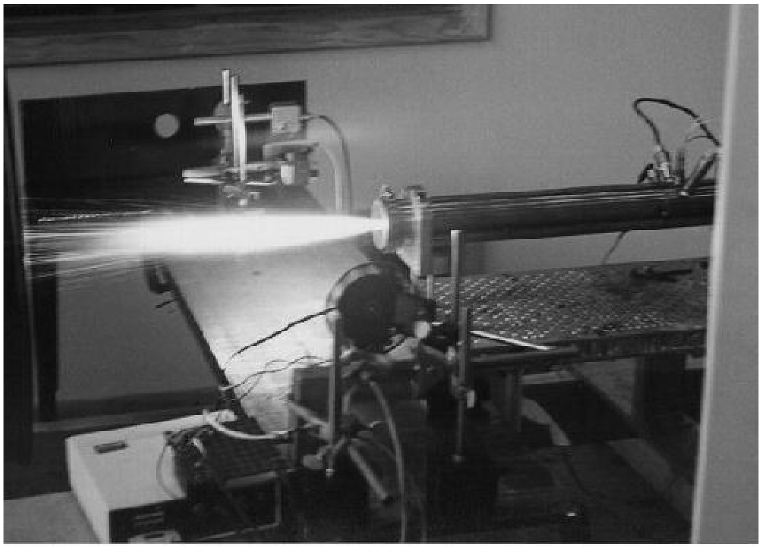


Figure 1. UALR hybrid rocket firing.

as boosters on the Space Shuttle Main Engine (SSME).[1] While these studies are of general interest, some may not be well known to the readers of this journal. For that reason, much of the introduction to this paper is devoted to briefly recounting those studies and providing literature references to them.

UALR's hybrid rocket motor uses hydroxyl-terminated polybutadiene (HTPB) as its fuel and gaseous oxygen as the oxidant. The rocket motor is operated in a controlled, variable oxygen-to-fuel ratio range of 1.5 to 4.5, by varying the oxygen mass flow in a range of 0.018 to 0.037 kg/s. At an oxygen-to-fuel ratio of 2.074, HTPB burns stoichiometrically to carbon monoxide (CO) and water vapor (H_2O). The temperature in the combustion chamber is above 3000 °C, providing sufficient energy for the atomization process.

Several studies were conducted using different spectral techniques. Spectral emission in the hybrid rocket plume was detected in the ultraviolet-visible (300–750 nm), near infrared (near IR) (750–800 nm), and mid-infrared (2–16 μm) regions,[2] and a baseline emission curve from 250 to 800 nm was produced.[3] The fuel was doped with metallic salts of varying concentration, and atomic line and molecular band emissions were measured, and intensity versus concentration curves for manganese, magnesium, and strontium were determined. Infrared studies were conducted with a Fourier-transform infrared (FTIR) spectrometer,[4] and work is underway to extend the infrared measurements to 1100 nm.

Absorption spectroscopy techniques were applied to determine nitrous oxide (NO) concentration and hydroxide (OH) concentration in the plume.[5,6] The OH concentration gives a measure of combustion efficiency and may be used in a feedback scheme to modulate the oxygen flow and to optimize the combustion efficiency during regression of the fuel. Although OH concentration has been measured only in the plume, pre-combustion chamber measurements might provide better control response.

Studies to characterize the physical parameters of the hybrid rocket such as pressure, plume flicker, acoustical output, and thrust have been performed at the UALR facility.[7,8] Additionally, pressure transducers have been placed in both the pre-combustion and the post-combustion chambers. The following studies have been completed: 1) correlation between the two pressure transducer signals; 2) preliminary analysis to determine chaos in the pressure signals, and 3) correlation between flicker in the plume and variations in the pressure signal. The frequency of oscillation is identical for the two pressure transducers and the plume flicker.

A novel ion detector was used to detect charged species in the plume.[9] This detector measures the current induced when the particles pass through a conducting cylinder. The induced current measurement can be used to determine what metallic species are present in the plume, and the ion detector signals have been correlated to the pressure signals. This has shown that downstream from the nozzle, the metallic ions dominate the response over the charge associated with combustion products, making the ion detector an excellent candidate for engine health monitoring.

In conjunction with the diagnostic measurements, the effects of energetic additives on thrust have been studied.[10] Guanidinium azo-tetrazolate (GAT) and amino-guanidinium azo-tetrazolate (AGAT) were added to the HTPB fuel mixture, and both additives increased the regression rate of the fuel.

NASA's John C. Stennis Space Center (SSC), a leader in exhaust plume diagnostics, uses plume spectroscopy for vehicle health management (VHM).[11] Diagnostics for VHM are provided by atomic spectral emission techniques. The measurement of excited atomic species in the motor plume can be correlated to the amounts of metallic species introduced by failures in engine components leading to predictions of possible failures. Most of these studies, however, have been conducted on liquid rocket motors. Should the space community adopt the hybrid rocket motor, which has a much more complicated plume, fundamental work must be performed to adapt these spectroscopic techniques.

Although UALR, SSC, and other rocket facilities have conducted extensive research on the external parameters of the hybrid rocket plume, no studies have been conducted viewing, characterizing, or collecting data from the pre-combustion chamber during firings (see Figure 2). Studies of the initial combustion zone would augment previous plume studies and offer informa-

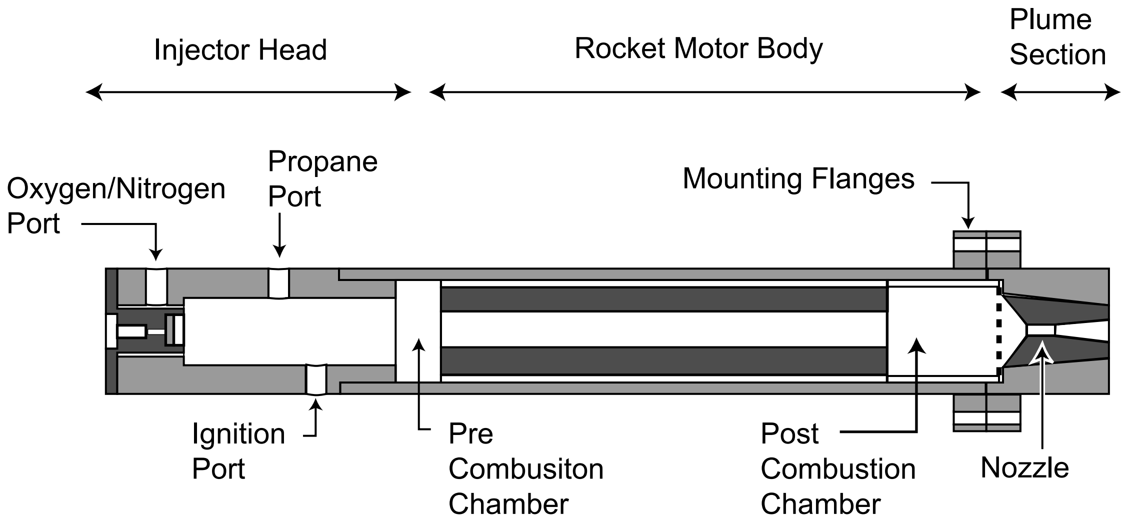


Figure 2. Schematic of UALR's labscale hybrid rocket motor.

tion for comparative analysis. Viewing the inside of the motor will provide oxygen-to-fuel ratio data and internal flow characteristics of a healthy engine.

Design

Injector Head

The oxygen injector head in UALR's lab-scale hybrid rocket motor is designed to include an optical port (see Figure 3).This port is located coaxially with the center-line of the rocket motor and allows direct viewing into the pre-combustion chamber (see Figure 2). A visual imaging fiber optic is used to transmit the image of the burning fuel grain to a charge-coupled device (CCD) camera. Alternately, an ultraviolet fiber optic is used to collect UV-Vis spectral data and transfer it to a spectrograph. Plans exist to observe the near IR region; however, difficulties with flicker make this measurement much more challenging than the other two measurements. Additional research and instrumentation will be required.[4]

The injector head design consists of two sections: the injector head shaft (IHS) and the fiber optic plug (FOP). The gas inlet ports are located on the side of the IHS so that the FOP could be axially located (see Figure 3).

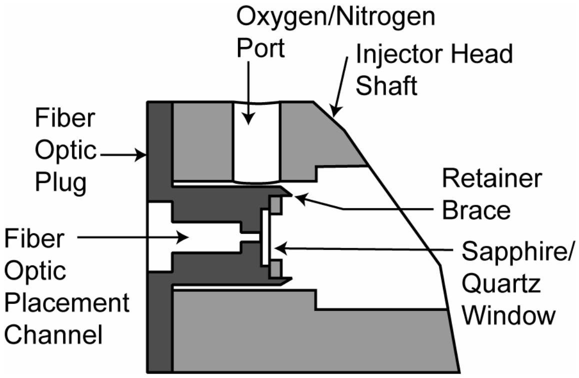


Figure 3. Cross section of injector head shaft (IHS) and fiber optic plug (FOP).

Protecting the fiber optics from the combustion chamber temperature and pressure was a primary design concern. A 2-mm thick quartz (for imaging or UV-Vis) or sapphire (for near IR) window separates the fiber optic from the combustion chamber pressures, temperatures, and reactive species. The FOP was designed to be easily removed, while maintaining the challenging sealing requirements. This design allows windows to be switched or cleaned without disassembling the rocket motor. O-rings are used to seal the FOP and the window, so that hot combustion gases cannot escape through the head of the motor.

Optical Systems

Two different optical setups have been used to date: imaging (borescope) and UV-Vis. The imaging optical system includes an imaging fiber optic (borescope), coupling devices, neutral density (ND) filters, a CCD camera, a video cassette recorder (VCR), and a television monitor (see Figure 4). A Hawkeye 17 focusing borescope is used to collect visual images. The borescope eyepiece is inserted into a ND filter holder that mounts to a bracket that supports the borescope and maintains the distance between the borescope eyepiece and the FOP window. Kodak Wratten gelatin film is used as the ND filter, which provides flat attenuation of light intensity across the visible spectrum. The CCD camera lens fits into the other side of the ND filter holder. A black and white CCD camera with NTSC output transmits the image to a VCR or TV. The images were not inverted by the borescope or the camera lens.

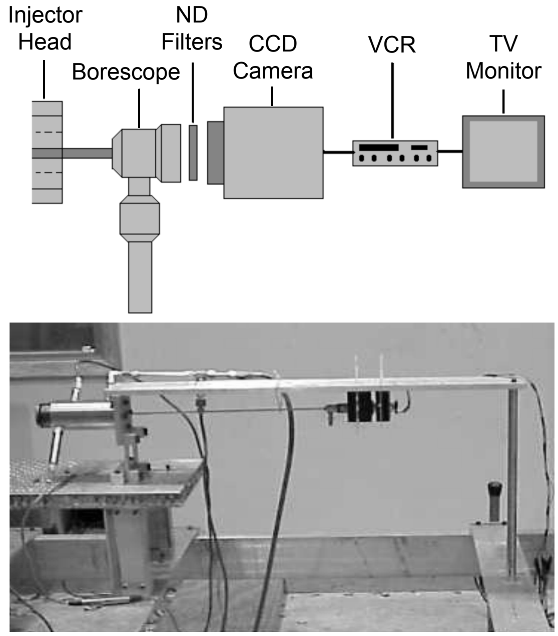


Figure 4. Schematic and picture of imaging system.

The UV-Vis system (see Figure 5) uses a quartz window in the FOP. For maximum transmittance efficiency, a 1-m long quartz fiber optic with 10:1 core/clad ratio is inserted into the FOP and connects to a SPEX270M spectrograph. The quartz fiber passes 300 to 750 nm light without distortion. The SPEX270M uses a grating to spread the incident light onto a 1024 pixel silicon photodiode array (PDA). A wavelength selector allows the wavelength at the center of the PDA to be set. The output of the spectrograph is interfaced to and controlled by a portable PC computer. The spectrograph system (for plume spectroscopy) has been described previously.[12]

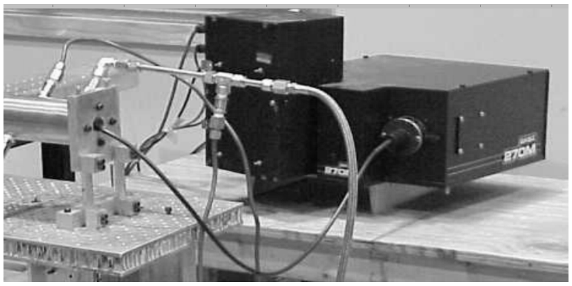


Figure 5. Picture of UV-Vis spectroscopic system.

Experimental

Imaging

Initially, eight experiments were performed, two each at chamber pressures of 1379 kPa (200 psi), 1724 kPa (250 psi), 2413 kPa (350 psi), and 3103 kPa (450 psi). The fuel used was HTPB cured using Desmodur N-100 (1,6-hexamethylene diisocyanate, Bayer) with 1% carbon added as an opacifier. The carbon provided particles that enhanced the visual images. Each firing lasted three seconds. Multiple firings were performed with the same fuel grain until the fuel was expended. Movies of representative firings are available for download.[13–15]

Steady state flow patterns occurred in less than one second after combustion began. The flow pattern in every firing indicated two effects: a clockwise rotational pattern about the axis of the motor and a pulsating pattern along the axis of the motor. The flow field was clearly three-dimensional and turbulent. At the end of each firing, the light at the center of the motor diminished and then intensified. This corresponded to the shutoff of the oxygen where the combustion became fuel rich.

The clockwise rotational pattern explains some observations of the fired fuel grains. The bore of spent fuel grains is generally smooth and circular. A one-dimensional flow along the bore would not generate these features, since variations in the fuel mixture would create lean and rich pockets at different points in the fuel, resulting in an uneven, pitted surface. However, the rotational flow field carries oxygen around the circumference of the grain such that more complete mixing occurs.

Many researchers have postulated a parabolic flow boundary layer along the grain.[4,16] This effect would appear much like water flowing down a drain, and it can be clearly seen in the current visual images.

There are two theories about how hybrid fuel grains burn. One theory presumes a double layer combustion in which the fuel melts and then vaporizes into a fuel/oxidant combination.[4] The other theory presumes that the fuel sublimes into a fuel/oxidant mixture.[16] Identifying the correct mechanism is important since the melting phenomena introduces combustion mechanistic steps and associated kinetic parameters (like rate constants) that may be very important as the model is scaled. Even though the melt layer may be small, it must be proven to be insignificant before it can be neglected. The rate constants associated with the melt layer may give rise to some of the combustion oscillations seen with hybrid rocket motors.

In a separate work,[17] it was discovered that liquid droplets of HTPB were present in UALR's hybrid rocket plume. In the current work, it appears in the visible images that a melt layer exists around the edge of the burning zone. Liquid droplets could not exist in the plume without a melt layer, and the visible images support this conclusion.

Including swirl in a theoretical model dramatically increases computational load.[18] It should be neglected unless the effect can be shown to be significant. However, failure to include the effects, if they exist, will result in underestimation of the key modeling features, such as thrust, specific impulse, and efficiency. The video images show definitively that this effect cannot be neglected in hybrid rocket motors.

Why the rotation was clockwise in all firings has not been explained. In a perfectly symmetric motor, there should be no predisposition for rotation to start in a particular direction, and it would be expected that the rotation would sometimes be clockwise and other times counterclockwise. The best explanation to date is that minor asymmetries in this particular rocket motor make clockwise the preferred rotational direction. For instance, the oxygen inlet may not be perfectly aligned with the motor center line.

The visual images show pulsations into the pre-combustion chamber. This can be seen by a brightening of the background light and by particulate matter moving toward the camera. The pulsating flow pattern is consistent with an expected longitudinal acoustic mode associated with a cylinder. The pressure measurements in both the pre-combustion chamber and the post-combustion chamber show evidence of acoustic modes among other oscillations.[7,8]

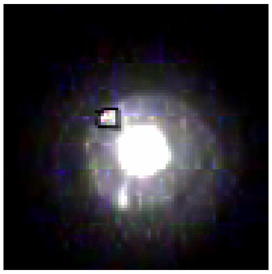
Since acoustic modes sometimes couple with the combustion process and give rise to chaotic behavior, chaos may exist in the hybrid rocket motor process. Preliminary investigation was made to detect chaos in the pressure signals, and, for the higher flows, it appeared to be present. The presence of chaotic oscillations and the oxygen mass flow where transition to chaotic behavior occurs needs to be investigated further since it will impact both the modeling and the design effort.

Although oxygen is being directed into the pre-combustion chamber at pressure, waves are free to propagate along the cylinder of the motor between the impedance set by the nozzle and chamber at the post-combustion end and the chamber at the pre-combustion end (see Figure 2). The visual evidence of a pulsating flow in the injector head further supports longitudinal acoustic modes as the basis for some of the pressure oscillations in hybrid rocket motors.

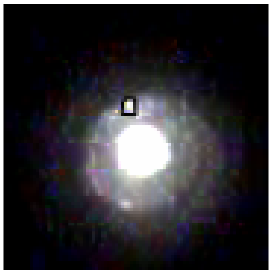
The swirling pattern was more clearly defined for fuel grains that had been fired one or more times than for fuel grains that were being fired for the first time. This could be due to the char layer deposited from previous firings acting as an opacifier. The soot particles may add to the visualization of the swirling effect. Further, with a larger center bore, the swirling pattern is larger.

In one of the 450 psi chamber pressure firings a large, clearly visible particle provided clear evidence of the rotational flow pattern (see Figure 6). Although it is obvious in the moving images, the particle in the still images has been outlined to enhance its visibility. The particle is first seen (upper most frame in Figure 6) at 11:00 (upper left quadrant) in the image near the periphery. One frame later (at the 30 Hz NTSC sample rate), the particle has moved to approximately the 12:00 position (middle frame in Figure 6). One frame later, it has moved to 1:00 (bottom most frame in Figure 6). This gives an approximate rotation rate of 24 radians per second for this flow condition.

Particle at 11:00



Particle at 12:00



Particle at 1:00

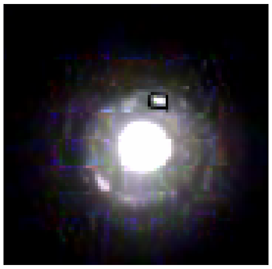


Figure 6. Sequential images looking down bore of hybrid rocket with rotating particle outlined.

UV-Vis

The initial study performed with the UV-Vis spectrograph was to gather baseline information for the combustion chamber area. The entrance slit width was set to 22 µm, the same as that used with previous plume emission studies at UALR.

The rocket motor was fired for three seconds twice at 1379 kPa (200 psi) and twice at 1724 kPa (250 psi). The wavelength selector on the spectrograph was set for different portions of the spectrum in the separate experiments (500–650 and 620–770 nm). The control computer initiated the spectrograph two seconds prior to firing and stopped the spectrograph after shutdown. The spectrograph collected the emission in the UV-Vis range 100 times every 0.1 seconds for each experiment.

A “waterfall” plot for each wavelength selector position is plotted (see Figures 7 and 8). The *z*-axis on this plot is the analog-to-digital converter (ADC) value from the spectrograph’s CCD camera as read by the computer card. The *x*-axis is the time throughout the firing. For clarity, the *x*-axis was down-sampled to provide a plot every 500 milliseconds. The *y*-axis is the wavelength from the spectrograph. The initial ignition event and the shutdown event can be seen. At shutdown, emissions approach the blackbody configuration due to soot and smoke that are formed in the fuel rich condition. This can be observed as well in the videos of the combustion chamber. During the middle portion of the firing, the emissions stabilize to a steady state condition for about one second. In Figure 7, the sodium resonance line continuum can be seen centered at 590 nm. In Figure 8, the potassium line/ continuum can be seen at 740 nm.

(There is a section of several pixels in the center of the CCD camera that consistently reads low. This results in an inverse peak in the center of each graph and does not represent a spectral feature.)

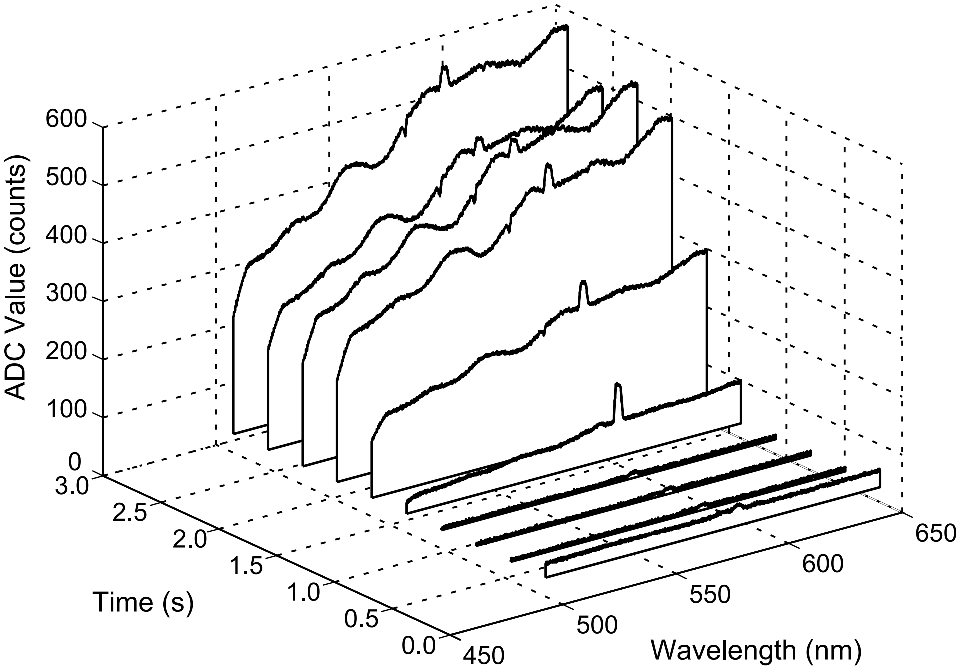


Figure 7. Waterfall plot for a hybrid rocket motor firing (sodium).

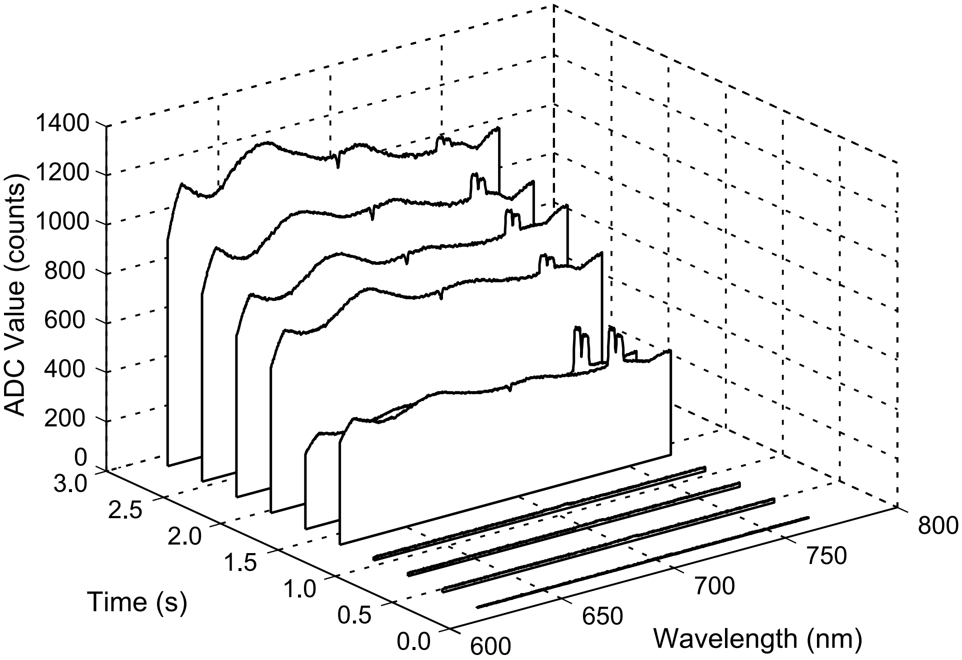


Figure 8. Waterfall plot for a hybrid rocket motor firing (potassium).

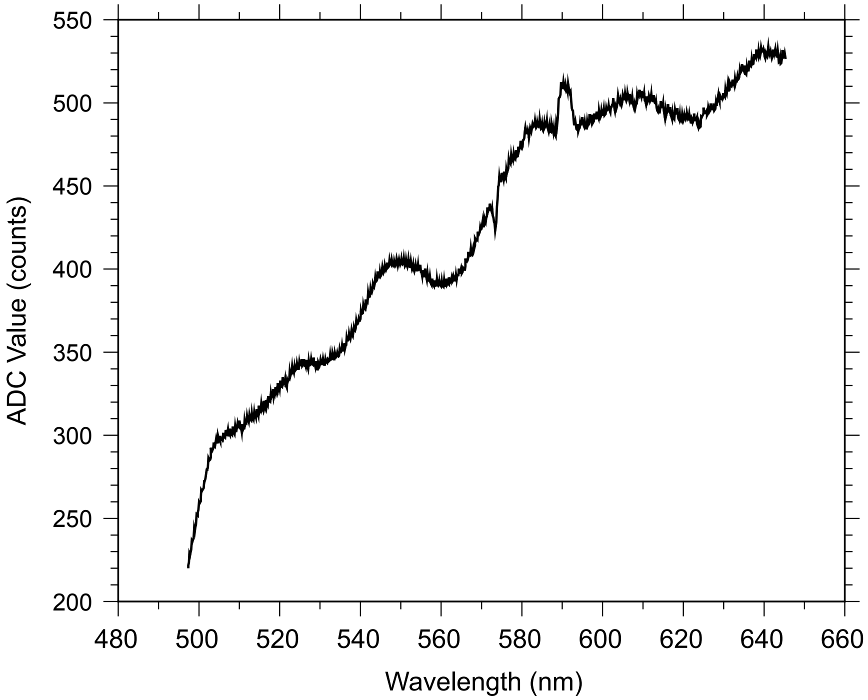


Figure 9. Averaged UV-Vis spectrum inside combustion chamber (sodium).

Several spectra were averaged for the steady-state emissions (between initiation of combustion and the blackbody shutdown spectrum). In Figure 9, the sodium resonance line/continuum can be seen centered at 590 nm. In Figure 10, the potassium line/continuum system can be seen centered at 740 nm. These spectra can be compared with plume spectra from previous studies using the labscale hybrid rocket motor for similarities.[3] Increased emissions are observed. These may be due to increased blackbody emissions, especially considering that the injector head view is directed to the graphite nozzle at the rear of the chamber. The spectra generated from in-plume measurements represent completed combustion; however, chamber combustion should have char and other materials coming off the fuel grain surface, which give rise to increased black body emissions. Molecular bands are present that appear to be similar to those in previous plume studies.[12] Further experiments are planned to fully characterize the baseline emissions in the combustion chamber. However, the current experiments validate the ability to extract useful information from the injector head mounted optics.

Conclusion

The swirling, pulsating flow observed in the combustion chamber indicates that the one-dimensional flow assumptions are not valid. This study provided visual information that characterizes the internal combustion chamber flow as three-dimensional.

The in-chamber UV-Vis measurements performed in this study are correlated with previous in-plume UV-Vis studies. This measurement in conjunction with plume measurements can be used to characterize the effects of combustion as it progresses through the rocket motor and the effects of afterburning.

The blackbody component in the chamber is higher than in the plume, probably due to the graphite nozzle at the end of the chamber. The nozzle forms a very good approximation of a blackbody source during firing due to its material, surface, and shape. At the end of the firing, the blackbody radiation due to soot swamps the rest of the spectrum. This is also seen in the visual images as the emission extinguishes at the end of the firing.

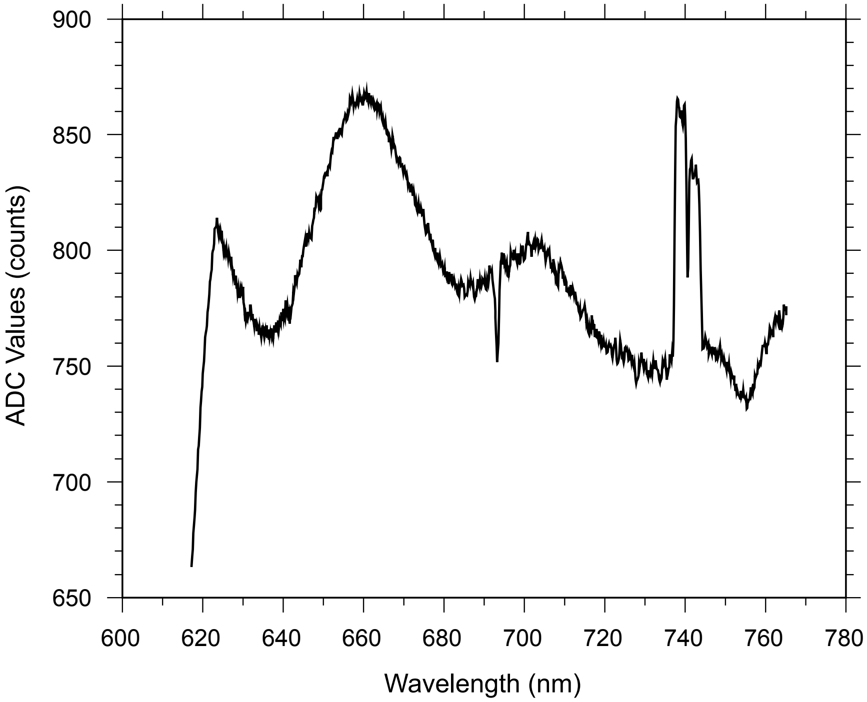


Figure 10. Averaged UV-Vis spectrum inside combustion chamber (potassium).

Acknowledgement

This work was funded by the Arkansas Space Grant Consortium and by NASA Grant Number NCC5-260.

References

1) R. Shanks and M. K. Hudson, "A Labscale Hybrid Rocket Motor for Instrumentation Studies", *J. Pyrotechnics*, No. 11, 2000, pp 1–10.
2) K. L. Maxwell and M. K Hudson, "Spectral Study of Metallic Molecular Bands in Hybrid Rocket Plumes", AIAA Paper No. 2000-3887, 2000.
3) M. K. Hudson, et al., "UV, Visible, and Infrared Spectral Emissions in Hybrid Rocket Plumes", *Int'l Journal of Turbo and Jet Engines*, Vol. 15, 1998, pp 71–87.
4) R. W. Sproles, J. D. Wilson and M. K. Hudson, "An Analysis of FTIR Emission Spectroscopy of Flickering/Pulsating Sources: Application to Rocket Plumes", *Int'l Journal of Turbo and Jet Engines*, Vol. 21, 2004, pp 211–215.
5) M. W. Teague, J. R. Welborn, T. M. Felix, M. K. Hudson, and J. Willis, "UV/Vis Absorption as a Diagnostic for NO in Rocket Plumes", *Int'l Journal of Turbo and Jet Engines*, Vol. 13, 1996, pp 211–215.
6) M. W. Teague, T.A. Jennings, A.M. Wright, and A.B. Wright, "UV Spectroscopic Monitoring of Rocket Motor Combustion Efficiency", 38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Indianapolis, IN, July 2002.
7) M. F. Desrochers, G. W. Olsen, C. Luchini, and M. K. Hudson, "Pressure, Plume Flicker, and Acoustic Data Correlation in Labscale Hybrid Rockets", *J. Pyrotechnics*, No. 13, 2001, pp 35–39.
8) A. B. Wright, A. Tomany, A. M Wright, and M. K. Hudson, "Pressure Measurement in the Post-Combustion Section of a Hybrid Rocket Motor", AIAA Paper No. AIAA-99-2536, 1999.
9) R. W. Dunn, et al, "Noninvasive Ion Detection in a Rocket Plume for Health Monitor-

ing", 36th AIAA/ASME/SAE/ASEE JPC, Huntsville, AL, July 17–19 July 2000.

10) M. K. Hudson, A. M. Wright, C. Luchini, P. Wynne, and S. Rooke, "Guanidinium Azo-Tetrazolate (GAT) as a High Performance Hybrid Rocket Fuel Additive", *J. Pyrotechnics*, No. 19, 2004, pp 37–42.
11) Gopal Tejwani, et al., "Space Shuttle Main Engine Exhaust Plume Spectroscopy", *Spectroscopy*, Vol. 11, No. 9, 1996, pp 31–43.
12) D. Snider, R. Shanks, R. Cole, and M. K. Hudson, "Inexpensive Photodiode Arrays for Use in Rocket Plume and Hot Source Monitoring and Diagnostics", *Measurement Science and Technology*, Vol. 14, 2003, pp 1725–1733.
13) http://theduchy.ualr.edu/nasa/JasonData/81199Run6.m1v
14) http://theduchy.ualr.edu/nasa/JasonData/8499Run8.m1v
15) http://theduchy.ualr.edu/nasa/JasonData/8499Run10.m1v
16) Marxman, G. A., "Combustion in the Turbulent Boundary Layer on a Vaporizing Surface," *Tenth Symposium on Combustion*, The Combustion Institute, 1965, pp 1337–1349.
17) A. P. Chouinard, A. J. Adams, A. M. Wright, and M. K. Hudson, "Multi-Wavelength Laser Opacity Study of Hybrid Rocket Plume", *J. Pyrotechnics*, No. 15, 2002.
18) Villasenor, R., "A Fully Coupled, Implicit, Numerical Scheme for Laminar and Turbulent Parabolic Flows," *International Journal for Numerical Methods in Engineering*, Vol. 40, 1997, pp 1821–1837.

Editorial Policy

Articles accepted for publication in the *Journal of Pyrotechnics* can be on any technical subject in pyrotechnics. However, a strong preference will be given to articles reporting on research (conducted by professionals or serious individual experimenters) and to review articles (either at an advanced or tutorial level). Both long and short articles will be gladly accepted. Also, responsible letters commenting on past Journal articles will be published, along with responses by the authors.

Choked Flow, a Frequently Misunderstood Term

Lawrence Weinman
Schneier/Weinman Consultants, LLC, Austin, TX USA

ABSTRACT

A brief description of compressible fluid flow is presented to clarify and, hopefully, reduce the incorrect usage of the term "choked flow" in the fireworks community.

Keywords: choked flow, fluid flow, gas velocity, mass flow, rocket, sonic flow

A term that is frequently used in the field of fluid mechanics is "choked flow". Unfortunately, it is also a frequently misused term. The author has found that this seems to be particularly true in the fireworks industry where it has been used as an explanation for, among other things, the transition between the initial slow buildup of pressure in fireworks mortars and a sudden and rapid increase in mortar pressure. (Choked flow has also been similarly invoked as one explanation of exploding gerbs.) This article is a brief explanation of those conditions under which the use of the term choked flow would be correct, and why and under what conditions, especially in fireworks, its use is incorrect.

Figure 1 presents two examples of gas flow from some pressure source region labeled P_0 and having a pressure of P_0 through a constricted throat section similarly labeled P_1 (at pressure P_1) to the atmosphere labeled P_2 (at ambient pressure P_2). The upper depiction in Figure 1 is typical of either a rocket motor or gerb, and the lower depiction shows the somewhat analogous situation of a spherical shell firing from a mortar. If the pressures P_0 and P_2 are equal, there will be no flow of gas. If the pressure P_0 is raised above P_2, the gas will begin to flow with some velocity, with the point of maximum constriction at P_1 being of particular interest. If P_0 is increased further, the velocity of the flow at point P_1 again increases. However, if the pressure P_0 continues to be increased, at some point the velocity of the gas flow at point P_1 will reach the speed of sound (which for a given gas is mostly a function of temperature). At that point, any further increase in P_0 will not result in a further increase in gas flow velocity at point P_1. This is the condition generally described as "choked flow".

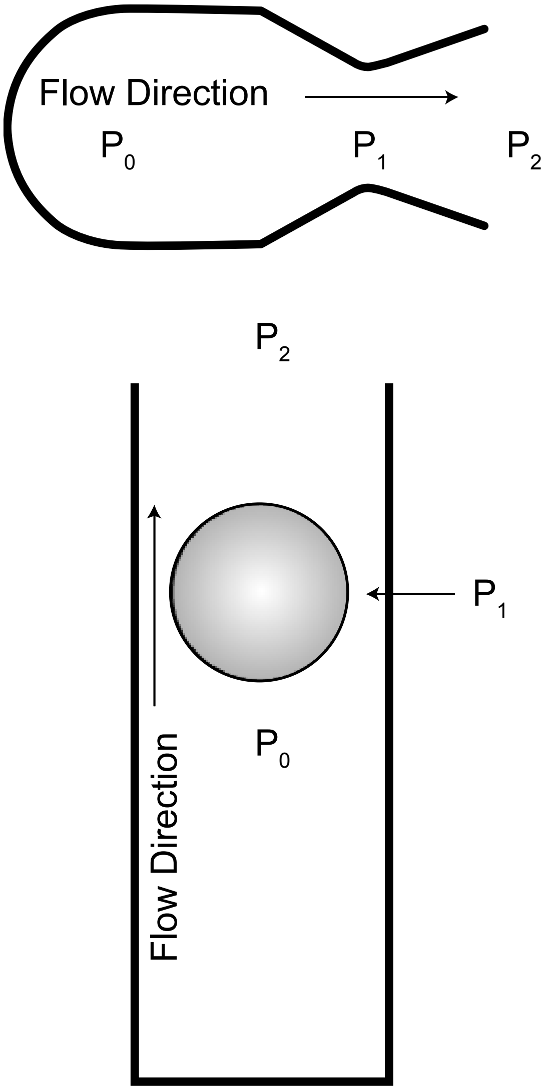


Figure 1. Examples of gas flow in items such as a rocket motor or gerb (above) and a discharging fireworks mortar (below).

Figure 2 is a somewhat typical graph of mortar pressure as a function of time during the firing of an aerial shell. Note that there is a rather long interval between igniting the lift charge with an electric match (at t_0) and the eventual rapid rise in mortar pressure (occurring from t_r to t_p). It has occasionally been suggested that the reason for the sudden onset and rapid increase in pressure was that the velocity of the gas escaping around the aerial shell has reached the speed of sound. Since there can be no further increases in the velocity of the escaping lift gas as mortar pressure continues to increase, it is suggested that this results in something like a piling up of gas that is unable to escape, and this is what causes the precipitous rise in mortar pressure. However, as is demonstrated below, an examination of gas flow dynamics finds that this argument cannot be supported.

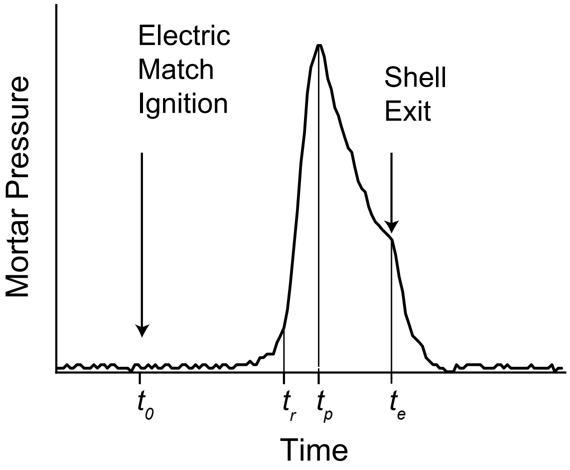


Figure 2. A graph of mortar pressure (gauge pressure) as a function of time during the firing of an aerial shell.

Before beginning the discussion of gas dynamics in general, and choked flow in particular, it is appropriate to point out that the information presented in this article can be found in any number of text books. For this reason, specific references are not included, but rather a list of general references is provided at the conclusion of the article.

The first step in discussing choked flow is to demonstrate that under the conditions assumed for this article, the density of a gas is proportional to its pressure. Equation 1 is known as the Ideal Gas Law and is a reasonably accurate equation of state for most commonly encountered gases under the conditions of pressure and temperature encountered in fireworks and rocketry.

$$PV = nRT \tag{1}$$

where P is absolute pressure (as opposed to gauge pressure, or pressure above atmospheric), V is volume, n is the number of moles of gas, R is a constant of proportionality (the Universal Gas Constant, the magnitude of which depends on the system of units being used), and T is the absolute temperature.

In this discussion, only pressure sources venting to the ambient atmosphere will be considered, and the temperature (T) at the pressure source will be considered to be constant. Therefore, eq 1 reduces to

$$PV \propto n \quad or \quad P \propto \frac{n}{V} \tag{2}$$

(Equation 2 is also known as Boyles Law.) Since density (ρ) is defined as mass divided by volume, and number of moles of a gas is proportional to the mass of that gas (m), then

$$\rho = \frac{m}{V} \propto \frac{n}{V} \tag{3}$$

For eqs 2 and 3 both to be true, for an ideal gas its density must be directly proportional to the pressure, ($\rho \propto P$) (i.e., gas density increases linearly with gas pressure).

The second step in this discussion is to derive a general equation for the mass flow rate for a gas in motion. Consider a gas flowing through a pipe, such as illustrated in Figure 3, with a known constant velocity (v). During a given time interval (t), not considering the random motions of the individual gas molecules, the gas starting at point 1 will have traveled to point 2. In this case, the distance traveled (D) will equal gas velocity times time.

$$D = v \cdot t \tag{4}$$

During that same time interval, the volume of the gas (V) passing point 1 will be that amount of gas in the volume of the pipe between points 1 and 2, which is equal to the cross sectional area of the pipe (A) times the distance between points 1 and 2 (D).

$$V = A \cdot D = A \cdot v \cdot t \qquad (5)$$

Since density is defined as equaling mass (m) divided by volume (V), the mass of gas passing point 1 during this same time interval is equal to the density of the gas times its volume.

$$m = \rho \cdot V = \rho \cdot A \cdot v \cdot t \qquad (6)$$

Mass flow rate ($\dot{m}$) is defined as the mass passing point 1 divided by the time that has elapsed.

$$\dot{m} = \rho \cdot A \cdot v \qquad (7)$$

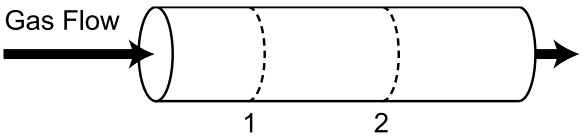


Figure 3. An illustration of a gas flowing through a simple pipe.

In the discussion of choked flow, it is the mass flow rate ($\dot{m}$) through the point of constriction that will be of primary interest. Also, when the terms “sub-sonic”, “sonic”, and “super-sonic” flow are used, they refer to the local speed of sound in the gas at the section being referred to (i.e., in sections P_0, P_1, or P_2). They do not refer to the speed of sound in the surrounding atmosphere. Finally, it should be noted that the local speed of sound is, for a given fluid (gas), primarily, but not exclusively, dependent on the temperature of the fluid. In the cases being discussed here, the actual value for the local speed of sound will not be specified, and it will be assumed to be a constant through out the device, as will the temperature and the chemical and molecular composition of the gas.

The basic equation for sub-sonic mass flow rate (eq 8) has been taken from standard reference texts and is presented here without derivation (for more information, see the list of references at the end of this article).

$$\dot{m} = A\sqrt{2\rho P_0} \times \left(\sqrt{\frac{k}{k-1}}\right) \times \sqrt{\left(\frac{P_2}{P_0}\right)^{\frac{2}{k}} - \left(\frac{P_2}{P_0}\right)^{\frac{k+1}{k}}} \qquad (8)$$

In eq 8, P_0 is the chamber pressure in section P_0, P_2 is the ambient pressure in section P_2, A is the cross sectional area of section P_1, ρ is the density of the gas, and k is the ratio of the specific heat at constant pressure divided by the specific heat at constant volume (i.e., $k = C_p / C_v$) for the gas in the system. For common atmospheric gases, k is approximately 1.4.

Assume for the purposes of discussion that density is constant (and not proportional to pressure as was shown above). Then, if k is assumed to be 1.4, the pressure in section P_2 is held constant at atmospheric pressure and the pressure in section P_0 is increased from atmospheric to that which produces sonic flow in section P_1, eq 8 can be used to calculate mass flow rate. In this case, Figure 4 is a graph of the resulting mass flow rate, normalized to that when P_0 is 1.89 atmospheres.

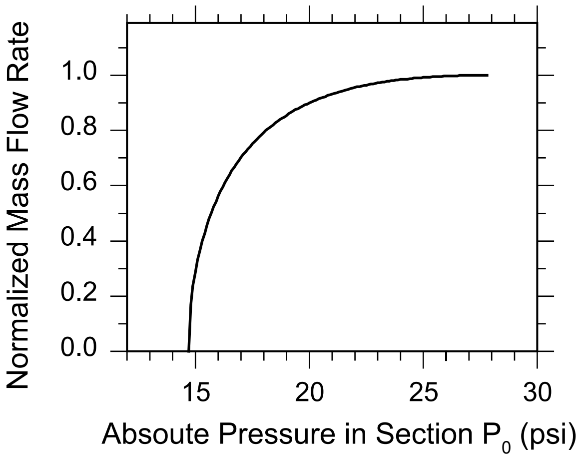


Figure 4. A graph of normalized sub-sonic mass flow rate as a function of absolute chamber pressure, incorrectly assuming gas density is constant, independent of pressure.

This type of curve can give rise to the term “choked flow”, as it appears that no matter how high the pressure rises, the mass flow rate reaches a limit. (This is actually the case when the pressure, in the source chamber, P_0 is held constant and the exhaust pressure P_2 is reduced, such as would happen if a rocket were to travel into space.). However, recall that the graph in Figure 4 was based on the incorrect assumption that gas density in section P_2 was constant and not proportional to pressure (P_2).

Therefore, a term needs to be introduced in the first radical that will cause the density of the gas to be proportional to the pressure above ambient. Notice in eq 9, that when the pressure P_0 is the same as the ambient pressure, P_2, the term is equal to 1, and if the source pressure is twice ambient, the term is equal to 2, and so forth. (In eq 9, ρ_2 is the density of the gas at atmospheric pressure, P_2.)

$$\dot{m} = A\sqrt{2\rho_2\left(\frac{P_0}{P_2}\right)P_0} \times \left(\sqrt{\frac{k}{k-1}}\right) \times \sqrt{\left(\frac{P_2}{P_0}\right)^{\frac{2}{k}} - \left(\frac{P_2}{P_0}\right)^{\frac{k+1}{k}}} \qquad (9)$$

Equation 9, when plotted similarly to eq 8, results in the graph in Figure 5.

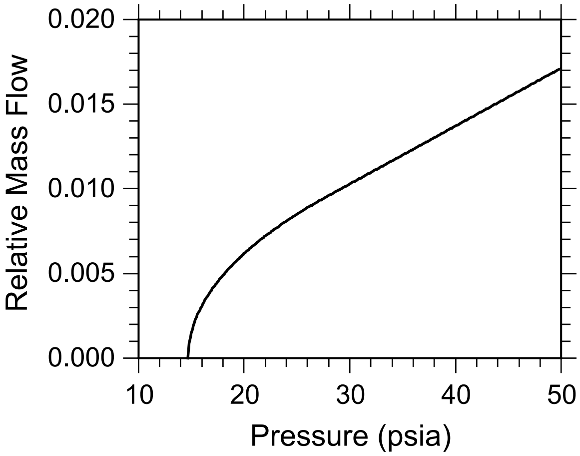


Figure 5. A graph of normalized sub-sonic mass flow rate as a function of absolute chamber pressure, correctly considering gas density to be proportional to pressure.

Equation 9 holds true so long as the flow remains sub-sonic (i.e., until the 'critical' pressure is reached). This critical pressure is defined as when the ratio of the pressure P_0 divided by P_2 exceeds the number given by

$$\left(\frac{k+1}{2}\right)^{\frac{k}{k-1}} \qquad (10)$$

At this critical pressure, the velocity in the 'throat' section P_1, is at sonic velocity, and for all higher source pressures (P_0) the following equation governs:

$$\dot{m} = A\sqrt{k\rho P_0} \times \left(\frac{2}{k+1}\right)^{\frac{k+1}{2k-2}} \qquad (11)$$

And, similarly to eq 9, a term is added to account for gas density in the chamber region being proportional to chamber pressure, giving

$$\dot{m} = A\sqrt{k\rho_2\left(\frac{P_0}{P_2}\right)P_0} \times \left(\frac{2}{k+1}\right)^{\frac{k+1}{2k-2}} \qquad (12)$$

A plot of eq 12 results in the graph shown in Figure 6.

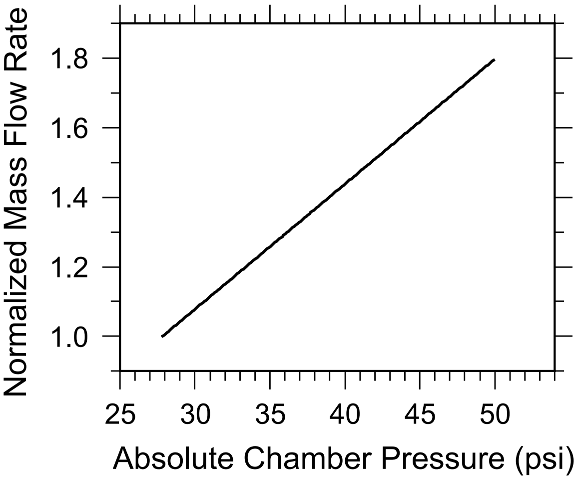


Figure 6. A graph of normalized super-sonic mass flow rate as a function of absolute chamber pressure.

Combining the sub-sonic and super-sonic data results in the graph shown in Figure 7.

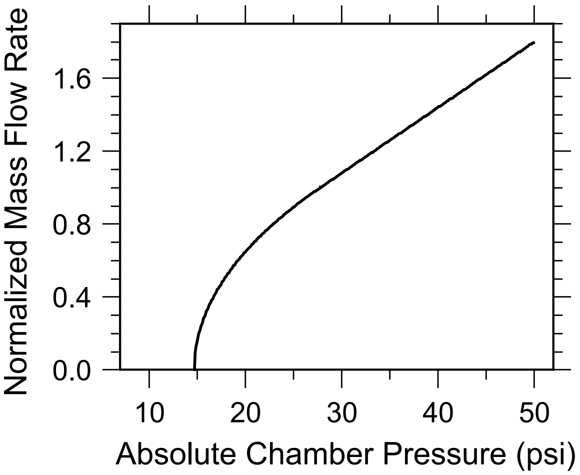


Figure 7. A graph of normalized mass flow rate as a function of absolute chamber pressure, spanning both sub- and super-sonic flow regions.

In the cases presented above, the transition from sub-sonic to supersonic flow happens at (i.e., the critical pressure is) approximately 27.8 psia. The above curves are generic; the exact shapes of the mass flow curves depend on other factors such as the composition of the gas, gas temperature, and such.

As can be seen from Figure 7, while there is a decrease in the slope of the mass flow curve with increasing pressure—until the flow reaches sonic velocity—clearly the mass flow rate continues to smoothly increase even after the flow has reached sonic velocity in the throat section. Accordingly, there is no basis for invoking a theory of choked flow as the reason for the precipitous rise in mortar pressure during the course of firing aerial shells.

The author used the following references, but a quick perusal of technical library shelves will show this list is far from exhaustive.

General References

1) *Marks' Standard Handbook for Mechanical Engineers*, Avallone & Baumeister, 9th ed., McGraw-Hill Book Company, 1987.

2) *Perry's Chemical Engineers' Handbook*, Perry & Green, 6th ed., McGraw-Hill Book Company, 1984.

3) *Fluid Mechanics*, Streeter & Wylie, 7th ed., McGraw-Hill Book Company, 1979.

4) *Fluid Mechanics*, De Nevers, Addison-Wesley Publishing Company, 1970.

5) *Elementary Fluid Mechanics*, Vennard, 3rd ed., John Wiley & Sons, 1954.

6) *The Dynamics and Thermodynamics of Compressible Fluid Flow*, Shapiro, V1., The Ronald Press Company, 1953.

Events Calendar

Pyrotechnics and Fireworks

2nd Workshop on Pyrotechnic Combustion Mechanisms

July 27, 2005, Pfinztal-Bergenhausen, Germany

Contact: Dr. Ernst-Christian Koch
Diehl Munitionssysteme GmbH & Co. KG
Fischbachstrasse 16
D-90552 Röthenbach a. d. Pegnitz, Germany
Phone: +49 (0) 911-957-2728
FAX: +49 (0) 911-957-2111
email: ernst.christian.koch@diehl-mun.de

36th Int'l Annual Conference of ICT and 32nd Int'l Pyrotechnics Seminar

June 28 to July 1, 2005, Karlsruhe Germany

Contact: Manuela Wolff
PO Box 1243
D-76318 Pfinztal, Germany
Phone: +49-721-464-0121
FAX: +49-721-464-0111
email: mw@ict.fhg.de
web: www.ict.fhg.de or www.ips.org

Pyrotechnics Chemistry

July 4 to 6, 2005, Grafham Water Sailing Club, Cambridgeshire, UK

Contact: Tom Smith
Davas Ltd, 8 Aragon Place
Kimbolton, Huntingdon, Cambs, PE28 0JD, UK
Phone: +44 1480 860124
Fax: +44 1480 861108
e-mail: pyrocourses@davas.co.uk
web:www.pyrochemistry.net/docs/
Pyrocourse UK 2005.pdf

Chemistry of Pyrotechnics & Explosives

July 24 to 29, 2005, Washington College, Chestertown, MD, USA

Contact: John Conkling
PO Box 213
Chestertown, MD 21620, USA
Phone: +1-410-778-6825
FAX: +1-410-778-5013
email: JConkling2@washcoll.edu
web: www.John.Conkling.washcoll.edu

HSBC Celebration of Light, International Fireworks Competition

July 27, July 30, Aug 3, and Aug 6, 2005, Vancouver, British Columbia, Canada

Contact: Alicia Maluta, General Manager
Ste 800, 888 Dunsmuir St
Vancouver, BK V6C 3K4, Canada
Phone: +1-604-641-1193
FAX: 604-641-1925
email: gm@celebration-of-light.com
web: www.celebration-of-light.com

Pyrotechnics Guild Int'l Convention

Aug. 6 to 12, 2005, Mason City, IA, USA

Contact: Frank Kuberry, Sec. Treas.
304 W Main St
Titusville, PA, 16354, USA
Phone: +1-814-827-6804
e-mail: kuberry@earthlink.net
web: www.pgi.org

33rd Int'l Pyrotechnics Seminar

July 16 to 21, 2006, Fort Collins, CO, USA

Contact: Linda Reese, Appl. Res. Assoc. Inc.
10720 Bradford Rd., Ste 110
Littleton, CO 80127, USA
Phone: +1-303-795-8106
FAX: +1-303-795-8159
email: lreese@ara.com
web: www.ips.org or www.ipsusa.org

Listing of Fireworks Events – Worldwide

web: http://fireworksguide.com

Energetic Materials

Computational Mech. Assoc. Courses–2005

Contact: Computational Mechanics Associates
PO Box 11314,
Baltimore, MD 21239-0314, USA
Phone: +1-410-532-3260
FAX: +1-410-532-3261
email: compmechanics@verizon.net
web: www.compmechanics.com

2nd Int'l Symp. on Energetic Materials and their Applications (ISEM 2005)

May 26 to 27, 2005, Tokyo, Japan

Contact: Noriaki Nakashima, Sec. ISEM 2005
Research Center for Explosion Safety
Nat'l Inst. Adv. Indust. Science & Technology
Kanda-Surugadai Branch
Office 6 Floor, Chemical Soc. of Japan Bldg.
1-5, Kanda-Surugadai, Chiyoda-ku
Tokyo 101-8307, Japan
FAX: +81-3-5282-4388
email: isem2005@m.aist.go.jp
web: www.eblo-ti.com/isem2005

Franklin Applied Physics Lectures

July 25 to 29, 2005, Oaks, PA, USA

Contact: James G. Stuart, Ph.D., Pres.
Franklin Applied Physics, Inc.
98 Highland Ave., PO Box 313
Oaks, PA 19456, USA
Phone: +1-610-666-6645
FAX: +1-610-666-0173
email: JStuartPhD@aol.com

3rd EFEE World Conference on Explosives and Blasting

September 13 to 16, 2005, Brighton, UK

Contact: Mark Hatt, Chairman
EFEE
Hoton Hills Barn
82 Loughborough Rd
Holton, Leics LE12 5SF, UK
Phone: +44 (0) 1509-631-530
FAX: +44 (0) 1509-234-911
email: efee@tylerevents.co.uk
web: www.efee-web.org

2005 International Autumn Seminar on Propellants, Explosives and Pyrotechnics

October 25 to 28, 2005, Beijing, China

Contact: Prof. Feng Changgen
School of Mechano-electronics Engineering
Beijing Institute of Technology
PO Box 327
Beijing 100081, China
Phone: +86 10 6891-3997
FAX: +86 10 6891-1849
email: lsc@iaspep.com.cn or
email: hmcspadden@aol.com [US, Canada]
web: www.iaspep.com.cn

International Pyrotechnic Automotive Safety Symposium (IPASS)

November 22 to 23 2005, Bordeaux, France

Contact: Assoc. Francaise de Pyrotechnic Le Diamant
email: ipass@afpyro.org
web: www.afpyro.org

32nd Annual Conference on Explosives and Blasting Technique

Jan. 29 to Feb. 1, 2006, Dallas, TX, USA

Contact: Lynn Mangol
Phone: 440-349-4400
email: mangol@isee.org

Propulsion

41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference

July 10 to 13, 2005, Tucson, AZ, USA

Contact:
Phone: +1-703-264-7500 / 800-639-2422
web: www.aiaa.org

High Power Rocketry

LDRS 2005

Contact: see web site:
www.tripoli.org/calendar.htm

Model Rocketry

NARAM 2005

Contact: — see web site for details:
web: www.naram.org
For other launch information visit the NAR Web site: www.nar.org

Future Events Information

If you have information concerning future—explosives, pyrotechnics, or rocketry—meetings, training courses or other events that you would like to have published in the *Journal of Pyrotechnics*, please provide the following information:

Name of Event

Date and Place (City, State, Country) of Event

Contact information — including, if possible, name of contact person, postal address, telephone and fax numbers, email address and web site information.

This information will also be published on the Journal of Pyrotechnics Web Site:

http://www.jpyro.com

Errata

***Issue 17, Summer, 2003, page 22.* “A Study of the Combustion Behaviour of Pyrotechnic Whistle Devices (Acoustic and Chemical Factors)”**

The word in bold text in the following sentence, which appeared on paged 22, had been “high” instead of “low. The **corrected** text follows:

While the experimental data show such a relationship between the mode frequencies (see Figure 2), it does not fit the half-wave resonator model, which yields unrealistically **low** acoustic propagation velocities when calculated as the product of frequency and wavelength, with the wavelength equal to twice the effective chimney length.

***Issue 20, Winter, 2004, page 71.* “A Simplified Method for Determining the Strength of a Tube Subjected to Internal Pressure”**

The example in the article had an error; the **corrected** example follows:

Example: A mortar tube is made of a plastic having a safe stress level of 2000 psi, with an ID of 4 in. and an OD of 4.5 in. Given that the expected internal pressure generated when the mortar is fired has always been less than 200 psig, is the mortar safe?

Solution: *w*, the ratio of the OD to the ID is

$$4.5 \div 4.0 = 1.125$$

From the graph the stress multiplier from the graph, at a ratio of 1.125 is approximately 9.5. Therefore, the tangential, or hoop, stress in the tube is

$$200 \text{ psi} \times 9.5 = 1900 \text{ psi}$$

The mortar is not safe to use since the allowable stress is approximately equal to the expected stress, thus a thicker tube wall is needed.

Special Materials in Pyrotechnics: IV.[1] The Chemistry of Phosphorus and its Compounds

Ernst-Christian Koch
Morlauterer Straße 103a, D-67657 Kaiserslautern, Germany

ABSTRACT

The combustion chemistry of phosphorus and its compounds in pyrotechnic applications is discussed. Whereas red phosphorus (RP) and phosphorus sulfides can be used as fuels, the phosphates can be used as oxidizers in metal-containing pyrolants. Phosphorus combustion mainly occurs in the gas phase after volatilization of the parent phosphorus source, be it P_4 *or* P_{red}. *The enormous sensitivity of RP and its mixtures is mainly due to high strain in red phosphorus building blocks and trace amounts of phosphoric acids formed in non-stabilized RP. The inherent danger of RP/chlorate mixtures is believed to result for the most part from acid-base reactions in non-stabilized RP mixtures leading to the highly reactive species* ClO_2, *which will trigger ignition.*

Keywords: red phosphorus, phosphate, phosphide, white phosphorus, chlorate, smoke, Armstrong's mixture

Introduction

Aside from group one of the periodic system of elements (Li–Cs), only the 15th group (N–Bi) finds full application in pyrotechnics. Whereas nitrogen is nearly ubiquitous as nitrate (NO_3^-), dinitramide ($N(NO_2)_2^-$) or nitroformate ($C(NO_2)_3^-$) in oxidizers, arsenic (As) has found application as realgar (As_4S_4) in white fire Bengal applications. Likewise antimony (Sb) is used as metalloid or sulfide (Sb_2S_5) in white fire and glitter applications. Finally bismuth (Bi) is applied as the oxide, Bi_2O_3, as an oxidizer in both delay elements and micro-crackling star applications[2,3] and most recently the sulfide (Bi_2S_3) has found introduction as non-toxic fuel in delay compositions.[4]

Phosphorus (P), the element from the second row of group 15, is very well known as a potent fuel in pyrotechnics. Nevertheless phosphorus is not an everyday fuel, although applied in everyday products such as safety match strikers. This striking situation arises from the special properties of phosphorus, which are high flammability at room temperature and inherent sensitivity to electrostatic discharge, mechanical impact and heat.

Among the fuels applied in pyrotechnics, phosphorus plays a prominent role. The proverbial polymorphy of the element and the application of the element in everyday articles like safety matches, in countermeasure ammunition, and finally in such inhumane devices as incendiary bombs require a detailed look at the element and its compounds in pyrotechnic applications.

It is the purpose of the present paper to give an overview of the chemistry of phosphorus and its combustion in pyrotechnics. An exhaustive review on red phosphorus and its application in screening smoke compositions has been written by Davies.[5] The discussion of general military applications of phosphorus is the subject of an upcoming paper.

Modifications of Phosphorus

When discussing phosphorus, one has to look at the modifications of the element (allotropes) in general. Virtually no other element occurs in such a large number of modifications. Nevertheless within the scope of this paper only two modifications will be addressed, the white tetrahedral (P_4) and the red amorphous (P_x).

ELEMENTA
CHEMIÆ,
QUÆ
ANNIVERSARIO LABORE DOCUIT,
IN PUBLICIS, PRIVATISQUE
SCHOLIS,
HERMANNUS BOERHAAVE.
TOMUS PRIMUS.
QUI CONTINET HISTORIAM ET ARTIS
THEORIAM.
CUM TABULIS ÆNEIS.

VENETIIS, MDCCLIX.
Apud SEBASTIANUM COLETI.
SUPERIORUM PERMISSU, AC PRIVILEGIO.

DE ARTIS THEORIA. 189

Figure 1. Elementa Chemiæ of Hermannus Boerhaave, Vol. 1 from 1759, page 178 refers to white phosphorus probably for the first time in chemical literature.[7]

Phosphorus was originally discovered by the German pharmacist Hennig Brand in the year 1669 while fusing a mixture of urine, limestone and coal in a porcelain retort. After several hours of heat treatment Brand observed a green glowing substance, which was condensed white phosphorus. A fascinating-to-read book about the discovery, application and history of this element has been written by J. Emsley.[6] Figure 1 shows one of the first monographs on chemistry mentioning igniting phosphorus[7] written by Hermannus Boerhaave, who was born just one year before the element's discovery in 1668. Although phosphorus was discovered in the 17th century, Lavoisier in the 18th century was the first to recognize it as an element.

Table 1 displays the most important modifications of phosphorus.

White Phosphorus (WP)

White phosphorus (P_4) is the modification that originally gave the element its name (Greek: fosforos = light carrier) due to its white-green chemiluminescence in the air,[8] most impressively observed in a dark room. White phosphorus is the starting material for the synthesis of any other phosphorus allotrope as can be seen from Figure 2.

In the cold, white phosphorus (WP) is a brittle substance showing conchoidal fracture and becoming waxy at ambient temperature. Under an inert atmosphere—otherwise it would enflame—WP fuses at 44.1 °C to give a clear and highly refractive liquid. The melt vaporizes at 280 °C. In both the condensed and gas phases, phosphorus is composed of P_4 molecules. Above 800 °C, in the gas phase, the P_2 units start to form which dissociate again at $T > 2000$ °C to give monatomic $P_{(g)}$.

$$P_{4(s)} + 54.4\ \text{kJ} \longleftrightarrow P_{4(g)} \qquad (1)$$

$$\tfrac{1}{2}\, P_{4(g)} + 139.8\ \text{kJ} \longleftrightarrow P_{2(g)} \qquad (2)$$

$$P_{2(g)} + 489.5\ \text{kJ} \longleftrightarrow 2\, P_{(g)} \qquad (3)$$

Due to the tetrahedral geometry of the P_4 molecule, it is highly reactive as can be seen from its low ignition temperature of 35 °C. Finely dispersed white phosphorus ignites spontaneously at ambient temperature. WP is soluble in many organic solvents and also in PCl_3 and PBr_3. At $T > 200$ °C white phosphorus slowly transforms into modifications having higher thermodynamic stability such as red, violet and black phosphorus as can be seen in Figure 2.

Table 1. Properties of Phosphorus Modifications.

Parameter	Unit					
Designation		P	White	Red	Hittorf	Metallic
CAS-No.			[12185-10-3]	[7723-14-0]	[7723-14-0]	[7723-14-0]
Constitution	—		$P_{4(s)}$	P_x	$(–P_8P_2P_9–)_x$	$(–P_6–)_n$
Atomic mass	A.U.	30.9738				
Color			White-yellow	Orange-violet red	Violet-brown	Silvery, graphite like
Density	$g \cdot cm^{-3}$		1.82	~ 2.3	2.36	2.69
Melting point	°C		44.25	~590 subl.	~ 620 subl.	>620 subl.
Boiling point	°C		281	n.a.	n.a	n.a.
Structure			P_4	amorphous	$((P_8)(P_2)(P_9))_n$	$(P_6)_n$
Resistivity	Ω cm		none	$>10^9$	none	>1000
Solubility			in organic solvents	no	no	no
Toxicity			yes	no	no	no
Odor			fishy	fishy	fishy	mild fishy
Ignition Temperature	°C		ambient temperature	~ 300	~ 400	~ 500

Due to both its high reactivity and solubility in organic media, white phosphorus is highly toxic. MAW (*M*aximum *A*llowable *W*orkplace concentration) according to German regulations is 0.15 mg m^{-3}.

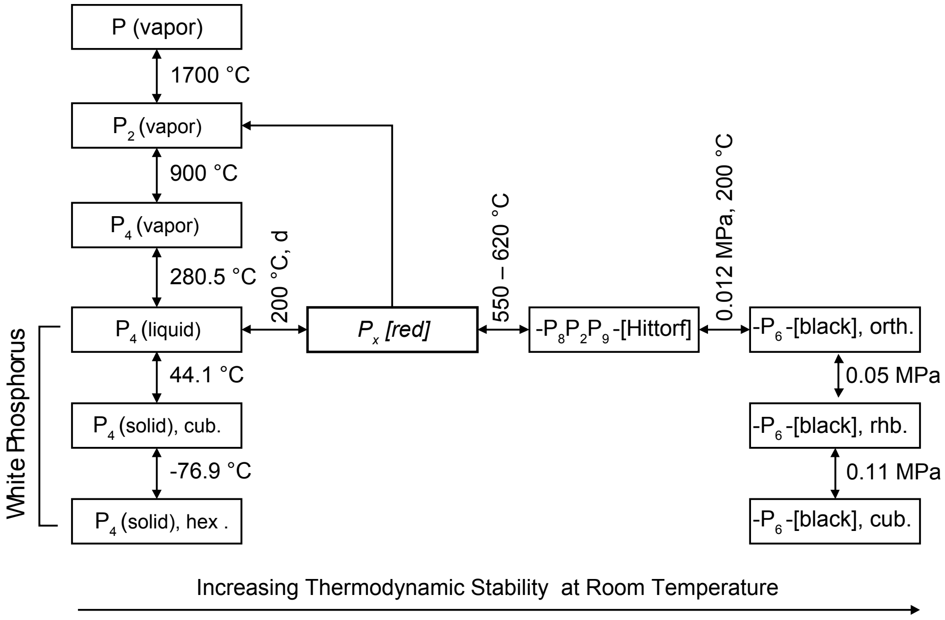


Figure 2. Simplified phase diagram of phosphorus.

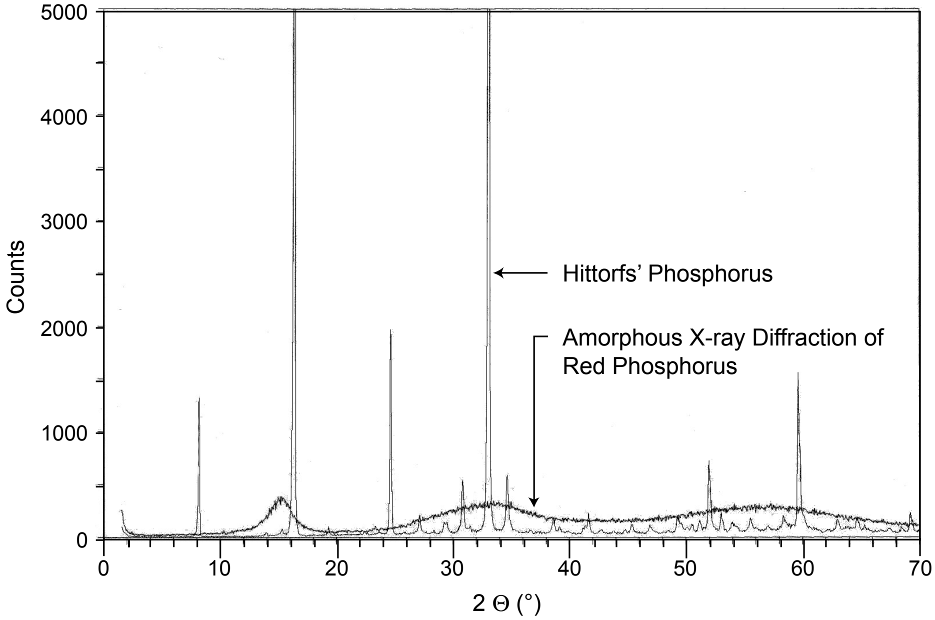


Figure 3. X-ray diffraction of red phosphorus overlaid with crystalline Hittorf's phosphorus

Red Phosphorus (RP)

Whereas defined structures can be assigned to white, violet and the black modification, red phosphorus is an amorphous material whose microscopic structure properties and appearance are strongly dependent on the type of synthesis. Hence red phosphorus cannot be designated as an allotrope but rather as an undefined mixture of phosphorus allotropes. Since the type of production strongly influences the properties of the red phosphorus, it is not possible to give exact physical values for any of the properties of the material but only broad ranges.

With decreasing grain size RP will appear as a violet-brown to orange-red powder.[9]

Although amorphous with respect to X-ray diffraction (Figure 3) several molecular building units of the red phosphorus have been resolved in the last years. According to Pfitzner[10] and Hartl[11] the main constituents of RP are chains made from alternating $(P_2)(P_{10})$-units. Those have been assumed to form upon dimerisation of bullvalene-type P_6 units as has been found by Schröder.[12]

$$P_{2(g)} + P_{4(g)} \xrightarrow{\Delta} P_{6(g)} \tag{4}$$

$$2n\ P_{6(g)} \longrightarrow ((P_2)(P_{10}))_{n(s)} \tag{5}$$

The structural building blocks of the $(P_2)(P_{10})$ strongly resemble the known pentagonal tube units found in the violet allotrope that is the "Hittorf's phosphorus", which is composed of cross-layers of $((P_8)(P_2)(P_9))_n$ units. This explains the ease of formation of the latter modification upon slow heating of red phosphorus, which can be interpreted in terms of a rearrangement of bonds into the more stable and less strained pentagonal tube conformation.

In addition red phosphorus is said to comprise units made from condensed butterfly units. These units are formally built by opening an edge of the P_4-tetrahedron and fusing the free valences to give a new σ-bond between the still highly strained butterfly units.

At present a minimum of two identified different structural building units are responsible for the entire macroscopic structure and behavior of RP. It is also clear that the ratio of both units will strongly depend on the formation mechanism and thus properties vary dependent on the manufacturing process.

Recently Pfitzner and co-workers succeeded in isolating two new allotropes of phosphorus, **1** and **2** by treating both $(CuI)_8P_{12}$ and $(CuI)_3P_{12}$ with aqueous KCN solution. Phosphorus **1** consists of nano-rods made from P_8-cages connected by P_4 rings $((P_8)(P_4))_n$, and phosphorus **2** consists of P_{10} cages that are linked by P_2 units $((P_{10})(P_2))_n$.[13]

Whereas the latter $((P_8)(P_4))_n$ and $((P_{10})(P_2))_n$ units are thermodynamically stable and relatively unstrained, the above mentioned butterfly units impart high strain into the red phosphorus. It is hence that the strain may be released upon energy input such as impact, friction, heat or electrostatic discharge to give free valences which in turn cause self ignition of the material. In addition slow phase transition processes yielding free valences have to be considered when focusing at the long-term stability of red phosphorus.

The "crystallization" of red phosphorus was the object of a diploma thesis by Rudolf.[14]

Reactions of Phosphorus

Long-Term Reactions

Red phosphorus is prone to reactions that pose some difficulties when considering long term storage of pyrotechnic compositions. Oxidative and hydrolytic degradation of red phosphorus is especially pronounced with small particles sizes (<10 µm). Shechkov and coworkers[9] have found that oxidation of small fraction RP (<10 µm) occurs much faster than could be solely explained on the basis of greater surface area. This is explained on the basis of differing chemical constitution of the different fractions, as was demonstrated by different absorption band edge. The primary degradation reaction either in the presence or absence of water is the oxidation of red phosphorus to give phosphorus trioxide.

$$4\ P_{(red)} + 3\ O_2 \xrightarrow{slow} P_4O_{6(s)} \qquad (6)$$

$$P_4O_{6(s)} + 2\ O_2 \xrightarrow{slow} P_4O_{10(s)} \qquad (7)$$

These products in turn react with atmospheric moisture to give

$$P_4O_6 + 6\ H_2O \longrightarrow 4\ H_3PO_3 \qquad (8)$$

$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4 \qquad (9)$$

$$2\ P_{(red)} + 3\ H_2O \longrightarrow PH_3 + H_3PO_3 \qquad (10)$$

Figure 4 shows the FTIR spectrum of non-stabilized red phosphorus. The labeled peaks on the spectrum clearly display the signatures of P_4O_6, H_3PO_3 and H_3PO_4. These byproducts would lead to severe degradation of any pyrotechnic composition if included. Thus red phosphorus has to be treated in order to impede the formation of these byproducts. Norris[15] has investi-

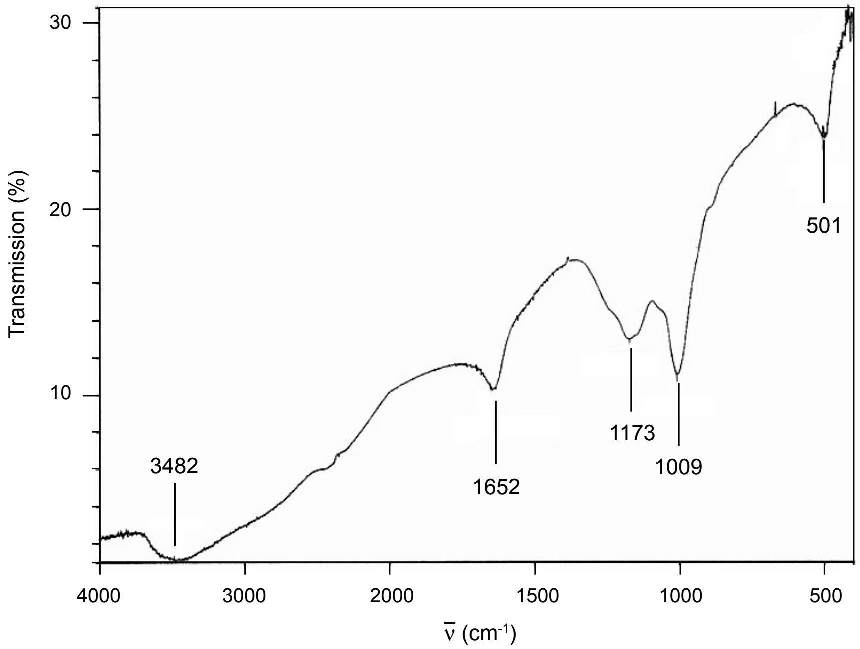


Figure 4. FTIR-spectrum (KBr) of non-stabilized red phosphorus.

gated the degradation of red phosphorus under the influence of air and moisture. Walz and Beard have investigated the action of water on RP.[36]

Stabilisation of Red Phosphorus

To avoid problems with long term stability of red phosphorus, manufacturers treat the raw material in several ways. These treatments include:

- oiling with low melting paraffins, as dust suppressants,
- microencapsulation, as a protective measure against impact, friction and action of chemical agents,
- basic and amphoteric substances to buffer traces of phosphorus acids that themselves have been found as to catalyze the above side reactions and
- stabilizers to impede the phosphane (PH_3) formation.

Epoxy resins are employed as microencapsulation agents, which cover the pure RP grain. In addition the encapsulation process reduces the free surface by scavenging the dust that would be otherwise very prone to ignition due to, for example, adiabatic compression. These encapsulating agents are additionally treated with phthalic acid esters to render the protective coat more flexible in order to reduce the mechanical sensitivity. In the past the hydroxides of both magnesium and aluminum have found application as buffer substances. Today tin-oxide hydrates ($SnO{\cdot}(H_2O)_n$) are applied as state-of–the-art inhibitors against phosphane formation.

Figure 5 displays the FTIR spectrum of HB 700 red phosphorus manufactured by Clariant, the world's leading manufacturer of red phosphorus. Only trace signatures of the above discussed byproducts are discernible. The development of stabilized red phosphorus has been described by Hoerold, Ratcliff[16] and Eisenträger.[17] Lissel[18] from German WIWEB has conducted a comparative investigation on the stability of several commercially available red phosphorus types.

Incompatibilities of Red Phosphorus

Many severe accidents are reported in the literature from the handling of red phosphorus especially when inexperienced persons such as children are involved. These accidents are due to some chemical incompatibilities of the red phosphorus.

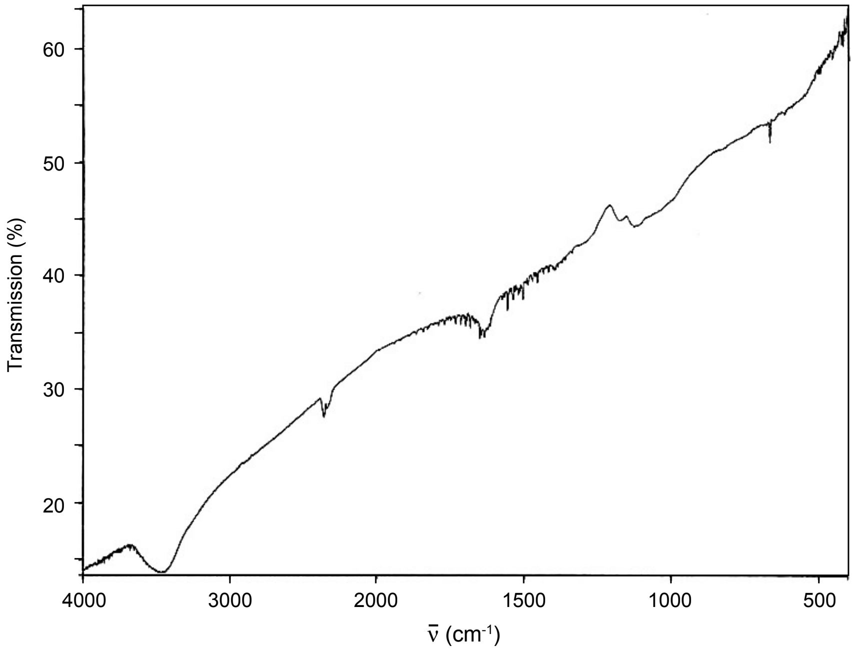


Figure 5. FTIR-spectrum (KBr) of stabilized red phosphorus.

Mixtures with Chlorates

The most “prominent” reported combinations are mixtures of red phosphorus with the chlorates of either sodium or potassium. Potassium chlorate/RP is reported as Armstrong’s mixture in the literature. The extreme sensitivity of these mixtures and the unpredictable behavior with respect to ignition is still somewhat obscure. Nevertheless several plausible causes will be discussed in the following.

The chlorates of both sodium and potassium possess exothermic enthalpies of decomposition according to the general dissociation process:

$$\begin{aligned}&2\ \mathrm{MClO_3} \xrightarrow{\Delta} 2\ \mathrm{MCl} + 3\ \mathrm{O_2}\\ &\Delta_D H^\circ(\mathrm{NaClO_3}): -90\ \mathrm{kJ\ mol^{-1}} \qquad (11)\\ &\Delta_D H^\circ(\mathrm{KClO_3}): -78\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

In addition the thermal decomposition of chlorates occurs at relatively low activation energies of ~ 200 kJ $\mathrm{mol^{-1}}$[19] calling again for low ignition stimulus and fast reaction rates with suitable fuels.

Given the amount of acid present in untreated RP (as indicated by its FTIR spectrum), it is not very surprising that upon contact of this material with chlorates the respective chlorine oxides may be formed, which are known as to decompose fiercely. In 1971 Rollins[20] investigated the chemistry of Armstrong’s mixture and found experimental confirmation of the following exothermic reaction taking place in RP/$\mathrm{KClO_3}$ mixtures with non-stabilized or UV sensitized (that is, sun light!) RP.

$$\begin{aligned}&3\ \mathrm{KClO_3} + 2\ \mathrm{H_3PO_2} \xrightarrow{\text{moisture}}\\ &\qquad 2\ \mathrm{ClO_2} + \mathrm{KCl} + 2\ \mathrm{KH_2PO_4} + \mathrm{H_2O}\end{aligned} \qquad (12)$$

In addition, trace amounts of white phosphorus in RP may trigger accidental reactions.

Mixtures with Miscellaneous Partners

A series of other contact pairs have also been recognized to be highly dangerous due to very high mechanical and thermal sensitivity. These materials are

- perchlorates,
- nitrates of the transition metals (e.g., $\mathrm{AgNO_3}$),
- permanganates, chromates, dichromates,
- inorganic peroxides and
- coruscative[a)] partners having low enthalpy of fusion (e.g., Mg and Zn).

Despite the incompatibility with Mg and Zn, the above pairs suffer from the described acid-base reaction when working with non-stabilized RP. The coruscative partners owe their danger to the low ignition stimulus needed to initiate these mixtures.

Although incompatible, in view of the above compilation, Shimizu[22] reported on the combustion behavior of ternary systems made from gallic acid, potassium perchlorate and RP as well as phthalic acid anhydride/potassium perchlorate/RP mixtures. He observed three stoichiometric ranges showing (1) linear combustion, (2) sizzling combustion and (3) explosion phenomenon. In addition mixtures of barium chlorate (*sic*!) and red phosphorus have been disclosed as incendiary payload constituent for military application.[23] In view of the above, stabilized RP may be indeed stable enough not to undergo spontaneous explosion in these mixtures.

Combustion Properties of Red Phosphorus

When heated to T > 300 °C, RP ignites in ambient air showing a brilliant yellow flame with evolution of a dense white smoke.

Figure 6 displays the DTA/TG plot of red phosphorus (type SF/Clariant). At T ~ 260 °C both the start of an exothermic reaction as well as a mass increase are discernible. The peak temperature for the oxidation process is 405 °C. This coincides with the maximum in the TG plot, which calls for ~ 25 % increase in mass. At higher temperatures a series of consecutive oxidation processes are resolved all accompanied with a decrease in weight to –99 % at 600 °C.

The combustion process of phosphorus occurs in the gas phase and thus has to be understood as a successive process involving phase changes according to the following equations:

[a)] The term coruscative, originally coined by F. Zwicky,[21] refers to mixtures that upon combustion only yield (a) solid product(s). According to the general equations X + Y → XY and AB + CD → AD + CB; the latter describing metathetical reactions thus including also thermitic systems.

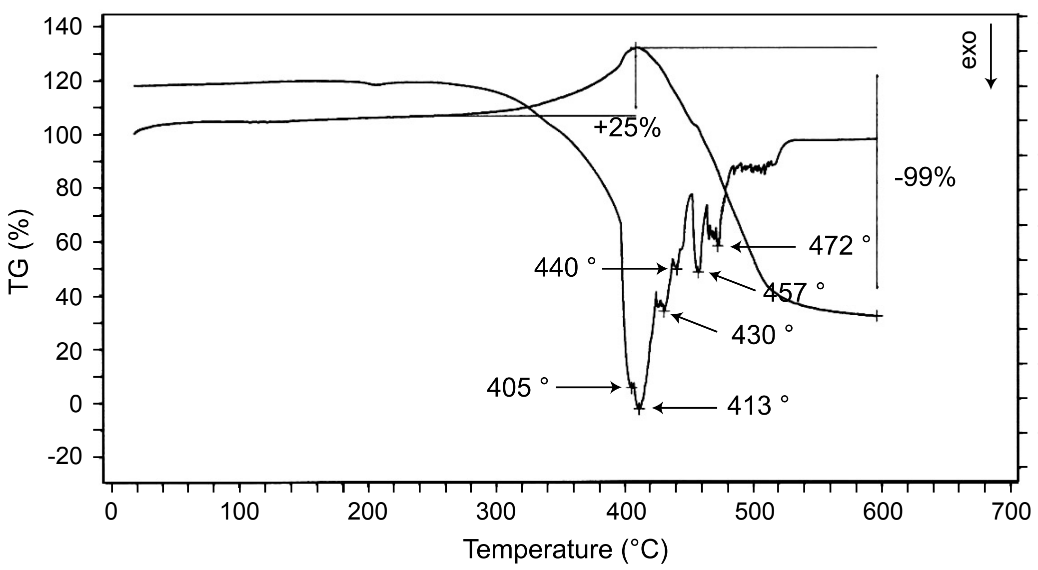


Figure 6. DTA/TG plot of stabilized red phosphorus.

$$4\,P_{(red)} + 17.7\ kJ\ mol^{-1} \xrightarrow{\Delta} P_{4(g)} \qquad (13)$$

$$P_{4(g)} + 5\,O_2 \xrightarrow{\Delta} P_4O_{10(s)} + 2988\ kJ\ mol^{-1} \qquad (14)$$

Under oxygen deficient conditions or under quenched conditions, when much heat is carried away by the environment, the following process also occurs:

$$P_{4(g)} + 3\,O_2 \xrightarrow[quenching]{oxygen.deficiency} P_4O_{6(s)} + 2214\ kJ\ mol^{-1} \qquad (15)$$

The P_4O_6 suboxide often yields white to yellowish stains that can be found on flat surfaces around burning RP pellets.

At T >70 °C this oxide again ignites to combust with atmospheric oxygen to give the pentoxide according to the following equation:

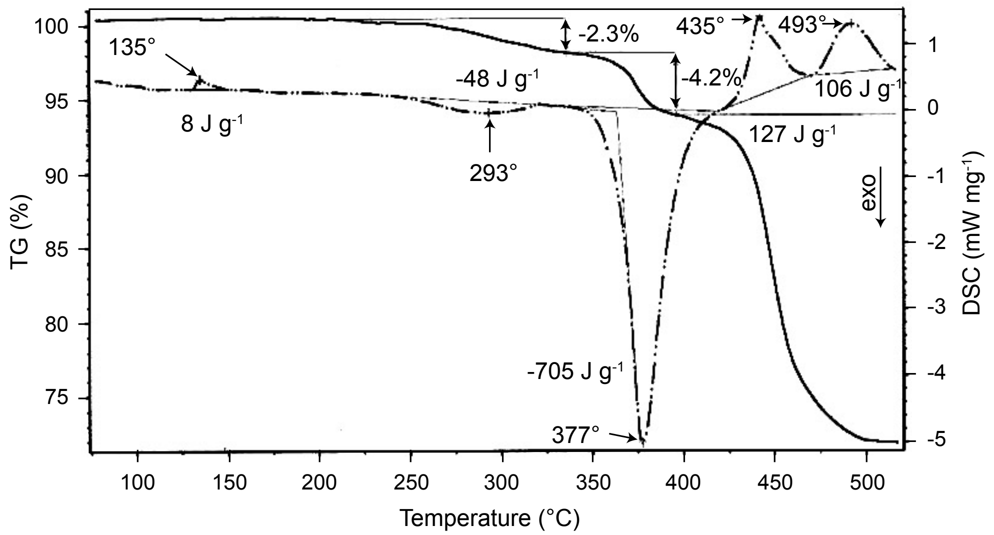


Figure 7. DSC/TG plot of smoke composition under helium.

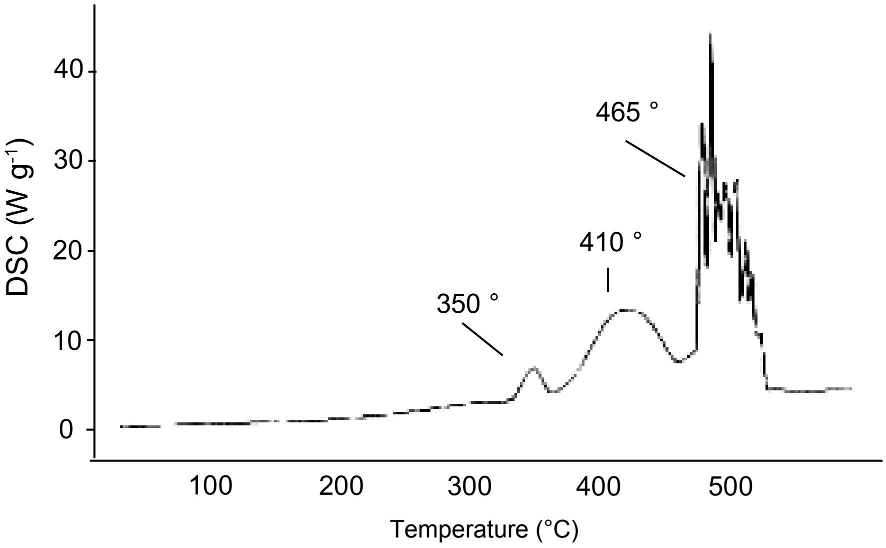


Figure 8. DSC plot of smoke composition under air.

$$P_4O_{6(l,g)} + 2\ O_2 \xrightarrow{\Delta} P_4O_{10(s)} + 774\ \text{kJ mol}^{-1} \quad (16)$$

In mixtures with oxidizers such as alkali nitrates the combustion behavior differs from pure red phosphorus in that the ignition occurs at lower temperatures.

Figure 7 displays the DSC and TG plots for the investigation of a smoke composition based on RP, potassium nitrate, zirconium and polychloroprene binder (60, 25, 10, 5 wt-%) under a helium atmosphere at heating rate of 10 K min^{-1}.

The (*rhombic* → *trigonal*) crystal transition for KNO_3 is observed at 135 °C. A shallow exothermal process has its maximum at ~ 300 °C; the nature of which is unclear at present. A strong exotherm at 377 °C is due to reaction of molten potassium nitrate (mp: 341 °C) with zirconium, which nicely matches with values found by Kubota.[24] The strong mass loss from 400 to 500 °C is due to the vaporization of phosphorus.

Figure 8 displays a DSC plot for the same smoke composition but under a constant stream of air (50 ml min^{-1}). The crystal transition of potassium nitrate has now vanished. Three exotherms are observed at 350, 410 and 465 °C, respectively, which are due to the oxidation of both zirconium and phosphorus.

The absence of atmospheric oxygen in the first experiment allows for distinction between single exothermic reactions in the PIR (Pre-Ignition-Reaction) temperature range. In addition the phosphidation reaction such as Zr + P → ZrP is likewise possible, but it has only been observed to start at T >500 °C having activation energy of 21 ± 12.5 kJ mol^{-1}.[25]

Combustion of the above mentioned consolidated composition in air occurs at T ~295 °C. Thus the unexplained PIR reaction—detected in both the anaerobic an aerobic experiment at T ~295 °C—triggers the actual ignition of the composition.

The high heat of combustion of phosphorus is a prominent feature of the element. In addition there is a large negative neutralization enthalpy available for the pentoxide to react with basic metal oxides according to the general Eq. 17:

$$P_4O_{10} + M_aO_b \longrightarrow M_c(PO_4)_d + Q \quad (17)$$

Since most phosphorus containing compositions are oxygen deficient with respect to the amount of red phosphorus included, other ingredients can react with the red phosphorus. Such ingredients can be metallic fuels, such as Mg, Al, Ti, Zr.

In the case of group 2 elements and aluminum phosphorus yields ionic phosphides according to Eqs. 18a and b[26]

$$3\,\mathrm{Mg} + 2\,\mathrm{P}_{(red)} \xrightarrow{\Delta} \mathrm{Mg_3P_{2(s)}} + 465\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Al} + \mathrm{P}_{(red)} \xrightarrow{\Delta} \mathrm{AlP_{(s)}} + 164\ \mathrm{kJ\ mol^{-1}} \tag{18a+b}$$

The phosphides of both aluminum and magnesium react with water and dilute acids to produce phosphane (PH_3) and the corresponding hydroxide. Since phosphane is highly toxic (MAW < 0.1 mg m^{-3}) and highly flammable, it is no longer acceptable to manufacture pyrotechnic compositions based on red phosphorus that use either of these fuels. Likewise other materials using magnalium (Mg_3Al_4) or calcium silicides $CaSi_x$ (x = 1, 2) that would yield calcium phosphide (Ca_3P_2), are now obsolete (note that Ca_3P_2 is the main product formed upon reaction of Al/Ca_3PO_4 mixtures in rodenticide type matches against moles).

$$\mathrm{Mg_3P_2} + 6\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{PH_{3(g)}}\uparrow + 3\,\mathrm{Mg(OH)_2}$$

$$\mathrm{AlP} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{PH_{3(g)}}\uparrow + \mathrm{Al(OH)_3} \tag{19a+b}$$

Since this chemical incompatibility has led to numerous fires on training grounds using several ammunition types, an improved formula needed to be developed.

The author[27] developed a series of smoke compositions based on both titanium and zirconium. With the application of zirconium and/or titanium as an additional fuel, the side reaction products TiP and ZrP are metallic type phosphides that do not react with moisture or even dilute acids such as “acid rain”.[28] Hence smoke compositions based on red phosphorus and Ti or Zr do not yield poisonous combustion products.

The constituents of the combustion products of several smoke compositions, based on red phosphorus, sodium nitrate, organic binder and magnesium have been investigated by Klusáček and Navrátil[29] by means of ^{31}P-NMR-spectroscopy. In systems having magnesium as an additional fuel, the major combustion/hydrolysis product is hydrogen phosphate (HPO_4^{2-}) along with modest amounts of diphosphate ($P_2O_7^{4-}$) and minor amounts of dihydrogenphosphate ($H_2PO_4^-$) and *cyclo*-triphosphate ($(OHOPO)_3^{3-}$). In contrast magnesium-free systems provide a mixture of *cyclo*-(tri-, tetra- and hexa-)phosphates as the major combustion/hydrolysis products and modest amounts of both dihydrogen phosphate and dihydrogendiphosphate ($H_2P_2O_7^{2-}$). Freiwald and coworkers[30,31] also investigated the combustion constituents of RP based smoke compositions.

Combustion of Phosphates with Metals

The potential of alkali metal and alkaline earth salts of oxyacids such as carbonates, phosphates and sulfates to act as single oxidizers in stoichiometric magnesium-based pyrotechnic systems has been impressively demonstrated by Shimizu.[32,33] In this context calcium orthophosphate ($Ca_3(PO_4)_2$) [7758-87-4] ($\Delta_f H$: –4120 kJ mol^{-1}), calcium dihydrogenphosphate ($Ca(H_2PO_4)_2$) [7758-23-8] ($\Delta_f H$: –3104 kJ mol^{-1}) and phosphorus pentoxide (P_4O_{10}) have been evaluated as oxidizers in stoichiometric mixtures with magnesium. An intimate mixture of P_4O_{10} and Mg ignites with a bright flash when contacted with water. A pulverized mixture of magnesium with $Ca(H_2PO_4)_2$ ignites at ~ 330 °C. Even consolidated, this mixture burns fiercely to produce a luminous flame. Although calcium orthophosphate/Mg mixtures ignite in the pulverized state, they do not ignite in the pressed form.[32]

Combustion products of calcium orthophosphate aluminum mixtures contain Ca_3P_2, which subsequently reacts with water and humidity to produce toxic phosphane (PH_3).[34]

Combustion of Phosphorus Sulfides with Oxidizers

In strike anywhere (SAW) matches, red phosphorus has been replaced by tetraphosphorus trisulfide (P_4S_3) [1314-85-8] ($\Delta_f H$:–224 kJ mol^{-1}). P_4S_3 is a light yellow crystalline that melts at 174 °C and vaporizes at 408 °C. It displays a chemiluminescence at temperatures from 40 to 60 °C comparable to that of WP and ignites at ~ 100 °C. It is very soluble in carbon disulfide (CS_2). Its friction sensitivity surely is due to high strain of the three-membered phosphorus ring present in the molecule.

Inhibiting Combustion with Phosphorus

Although highly flammable, red phosphorus is also a very potent flame retardant. Thus many commercial polymers in structural units subjected to thermal stress are often loaded with red phosphorus and also organic phosphorus compounds such as dimethyl methylphosphonate (DMMP, $C_3H_9O_3P$) and trimethyl phosphate (TMP, $C_3H_9O_4P$)). In fact the largest amount of red phosphorus produced today is used in applications as flame retardants. The mechanism is based on the flameless recombination of H and OH radicals in hydrocarbon flames. The actual process has been recently elucidated to occur via the following sequence:

$$\begin{aligned}
&H + PO_2 + M \overset{\longleftarrow}{\longrightarrow} HOPO + M \\
&H + HOPO \overset{\longleftarrow}{\longrightarrow} H_2 + PO_2 \qquad (20a\text{–}c) \\
&OH + HOPO \overset{\longleftarrow}{\longrightarrow} H_2O + PO_2
\end{aligned}$$

Thus the intermediate phosphorus dioxide (PO_2) scavenges hydrogen radicals to successively yield water and the PO_2 again. It is said that the termolecular reaction is the most efficient one in removing H radicals (with *M* being an inert collision partner).[35]

References

1) E.-C. Koch, “Special Materials in Pyrotechnics: III. Application of Lithium and its Compounds in Energetic Systems”, *Propellants, Explos., Pyrotech.*, Vol. 29, 2004, pp 67–80.

2) N. Davies, T. T. Griffiths, E. L. Charsley, and J. A. Rumsey, “Studies on Gasless Delay Compositions Containing Boron and Bismuth Trioxide”, *Proc. 16th Int’l. Annual Conference of ICT, Karlsruhe*, 1985, p 15ff.

3) R. Lancaster, *Fireworks – Principles and Practice*, 3rd ed., Chemical Publishing Co. Inc., New York, 1998, p 209.

4) H. J. John Jr., C. Yeager, D. Pile, and T. Webb, U.S. Patent 6 478 903, 2002, Nontoxic Primer Mix, RA Brands LLC, Madison, WI, USA.

5) N. Davies, “Red Phosphorus for Use in Screening Smoke Compositions”, *Report prepared under Contract No. NBSA5B/2701 Task 8*, February 1999, Royal Military College of Science Cranfield University Shrivenham, 1999.

6) J. Emsley, *The Shocking History of Phosphorus*, Pan MacMillan, London, 2000.

7) Literature archive of the author.

8) H.-B. Qian, P. B. Davies, and P. A. Hamilton, “High-Resolution Spectroscopic Study of the Oxidation of White Phosphorus”, *J. Chem. Soc., Faraday Trans.* ,Vol. 91, 1995, pp 2993–2998.

9) G. T. Shechkov, A. V. Domin, and N. M. Neskorodova, “Low-Temperature Oxidation of Red Phosphorus”, *Russ. J. Appl. Chem.*, Vol. 66, 1993, pp 1501–1504.

10) E. Freudenthaler Pfitzner, “$(CuI)_3P_{12}$: Ein Festkörper mit einer neuartigen theoretisch vorhergesagten Form des Phosphors”, *Angew. Chem.*, Vol. 107, 1995, pp 1784–1785.

11) H. Hartl, “Neues zur Struktur des amorphen roten Phosphors”, *Angew. Chem.*, Vol. 107, 1995, pp 2857–2859.

12) D. Schröder, H. Schwarz, M. Wulf, H. Sievers, P. Jutzi, and M. Reiher, “Experimenteller Nachweis von neutralem P_6: ein neues Allotrop des Phosphors”, *Angew. Chem.*, Vol. 111, 1999, pp 3723–3726.

13) A. Pfitzner, M. F. Bräu, J. Zweck, G. Brunkhaus, and H. Eckert, “Phosphorus Nanorods – Two Allotropic Modifications of a Long-Known Element”, *Angew. Chem.*, Vol. 116, 2004, pp 4324–4327.

14) P. Rudolf, “Zur Kristallisation des Roten Phosphors”, *Diploma thesis*, Fachhochschule Reutlingen, 1983.

15) V. J. Norris, “Investigation of the Mechanism of the Oxidation of Red Phosphorus”, *27th Int’l. Pyrotech. Semin.*, July 16–21, 2000, Grand Junction, Colorado, USA, pp 207–216.

16) S. Hoerold and A. Ratcliff, “Commercial Development in Red Phosphorus Perform-

ance and Stability for Pyrotechnics", *J. Pyrotech.,* Vol. 13, 2001, pp 54–60.

17) F. Eisenträger, "Key Parameters for the Stability of Red Phosphorus", *31st Int. Pyrotech. Semin.*, July 10–15, 2004, Fort Collins, Colorado, p 503.

18) E. Lissel, "Electrochemical Detection of Gaseous Products To Determine the Stability of Pyrotechnics – Construction of a Test Apparatus and First Results", *2nd Int. Workshop Mikrokalorimetrie/Stabilität von Treibladungspulvern – Forum Explosivstoffe 1999*, WIWEB, Swisttal Heimerzheim, 9.–10.03.1999.

19) G. Krien, *Thermoanalytische Ergebnisse von pyrotechnischen Ausgangsstoffen*, Report Az.: 3.0-3/3712/75, 1975, BICT, Swisttal Heimerzheim, Germany.

20) R. R. Rollins, "Potassium Chlorate/Red Phosphorus Mixtures", *7th Symposium on Explosives and Pyrotechnics*, The Franklin Institute Research Laboratories, Philadelphia, USA, September 8–9 1971. p III-11.

21) F. Zwicky, U.S. Patent 3 135 205, 1964, Coruscative Ballistic Device, Hycon Mfg Company, Pasadena, CA, USA.

22) R. Lancaster, *Fireworks – Principles and Practice*, 3rd ed., Chemical Publishing Co., Inc. New York, 1998, pp 153.

23) E. Nourdin, EP 0.663 376 A1, 1994, Composition incendiaire et projectile incendiaire dispersant une telle composition, Giat Industries, France.

24) K. Miyata and N. Kubota, "Combustion of Ti and Zr Particles with KNO_3", *Propellants, Explos., Pyrotech.*, Vol. 21, 1996, pp 29–35.

25) F. Freund and K. A. Gingerich, "Phosphidation of Zirconium", *Ber. Deut. Keram. Ges.*, Vol. 43, 1966, pp 132–135.

26) V. B. Chernogorenko and K. A. Lynchak, "Thermodynamic Analysis of the Combustion of Metal Powders and their Oxides in Phosphorus and of the Combustion of the Phosphides Formed in Oxygen", *Combustion, Explosion, and Shock Waves*, Vol. 34, 1998, pp 298–304.

27) E.-C. Koch and A. Dochnahl, U.S. Patent 6.581.520, 1999, Pyrotechnic active mass for producing an aerosol highly emissive in the infrared spectrum and impenetrable in the visible spectrum, Pepete GmbH, Hanau, Germany.

28) G. Brauer (Ed.), "*Handbuch der Präparativen Anorganischen Chemie*", Vol. 2, Ferdinand Enke Verlag, Stuttgart, 1978, pp 1382–1384.

29) L. Klusáček, P. Navrátil, "The Use and Application of Red-Phosphorus Pyrotechnic Composition for Camouflage in the Infrared Region of Radiation", *Propellants, Explos., Pyrotech.*, Vol. 22, 1992, pp 74–77.

30) H. Freiwald, G. Prähauser, and A. Schießl, "Improvements in Pyrotechnical Smoke", *6th Int. Pyrotech. Semin.*, July 17–21, 1978, Estes Park, Colorado, pp 185–208.

31) H. Freiwald, G. Prähauser, and A. Schießl, "Reaction Mechanism in a Smoke Mixture",*7th Int. Pyrotech. Semin.*, July 14–18, 1980, Vail, Colorado, pp 529–542.

32) T. Shimizu,"A Concept and the Use of Negative Explosives", *11th Int. Pyrotech. Semin.*, July 7–11, 1986, Vail, Colorado, pp 537–553.

33) T. Shimizu, "An Example of Negative Explosives: Magnesium Sulfate/Magnesium Mixture", *15th Int. Pyrotech. Semin.*, July 9–13, 1990, Boulder Colorado, pp 857–875.

34) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing Co. Inc., New York, 1968, p 359.

35) M. A. Macdonald, F. C. Gouldin, and E. M. Fisher, "Temperature Dependence of Phosphorus-Based Flame Inhibition", *Combust. Flame*, Vol. 125, 2001, pp 668–683.

36) R. Walz, A. Beard, "Chemical behaviour of Red Phosphorus in Water", Clariant GmbH, Sulzbach, Germany, 14. January 2000, 16 pp.

Impact Sensitiveness Analysis of Pyrotechnic Flash Compositions

S. P. Sivapirakasam,[1] M. Surianarayanan,[2a] P. Nagaraj,[1] G. S. Venkataratnam[2]

1) TIFAC-CORE in Industrial Safety, Department of Mechanical Engineering,
Mepco Schlenk Engineering College, Sivakasi - 626 005, India.

2) Cell for Industrial Safety & Risk Analysis, Chemical Engineering Department, Central Leather Research Institute, (Council of Scientific & Industrial Research), Adyar, Chennai - 600 020, India.

2a) Corresponding author: e-mail: msuri1@vsnl.com

ABSTRACT

Impact sensitiveness of pyrotechnic flash compositions consisting of mixtures of potassium nitrate (KNO_3), sulphur (S) and aluminium (Al) is experimentally analyzed using equipment similar to BAM (fall hammer) equipment. Results indicate that an increase in the sulphur content of the mixture raises its sensitivity to impact. The limiting impact energy (LIE) falls in the range of 5 to 8 J for the compositions studied, which may be categorized as class III explosives. The results obtained, using the statistical tool "Mixture Design", are helpful in correlating the characteristics of each component in the mixture with the overall impact sensitiveness. The model predictions and experimental results are found to match well within ± 0.5% error. Cost analysis and sound measurements are made for all compositions, and the results are compared with impact sensitivity to arrive at ratios of ideal compositions.

Keywords: flash composition, fireworks, impact sensitiveness, mixture design, pyrotechnics, potassium nitrate, sulphur, aluminum

1 Introduction

Pyrotechnic mixtures are energetic compounds susceptible to explosive degradations on ignition, impact and friction.[1] Several accidents have been reported in Indian fireworks manufacturing units during processing, storage and transportation.[2,3] An analysis of accident data recorded during the past ten years in Tamilnadu in India has shown that the main causes are inadequate knowledge of the thermal, mechanical and electrostatic sensitiveness of fireworks mixtures.[4] Unfortunately, the sensitivity of a mixture to explosion cannot be theoretically predicted as it depends on the reactive nature of the mixture components and the conditions employed during the preparation of the mixture and its handling. Though Material Safety Data Sheets (MSDS) of pure chemicals are readily available, no such data are available for mixtures. Additionally, the mixture's composition varies from company to company for the same type of application. There are no standard procedures or techniques to estimate performance related concepts applicable to mixing ratios. This leads to difficulties in providing a standard scale for assessing the quality of fireworks. Due to the lack of standard manufacturing equipment, tools, manufacturing procedures, combined with a poor understanding of the chemistry of pyrotechnics and their explosive nature, accidents continue to take place in the fireworks industry.

Most fireworks mixtures consist of an oxidizer, a fuel, a color enhancing chemical and a binder.[5] The chemicals employed and their compositions vary depending upon the type of fireworks being produced.[6] The fireworks' effectiveness depends not only on the mixture composition, but also on factors such as particle size, moisture content, packing density and purity of the chemicals.

As per the Indian Explosives Act, 1884, the use of chlorate and sulphur mixtures is prohibited due to its ease of ignition and sensitiveness to undergo explosive decompositions.[7] Alternate mixtures have been widely used in the fireworks industry. Nonetheless, accidents still occur, and the main reason is the poor understanding of the explosive nature and lack of mechanical and thermal sensitivity data for mixtures containing nitrate and sulphur compounds. In the past researchers[8–11] have studied the thermal stability and mechanical sensitivity of sulphur and chlorate mixtures. However, the impact sensitivity of mixtures containing potassium nitrate (KNO_3), sulphur (S), and aluminium (Al) has not yet been reported.

The present study has multiple objectives; the first is the classification of the mixture according to the Andreiev-Beliaev classification of explosivity of substances.[12–13] The other objectives are: to study the impact sensitiveness of mixtures containing KNO_3, S, and Al using the statistical tool "Mixture Design"; to develop a composition with reduced cost and optimum sensitivity that meets the sound levels specified by legislation. The study also assesses the impact sensitivity of flash compositions and helps to choose an ideal composition such that the cost and environmental pollution due to excessive usage of chemicals can be minimized.

2 Chemistry and Mechanism of Flash Composition Fireworks

Flash compositions used in fireworks compositions consist of an oxidizer, commonly potassium chlorate or barium nitrate with aluminum. Some companies use potassium nitrate as the oxidizer, so this paper also examines flash compositions containing potassium nitrate as the oxidizer. Sulphur acts as the ignition source, and aluminum acts as a fuel to oxidize the potassium nitrate. When a flash composition is ignited by its fuse, initially the sulphur melts. During melting, the interaction between atoms increases.[14] This results in more atoms with energies exceeding activation energy that will be in contact and react. As the reaction rate increases, the rate of energy release increases, which leads to thermal runaway at a lower temperature, and the flash composition explodes.

3 Experimental

3.1 Materials

The chemicals used for the preparation of the flash compositions were obtained from a firework manufacturing company situated in the southern state of Tamilnadu, India. The purity and assay of the chemicals were: KNO_3 - 91.6%, S - 99.84% and Al - 99.71%. The chemicals were passed through a 100-mesh brass sieve. The samples were stored in an airtight container and kept away from light and moisture.

3.2 Design of Experiments

The statistical tool "Mixture Design" was used to explore the influence of the three components of a flash composition (KNO_3, S, and Al) with regard to sensitiveness. The design of experiments for the mixture design model was generated by the software "Design Experts".[15] Based on the chemistry, as well as currently employed compositions in the industry, the three components were restricted as shown in Table 1. It was understood that the flash compositions had all the components within the specified levels of variation. The limits in Table 1 formed a triangle like that shown in Figure 1 as they were used in the experimental design. This is termed the simplex lattice mixture design model. The three vertices represent the maximum allowed quantity for a specific component. For example, the top vertex represents potassium nitrate with an upper limit of 65%; sulphur and aluminum have limits of 20 and 45%, respectively.

Table 1. Range of Flash Compositions Mixtures.

Component	% Range	
	Minimum	Maximum
KNO_3	50	65
S	5	20
Al	30	45

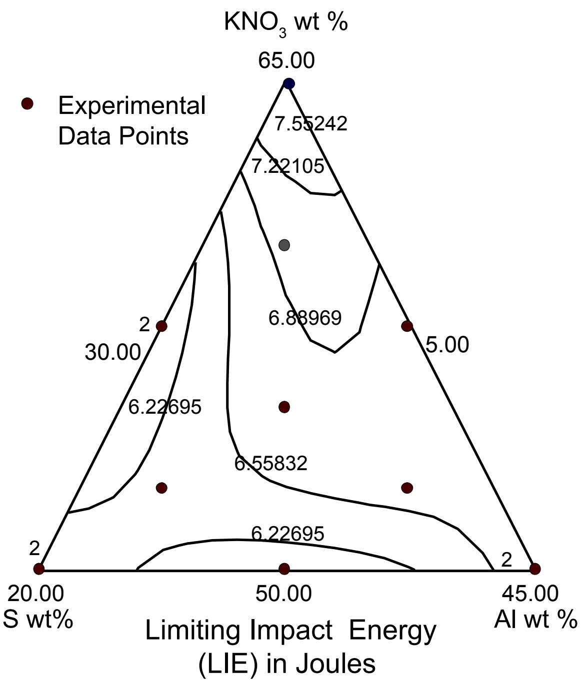


Figure 1. 2-D view of the results for the mixture design showing the results for flash compositions with respect to impact sensitivity.

Table 2 shows the various flash compositions generated by the simplex lattice mixture design model. The experiments were carried out as per the order mentioned in Table 2. In each experiment, 10 g of flash composition was prepared and mixed well, using a wooden spatula in a non-flammable container. The impact sensitiveness measurements were made using the equipment supplied by Electro Ceramics Private Limited, Pune, India as per the procedure described below.

3.3 Measurement of Impact Sensitivity

The diagram of the equipment used in this study for impact sensitiveness measurement is shown in Figure 2. The design and principle of the equipment is similar to that of the drop fall hammer equipment of BAM standards. For each test a 40 mg sample was placed in the anvil and a weight of mass 2 kg (standard weight) was allowed to drop from different heights. The dropping of the weight was controlled remotely. On triggering the remote, the weight fell on the sample through the guides fixed to the column so that the weight dropped directly on the striking head of anvil without rebound and distortion. Ignition of the mixture was observed using an optical sensor. The impact sensitiveness was measured in terms of the Limiting Impact Energy (LIE) and calculated using equation 1.

Table 2. Experimental Data of Flash Composition Mixtures Using the Mixture Design Model.

Exp. No.	Run Order	KNO_3 (wt %)	S (wt %)	Al (wt %)	Drop Mass Height (m)	LIE (J)	Maximum Sound Pressure Level (dB (Al_{max}))	Cost / kg of Mixture in INR
1	14	50	5	45	0.36	7	112	220
2	5	65	5	30	0.41	8.04	114	190.81
3	12	50	20	30	0.34	6.66	115.9	183.32
4	6	50	12.5	37.5	0.3	5.88	114.8	202.07
5	1	57.5	12.5	30	0.31	6.08	114.4	187.07
6	11	57.5	5	37.5	0.34	6.67	110.4	205.82
7	4	60	7.5	32.5	0.33	6.5	113.1	194.57
8	8	52.5	7.5	40	0.37	7.2	115.4	209.57
9	3	52.5	15	32.5	0.31	6.1	112.3	190.82
10	13	55	10	35	0.35	6.8	112	198.32
11	2	65	5	30	0.40	7.88	114	190.81
12	9	50	5	45	0.32	6.27	111.3	220.82
13	7	50	20	30	0.34	6.66	115.2	183.32
14	10	57.5	12.5	30	0.31	6.08	117	187.07

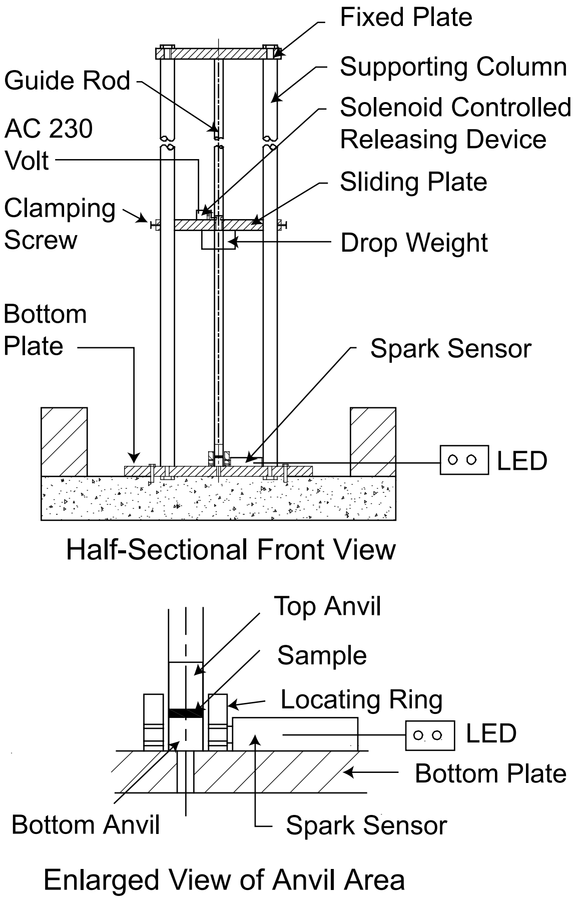


Figure 2. Diagram of the equipment for measuring impact sensitivity.

$$LIE = mgh \tag{1}$$

where

LIE - limiting impact energy in joules (J)
m - weight of the drop mass in kilograms (kg)
g - acceleration due to gravity (9.81 m/s^2)
h - fall height in meters (m)

The impact sensitivity measurements were carried out according to the procedure outlined in the United Nations (UN) *Recommendations on the Transport of Dangerous Goods*.[16] The UN test procedure recommends BAM (fall hammer) equipment for impact sensitivity measurements. The equipment used in this study was obtained from a local manufacturer, so the validity of the results was tested by matching them with the *LIE* of standard substances.[16] A comparison of the results appears in Table 3. The impact energy measured was within acceptable limits of errors (2–3%). Several runs were undertaken to check the reproducibility of the data.

Table 3. Validity of Test Data for Standardization of the Drop Weight Apparatus.

Substance	*LIE* (J) Tested by BAM (Fall Hammer)	*LIE* (J) Tested by Standardized Equipment	Error (%)
Lead azide (dry)	2.5	2.55	2
Tetryl (dry)	4	4.10	2.5

3.4 Measurement of Sound Level

Sound levels of the flash composition reported in this study were measured using the sound level monitor, Model No. 824 obtained from M/s. Larson-Davis, USA. A test charge of the flash composition was made, and the sound levels were measured according to the specification given in Government of India's gazette notification[17] for sound level measurement. The distance from the sample to the sound meter was 4 m. The test charge (see Figure 3) was approximately 25 mm in length, composed of a three-tier paper board (thickness 1.5 mm). The arrangement was compacted clay at the bottom, about 1.6 g of

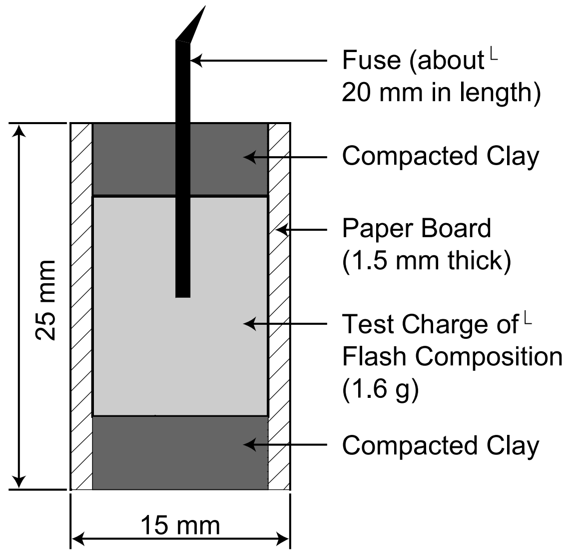


Figure 3. Sketch of test container.

flash composition in the middle, and compacted clay added to the top layer. A fuse (approximately 20 mm in length was placed at the center of the test charge. The results of the maximum sound pressure level in decibels dB (AI_{max}) for each sample are summarized in Table 2.

4 Results and Discussion

4.1 Effect on Impact Sensitiveness

The results of impact sensitiveness measurements for the different flash compositions are given in Table 2. It was observed that the impact energy varied when any one of the component concentrations of the mixture was changed. This behavior was due to the sensitivity and reactivity of each component. A rigorous analysis of the experimental data was carried out employing a simplex lattice mixture design model of Design Experts software. The results are shown in Figures 1 and 4. Figure 1 is the result of the special cubic model fit for the regression of LIE according to equation 2.

$$\begin{aligned} Y = {} & 0.78028\times A+10.36548\times B \\ & +1.49537\times C-0.21396\times A\times B \\ & -0.042330\times A\times C-0.33036\times B\times C \\ & +0.00687\times A\times B\times C \end{aligned} \qquad (2)$$

where

Y - *LIE* (J)
A - wt. % of KNO_3
B - wt. % of S
C - wt. % of Al

The centroid in the equilateral triangle was considered for discussion of the effects and interaction of each component. The points above the centroid were indicative of less sensitive (higher LIE) mixture compositions while the points below the centroid represented high sensitive (lower LIE) mixture compositions. Varying the quantity of potassium nitrate in the reaction mixture had only a minimal effect on impact sensitivity. However, increasing the concentration of sulphur had a marked influence on impact sensitivity. At lower concentrations of aluminium, the impact sensitivity was greater, but above 40% by weight of aluminium, the mixture became less sensitive. This trend showed that sulphur helped to ignite the reaction mixture rapidly, while aluminum was able to transfer the energy to the oxidizer to a limited level. Further increase in either sulphur or aluminum concentration made the mixture less impact sensitive, and the ability to explode appeared as a limiting factor in the mixture composition. The findings corroborated the previously reported results of sulphur–chlorate–aluminum mixtures.[8–11] This was further confirmed from the statistical model given in equation 2 (i.e., the co-efficient of each element indicated the severity of sensitivity in the mixture).

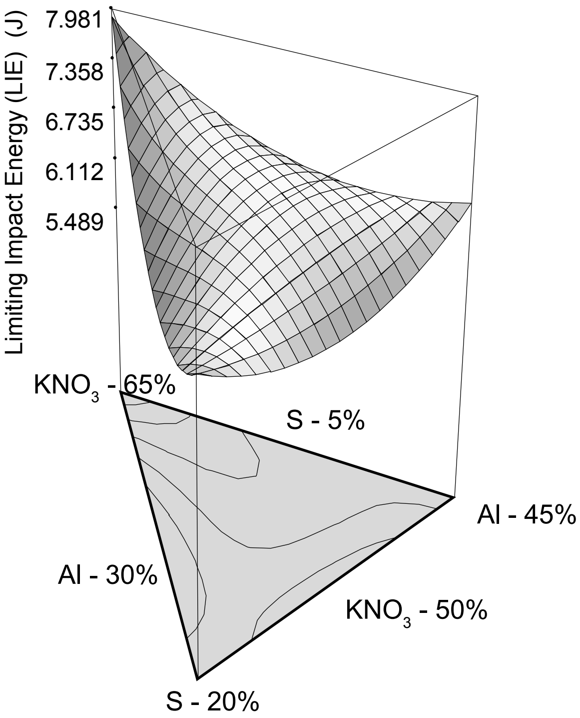


Figure 4. 3-D view of simplex lattice design model mixture contour graph showing the effect and interactions of the flash composition with impact sensitivity.

Moreover there was a narrow distribution of *LIE* (5–8 J) for the mixture ranges studied. Hence the possibility of arriving at optimal mixtures for flash compositions was not raised. From the impact sensitivity results given in Table 2, it was observed that the entire range could be grouped as category III explosives according to the classification of Andreieve-Beliaev.[12–13] Since all the compositions were sensitive to impact, there was no one optimal composition for explosivity. It should also be noted that the explosion effi-

Table 4. Analysis of Variance (ANOVA) for the Special Cubic Model – Partial Sum of Squares.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	Prob > F	Remarks
Model	4.581796	6	0.763633	5.419266	0.0216	Significant
Linear Mixture	1.20659	2	0.603295	4.281399	0.0610	
KNO_3/S	2.217775	1	2.217775	15.73886	0.0054	
KNO_3/Al	0.2887	1	0.2887	2.048815	0.1954	
S/Al	0.368433	1	0.368433	2.614655	0.1499	
KNO_3/S/Al	0.500298	1	0.500298	3.550464	0.1015	
Residual	0.986375	7	0.140911			
Lack of Fit	0.707125	3	0.235708	3.376306	0.1352	Not significant
Pure Error	0.27925	4	0.069813			
Corrected Total	5.568171	13				

ciency depends not merely on the flash composition but on the fuse, paper wrap (tube strength) and string wound around the flash composition.

Since the above impact sensitivity results indicated that the entire range of mixtures studied was prone to hazards from impact, all of them also produced good firecrackers. Surprisingly, there was wide variation in the compositions used among the Indian fireworks companies though they had to exhibit a specific level of explosivity. This meant that some manufacturers were employing unwanted quantities of chemicals. During hazardous situations, the use of excessive quantities of chemicals will lead to excessive damage to the ecosphere. Thus, from this study it is possible to arrive at an ideal composition by considering a few other parameters like sound pressure level and cost.

4.2 Sound Levels and Cost Analysis of Flash Compositions

The results of maximum sound pressure level for the flash compositions shown in Table 2 varied within the narrow range from 110 to 117 dB (AI_{max}) when measured at 4 m. The measured ranges all fell below the maximum sound level requirements of 125 dB (AI_{max}) prescribed by the Government of India in a gazette[17] for noise standards for firecrackers. A close look at Table 2, suggests that varying the compositions drastically did not alter the sound pressure level significantly. Thus, the sound pressure level studies prove that a cost effective mixture (within the ranges studied) can be chosen from the point of view of reduced impact hazards and environmenttal pollution. From Table 2 the cost of the compositions varies from INR 183 to 220 for various mixtures that exhibit similar explosivity and hazardous property (impact). Therefore, Composition No. 3 in Table 1 (consisting of 50% KNO_3, 20% S and 30% Al) appears to be an ideal composition in all respects (i.e., reduced impact sensitivity, required explosivity and sound pressure level, and minimum cost).

4.3 Stability of the Model

The stability of the statistical model can be verified from the Analysis of Variance (ANOVA) given in Table 4. The software output shows that the model is significant with probability (P) 0.0216 and no lack of fit with P = 0.1352, which is larger than the reference limit P of 0.005. The normal probability plot of the response residuals is shown in Figure 5. The convergence of the data indicates a minimum deviation from the fit. The goodness of fit ($R^2 = 0.82$) and the goodness of prediction ($Q^2 = 0.67$), confirm that the levels are within acceptable limits.[18]

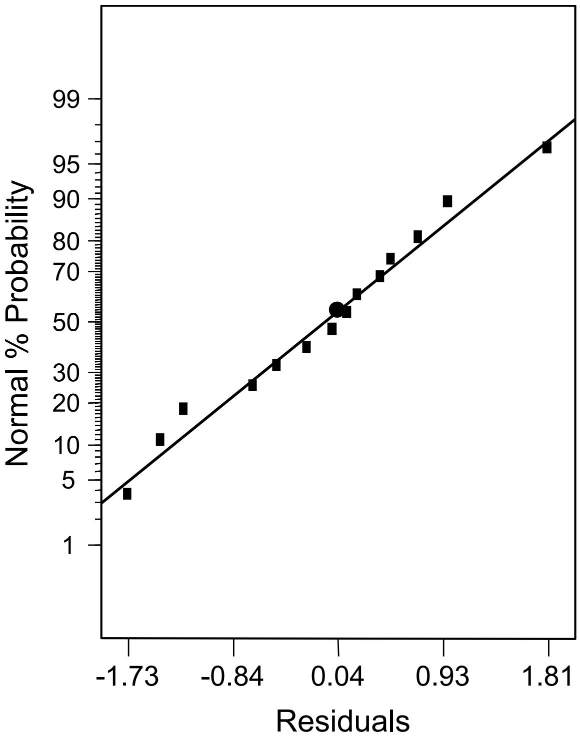


Figure 5. Normal probability plot of the response residues indicating deviation of experiments within the acceptable level.

5 Safety of Flash Composition

The impact sensitivity analysis indicates that the flash compositions studied can be categorized as class III explosives that are sensitive to impact. Hence, caution is required while handling these mixtures.

6 Conclusions

The impact sensitivity measurement studies show that the mixtures are sensitive to impact and can be categorized as class III explosives. The statistical results help to correlate the characteristics of each component in the mixture with respect to impact sensitivity. The model predictions and experimental results are found to match well within a range of ± 0.5% error. The cost and sound pressure level studies suggest an ideal flash composition (50% KNO_3, 20% S and 30% Al) for the fireworks manufacturing industry that has reduced impact sensitivity, meets the specified explosivity and sound pressure level, and has reduced cost.

Acknowledgements

S. P. Sivapirakasam is grateful to the management and Principal, Mepco Schlenk Engineering College, Sivakasi, for their constant encouragement. The author is also grateful to TIFAC, Department of Science Technology, and Government of India for offering facilities to carry out this research. The authors are thankful to Mr. T. Baskaran, Technician of the Institute for his assistance while carrying out the impact sensitivity experiments. The authors are thankful to the Head, Chemical Engineering Department and Director, CLRI for their kind permission to carry out this study at CLRI.

References

1) John A. Conkling, “Ignition Sensitivity of Fireworks Composition”, *Proceedings of the International Symposium on Fireworks*, Montreal Canada, 1992.

2) M. Veeramani and S. P.Sivaprakasam, “Safe Storage and Handling of Pyrotechnic Chemicals”, *Indian Chemical Engineering Congress*, Chennai, December 2002, p 126.

3) A. Celladhurai, *Fireworks Related Accidents How Caused and Who Is Responsible*, published by Standard Fireworks, Tamilnadu, India, 1990.

4) S. P. Sivaprakasam, M. Surianarayanan, G. S. Venkataratnam, and P. Nagaraj, “Hazard Evaluation Techniques for Fireworks Compositions”, *Indian Chemical Engineering Congress*, Hyderabad, 19–22, December 2003, p 126.

5) R.R. Lancaster, *Fireworks Principles and Practice*, Chemical Publishing Company, New York 1972, p 25.

6) K. N. Ghosh, *The Principles for Fireworks*, Department of Explosives, Govt. of India, copyright Economic Enterprise, Ahmedabad, India, 1982.

7) *A Guide to Explosive Act, 1884 and Explosive Rules, 1883 (India), Rule No. 6,* Eastern

Book company, Lucknow, 10th ed. 2002, p 139.

8) D. Chapman, R. K. Wharton, and G. E. Williamson, "Studies for the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixture Part I – Introduction", *Journal of Pyrotechnics*, No. 6, 1997, p 30.

9) D. Chapman, R. K. Wharton, and J. E. Fletcher, "Studies of Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 4 - Fireworks Compositions and Investigation of the Sulfur/Chlorate Initiation Reaction", *Journal of Pyrotechnics*, No. 12, 2000, p 43.

10) Clive Jennings-White and Ken Kosanke, "Hazardous Chemical Combinations: a Discussion", *Journal of Pyrotechnics*, No. 2, 1995, p 22.

11) Takeo Shimizu, *Fireworks: The Art Science and Technique*, Maruzen, Tokyo, Japan, 1981, p 317.

12) Andrelev Beliave, *Theory of Explosives*, Banyagytacsgyar, Budapest (in Hungarian), 1965.

13) Gyorgy Negyesi, "Sensitivity of Non-Explosive Compounds to Friction Testing", *Process Safety Progress*, Vol. 15, No. 1, 1996, p 42.

14) Wesley D. Smith, "Introductory Chemistry for Pyrotechnics, Part 1: Atoms, Molecules, and Their Interactions", *Journal of Pyrotechnics*, No. 1, 1994, p 12–25.

15) Helseth, et al. *Design-Expert*, version 6 for windows, Stat-Ease, Inc, Minneapolis, http://www.statease.com, as on December 2003.

16) United Nations: Recommendations on the Transport of Dangerous Goods, Test and Criteria, section 21 (BAM Fall Hammer) ST/SG/AC.10/11/Rev.1, 2nd ed., New York, 1990.

17) Government of India's Gazette Notification Noise Standards for Firecrackers, G.S.R.682 (E) (5.10.1999).

18) Torbjorn Lundstedt et al., "Experimental Design and Optimization", *Chemo metrics and Intelligent Laboratory Systems*, Vol. 42, 1998, p 3–40.

Spectral Study of Metallic Molecular Bands in Hybrid Rocket Plumes

K. L. Maxwell and M. K. Hudson

Department of Chemistry and Graduate Institute of Technology,
University of Arkansas at Little Rock, Little Rock, AR 72204, USA

ABSTRACT

A labscale hybrid rocket was used to study spectral bands produced by metal combustion. Bands in the ultraviolet-visible region (300–750 nm) are of interest. The rubber-like fuel, hydroxyl-terminated polybutadiene (HTPB), was doped with a metallic salt for introduction into the plume during combustion. When introduced, the metals produce atomic line emissions as well as molecular bands due to excited forms of metallic molecules in combustion. The most likely molecular band emissions are from the excited states of metal oxides or metal hydroxides formed by these metals in the presence of the oxygen flow of the hybrid rocket. As the concentration of metallic dopants increases in the flame, the molecular band emissions also increase. The fashion by which they increase is observed here.

The high concentrations observed for these metals result in intensity versus concentration curves that diverge from the expected linear progression for manganese, magnesium and strontium. The molecular band emissions observed for calcium, barium and copper in this study followed linear progression, as does the atomic line emission for barium. The line emissions for manganese, strontium and calcium lean toward the concentration axis. The curves are attributed to self-absorption or increased interactions among mixing species as metal concentration increases in the plume. This study indicates that molecular bands are useful for monitoring engine health and for plume diagnostics.

Keywords: combustion diagnostics, hybrid rocket, plume emissions, spectral signature, rocket exhaust, atomic spectroscopy, molecular spectroscopy, emission spectroscopy

Introduction

Atomic spectral techniques have been used in the past to provide diagnostics for engine health monitoring. The National Aeronautics and Space Administration (NASA) and Stennis Space Center in particular have taken interest in these studies as engine monitoring techniques for the Space Shuttle Main Engine (SSME).[1–4] These techniques depend on the relationship of excited atomic species in the motor plume to the amount introduced by failures in the engine system. It is important that a linear or otherwise describable and reproducible relationship exists, to quantify wear or other elemental introduction factors in the motor or engine system.

Molecular emissions as observed in the normal realm of atomic spectroscopy are viewed as interference. A classic example is that encountered with analysis of barium in the presence of calcium.[5] The analytical atomic line of barium is swamped by the presence of an overwhelming molecular emission from calcium, such as CaOH. Steps are usually taken to minimize the presence of these molecular bands in such work. However, these type precautions are not applicable to the field of engine health monitoring or in combustion diagnostics when applied to exhaust plumes. Molecular emissions are present in rocket combustion and should be factored in where quantitative data are required. A thorough study of the effect of molecular emissions in exhaust plumes is necessary to determine interference, fraction of species present as molecular versus atomic and other parameters.

The Hybrid Rocket Facility at the University of Arkansas at Little Rock (UALR) was constructed to provide combustion diagnostic testing and uses a 2 × 10-inch labscale hybrid thruster.[6,7] Previous studies have revealed the usefulness of the labscale hybrid rocket system as a plume simulator for other propulsion systems and characterized it for both atomic and molecular emissions.[8–11] The presence of metallic molecular bands was noted in these studies, both from the combustion of HTBP fuel and as formed by metallic dopants, such as manganese.

To study the molecular bands in rocket plumes, the labscale hybrid rocket fuel was doped with various levels of metallic salts. Combustion of these salts results in band emissions attributed to metal oxides or metal hydroxides. Some of the metals were chosen due to their presence in alloys used in certain engine components and because they appear to have produced molecular bands in previous combustion studies.[8,10–13] Other metals were added to the study based on their tendency to oxidize easily, thus being likely to produce refractory particles in combustion. Fuel grains were made using R-45 HTPB resin and Desmodur N100 curative. HTPB was placed in the mixing container and the amount of dopant was added. Then, N100 curative was added to begin the process of polymerization. The container was placed on the mixer between each addition. No plasticizers or other additives were used in this study. Previous work[8–11] indicated that mixing was sufficient to ensure a reasonably homogenous fuel grain.

Conversion Units

1 lbm = 1 pound mass = 454 grams
1 lb = 1 pound = 454 grams
1" = 1 in. = 1 inch = 25.4 mm

Experimental

The University of Arkansas at Little Rock labscale hybrid rocket motor, designed for combustion diagnostics, was used in this study. The two-by ten-inch fuel grains for the rocket are produced on site, which allows for seeding the fuel to produce desired spectral emissions. This is accomplished by doping the fuel with metallic chloride salts. Table 1 lists the chosen metals and the salts used in the study. The table also indicates the percent metal component for each salt.

Table 1. Percent Metal Used in Study.

Metal and Symbol	Salt Dopant	Metal (%)
Magnesium, Mg	$MgCl_2•6H_2O$	11.95
Calcium, Ca	$CaCl_2•2H_2O$	27.26
Barium, Ba	$BaCl_2•2H_2O$	56.22
Copper, Cu	$CuCl_2•2H_2O$	38.18
Strontium, Sr	$SrCl_2•6H_2O$	32.86
Manganese, Mn	$MnCl_2•4H_2O$	27.76
Aluminum, Al	$AlCl_3•3H_2O$	11.175

The procedure used to calculate the amount of dopant necessary to produce the desired concentrations of metal in the plume has been documented.[13] The equations used are based on total mass flow of the system during firing. These studies use an oxygen mass flow of 0.100 lbm/s. At this flow, the total mass flow is found to be 0.1344 lbm/s.

Initial emission studies indicated the capabilities of the rocket to produce emissions of metallic atomic and molecular species. Quantification studies have thus far focused only on the metal atomic emissions.[12,13] The goal of this study was to determine feasibility to quantitatively characterize molecular band emissions based on relative emission intensity.

The emission detection system consisted of a quartz collection lens with a 100 mm focal length placed 20 inches (510 mm) from the exhaust plume axis and 6 inches (152 mm) behind the exit nozzle plane of the rocket motor. A black metal tube housed the lens used to focus the plume emissions onto the entrance slit of a SPEX 270M spectrometer. The entrance slit was set to different widths for the various species observed, specified by trial during initial metal firings. The spectrograph utilized a grating capable of spreading incident light in a 150 nm window onto a 1024 pixel silicon photodiode array (PDA). A portable computer was used to collect the PDA output. Figure 1 is a sketch of the data

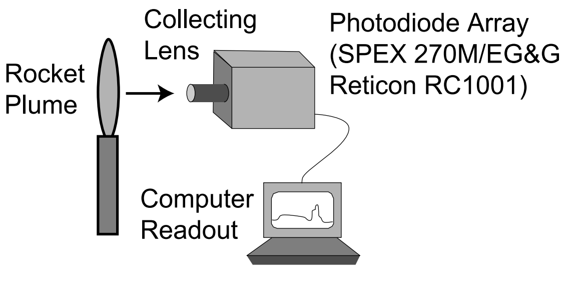


Figure 1. A sketch of the optical setup used.

collection setup. This spectrograph has been described previously.[14]

The 488 nm line of an argon ion laser was used to wavelength calibrate the spectrometer. The laser intensity was minimized and the beam was focused onto a nearly closed entrance slit to avoid damage to the photodiode array.

PDA detector scanning was initiated before firing and allowed to continue after shutdown to collect background scans, which were later subtracted. PDA scans were set to allow 100-ms time intervals for exposure. A total of 75 scans were collected for each experimental run. Each firing was programmed to last four seconds. Data was saved and transferred to a Pentium desktop PC for data reduction.

Data Analysis

Data was transferred to a desktop PC and the files were opened in WPLOT.[16] The plots were transformed from "raw" PDA pixel plots to spectra with the correct wavelength scale by simply applying a scaling factor. From the dispersion of the grating spectrometer, 150.99 nm was covered in the spectral window of the spectrometer (i.e., the 1024 pixels of the PDA). Therefore,

$$\left[\frac{150.99\text{ nm}}{1024\text{ diodes}} = 0.14706\text{ nm/diode}\right]$$

Each raw data point was multiplied by this factor, and the center wavelength of the window was used to provide a base point, or offset value. Application of the offset value resulted in a corrected x-axis with accurate wavelength values. Scans could then be displayed as regular two-dimensional or as three-dimensional plots. WPLOT provided that the data could then be saved as an ASCII file providing intensity vs. wavelength information for further post-processing as desired.

In reviewing the three-dimensional plots, it is obvious that the files show a distinct combustion initiation and post combustion period. The scans collected between these regions represent the stable combustion condition experimental run and are used for intensity versus metal concentration evaluation. This is consistent with previous studies.[6–9] The combustion initiation period shows a gradual increase in flame emissions. Very intense emissions are seen in the post combustion scans. These intense emissions are explained as blackbody emissions that occur during oxygen shutoff. Once the oxidizer flow has stopped, combustion in the chamber goes into a fuel rich condition before extinguishing.

The plot files were all opened in Microsoft Word to remove scans from combustion initiation and post combustion. The resulting text files of X wavelength and Y relative intensity data sets, corresponding to wavelength versus intensity, were saved and reopened in Microsoft Excel. The X data set remained constant. The Y data sets were averaged to obtain a single plot. The average plot obtained from an undoped fuel grain was used to subtract basic combustion emissions from the averaged plot of a metal study. This helped to provide a more clear representation of metallic emissions. These plots were compared for different concentrations of metallic dopants.

Results

A basic spectrum was collected for the UALR hybrid rocket using several undoped fuel grains. The consecutive firings were centered on different wavelength windows within the ultraviolet-visible region. The data were compiled, averaged and placed end-to-end for one continuous plot over the region of 200–800 nm. The figure starts at 250 nm. To see the combustion bands more clearly, the scale of intensity could be changed. Figure 2 is the result. This plot was used for identification of combustion products in the hybrid rocket plume. As expected, there were an abundance of hydrocarbon bands, plus the sodium and potassium atomic line emissions.

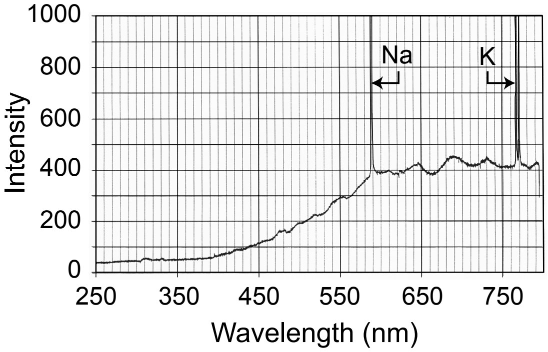


Figure 2. Combined hybrid rocket spectrum collected from 3 separate plain HTPB firings.

These line emissions were expected as they have been detected and identified as impurities in the rocket fuel materials.[3,11] The sodium line emission appears at 589 nm as an unresolved doublet. Potassium appears as a doublet centered at 767 nm. In the discussion below, spectral data as normally seen in the lab is compared with that seen in the plume.

I. Manganese

Manganese is a metal used in alloys for valves and flex joints in NASA's Space Shuttle Main Engine (SSME). During combustion, it is known to produce a strong atomic line emission at 403.3 nm. This is actually a triplet. It also produces a strong molecular band system centered at 560 nm. This is thought to be due to manganese hydroxide (MnOH).[14]

The plume emissions of HTPB doped with manganese chloride were monitored from 475 to 625 nm to evaluate the molecular band of manganese at different concentrations. Figure 3 shows an averaged scan for a manganese firing. The expected molecular band appeared at 560 nm. Firings were repeated with new fuel grains at increasing concentrations of this metallic salt. After collecting data for the molecular band of manganese, the wavelength selector was shifted to look at the atomic line emissions for this element, requiring a different wavelength window. Figure 4 is a typical manganese atomic line emission and appears at 403.3 nm as expected.

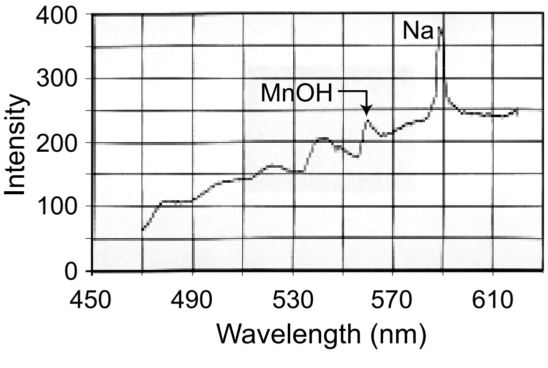


Figure 3. Manganese spectrum for 500 ppm Mn firing at 560 nm.

The evaluation for the atomic line emission intensity versus metal concentration coincides with earlier work.[11] The curve bends toward the concentration axis as concentration is increased (Figure 5). The nonlinearity for the atomic line emission with the increase in concentration can be attributed to self-absorption effects. At high concentrations, a significant fraction of photons emitted by atoms in an excited state are absorbed by atoms in the lower, ground state.[16] This results in a bend in the curve toward the concentration axis.

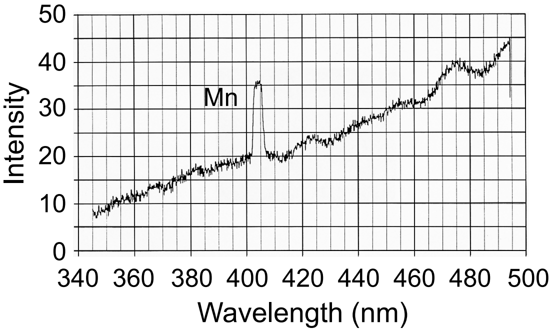


Figure 4. Manganese atomic line emission for 100 ppm at 403.3 nm

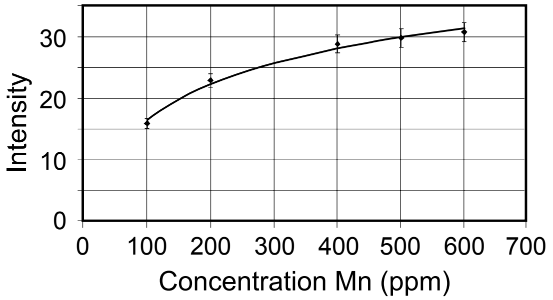


Figure 5. Manganese atomic line intensity versus metal concentration.

Note that the atomic line emission for Manganese exhibits a flat top. This is also characteristic of high concentrations of analyte species and self-absorption. At low concentrations, the line emission will grow by increasing "normal" peak intensity, but at higher levels these emissions are self-absorbed by other atoms in the ground state. The center of the line profile will thus widen as the concentration is increased, resulting in this characteristic emission peak shape. Also possibly contributing would be the rather wide entrance slits used in the study, somewhat decreasing the resolution of the spectrometer and making the lines appear broader.

In comparing the atomic line curve to the molecular band curve, we find that the increase in concentration affects the molecular band curve differently. Figure 6 shows the effect of molecular band intensity for increasing concentration. The result is a roughly exponential increase in intensity. With such large increases in concentration, there are more collisions created by the metal radicals in combustion. This leads to an increasing fraction of molecular formation and therefore more likely excitations of the molecular species.

II. Copper

Copper is used in several alloys in the internal components of the SSME. During combustion, it is known to produce two strong lines at 324.7 and 327.4 nm. The compound CuH has been identified as the cause for the band head at 428.0 nm. Copper hydroxide (CuOH) has been found to produce the band systems from 535 to 555 nm and 615 to 625 nm. Well-defined band systems at 605 and 615 nm have been attributed to copper oxide (CuO).[14]

The copper line emission was expected at 324.7 and 327.4 nm. Neither line appears. Previous studies did indicate the copper lines, but very weakly.[11] Since the same motor combustion parameters were used in this study (0.100 lb/sec oxygen flow and HTPB), the differences in spectral collection would be indicated as a possible cause for this behavior. Indeed, the use of the wider entrance slit in this work would mask out a very low intensity emission such as that seen previously for copper, as it would not be resolved above the noise baseline/background signals. While self-absorption would also be likely at these concentrations (100 to 600 ppm), the root cause for not being able to see the weak atomic lines for copper is most likely spectrometer setup.

In further analysis, the molecular band emissions of copper are not very intense emissions. The molecular band emissions due to CuH are evident in Figure 7 at 428, 435, and 444 nm. Figure 8 shows the band emissions attributed to CuOH from 535 to 555 nm and from 615 to 625 nm. The CuO band also appears from 605 to 615 nm. One can note the sodium line emission at 589 nm as a sort of "landmark" for this study, as it is always present.

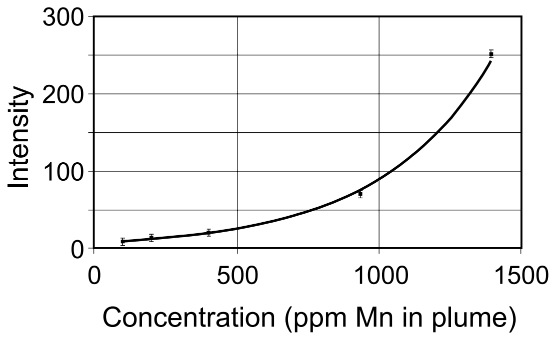


Figure 6. Manganese molecular band emission intensity versus metal concentration.

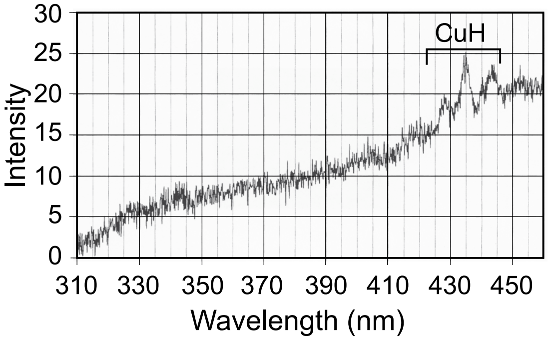


Figure 7. Copper molecular band emissions number 1 for 600 ppm Cu at 390 nm.

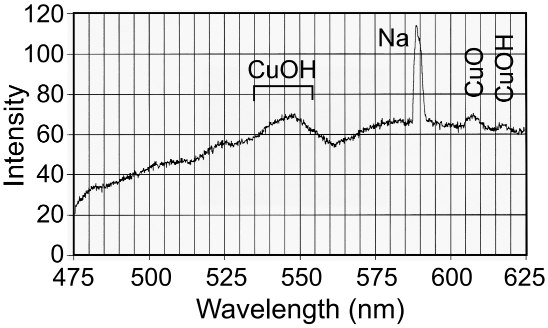


Figure 8. Copper molecular band emissions number 2 for 600 ppm Cu at 550 nm.

The intensity versus concentration for the molecular bands was evaluated and is reported in Figure 9. There is a linear relationship for the increase of intensity with increase in concentration. This suggests less fractional increase of molecular formations with increasing concentration, or closer to a constant proportionality of molecular formation.

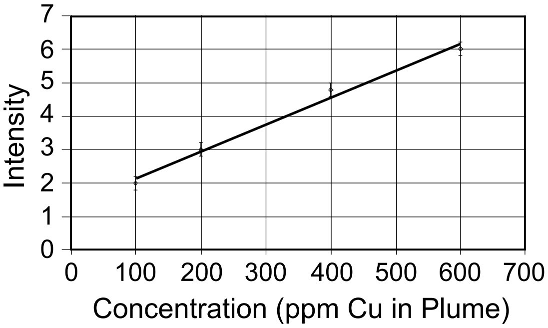


Figure 9. Copper molecular band intensity versus metal concentration.

III. Alkaline Earth Metals

The next four metals studied were members of group II-A of the periodic table, the alkaline earth metals. These metals produce flame spectra that have overwhelming molecular bands and much less intense atomic emissions. In fact, it is not uncommon for over 90% of the emissions for these metals to be in the molecular form.[15] Though this is usually the case, the most prominent line emissions for each element results from the transition between the lowest excited electronic state to the ground state. As such, all of these transitions produce singlets.

The atomic line emissions of these elements are dependent on temperature. Higher temperatures produce more atomic species and therefore more intense line emissions. Molecules dissociate at higher temperatures thus decreasing the intensity of molecular band emissions.

Magnesium

Magnesium produces its most prominent resonance line at 285.2 nm. Molecular bands appear between 353 and 415 nm. The two large band heads peak at 371 and 383 nm are both thought to arise from manganese monohydroxide, Mg(OH).[15,18] The existence of MgOH is favored at lower flame temperatures. The thermal decomposition of MgOH causes the relative intensity of the atomic line emission to increase at higher temperatures.[15]

The molecular bands at 371 and 383 nm, thought to be due to magnesium hydroxide, Mg(OH), can be seen in Figure 10. The intensities of the bands track together for changes in concentration. The figure also shows the absence of the magnesium atomic line emission at 285 nm. This indicates that metal exists in molecular form in the plume, as may be expected.

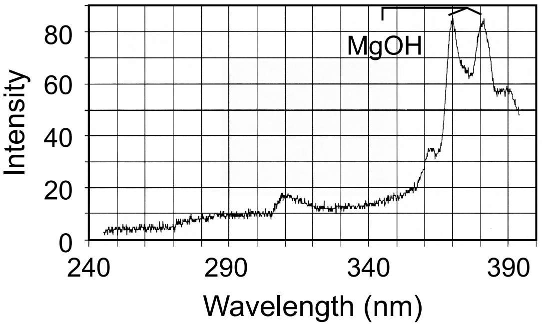


Figure 10. Magnesium molecular band emissions at 320 nm.

Figure 11 is the intensity versus concentration for the magnesium molecular band. The two bands were treated separately for this relationship. The upper line is the calibration curve for the molecular band seen at concentration. Like manganese, this indicates an increase in molecular formation with an increase in concentration. This behavior may be due to the change in thermal activity within the flame at different concentrations of metal. Higher analyte concentrations

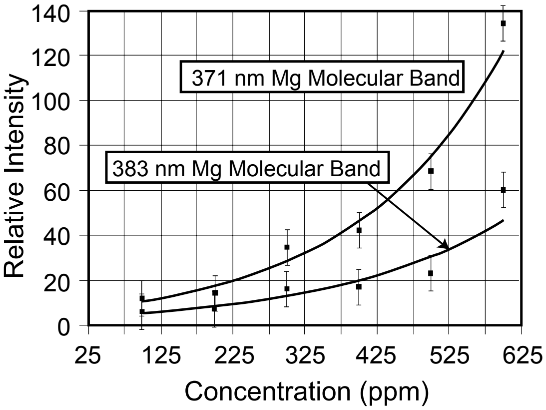


Figure 11. Magnesium molecular band emissions versus concentration, 371 and 383 nm bands.

will lead to an increase of interactions and thus a higher rate of metallic molecular formations. Therefore, the emission intensities for these bands will increase with the concentration of the metal in the fuel.

Strontium

The strontium molecular band systems make up the majority of the flame spectrum. The narrow band head at 606 nm and a wider system from 640 to 700 nm arise due to strontium monohydroxide (SrOH). The band heads in the wider system are seen at 650, 668 and 683 nm under conditions of narrow slit widths. Wider slit widths result in smoothing of that system into one large band. The last band system, near 595 nm, has been identified as arising from strontium peroxide (Sr_2O_2). Molecular band systems are favored in cooler flames.[14] The small strontium atomic line is found at 460.7 nm. In very hot flames, the strontium atom can be ionized to produce a doublet at 407.8 and 421.6 nm.[15,17] The hybrid rocket plume is not hot enough to produce these lines, and Figure 12 shows the resulting spectrum (Sodium at 589). The atomic resonance line of strontium also appears at 460.7 nm (Figure 13).

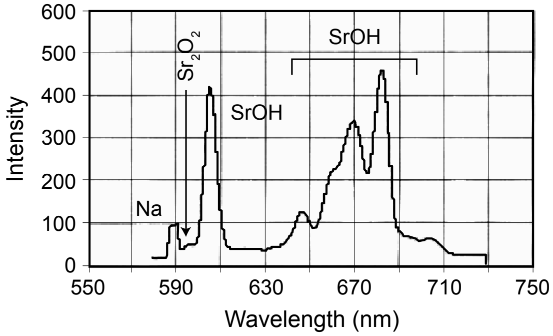


Figure 12. Strontium molecular band emissions for 200 ppm Sr at 650 nm.

Strontium molecular band intensities were plotted versus concentration in Figure 14. There is a slight bend toward the concentration axis as the concentration is increased. This is like the intensity versus concentration for the atomic line emission (Figure 15). This relationship is attributed to self-absorption of the molecular emitting species with high concentrations of analyte.

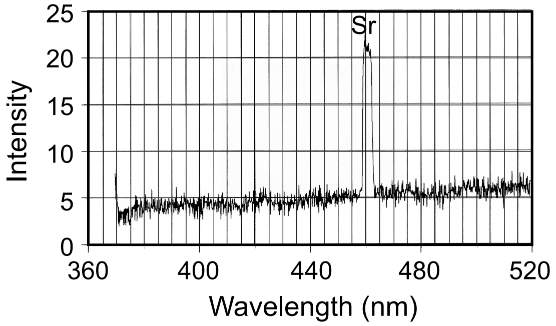


Figure 13. Strontium atomic line emissions for 220 ppm Sr at 460 nm.

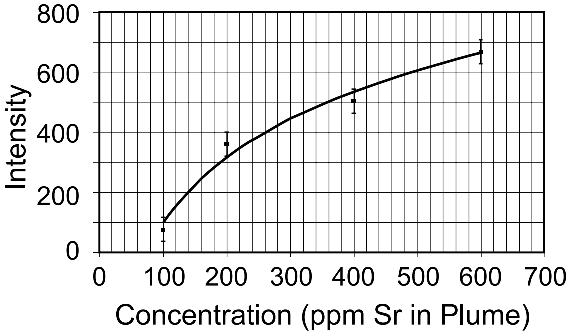


Figure 14. Strontium molecular band emissions versus metal concentration.

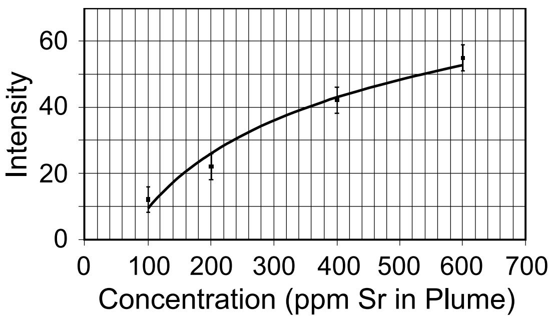


Figure 15. Strontium atomic line emission versus metal concentration.

Calcium

The calcium resonance line arises at 422.7 nm. When calcium is singly ionized it will produce a doublet at 393.3 and 396.8 nm. This only occurs under extremely high-energy conditions not attained by the hybrid rocket plume. Most of the calcium emissions result in two large band systems attributed to calcium oxide, (CaO), and calcium monohydroxide, (CaOH). The narrow green system stretches from 547 to 560 nm with a band head at 554 nm. The wider dark orange system extends from 580 to 650 nm with two band heads at 606 and 622 nm, when a narrow slit width is employed.[15, 19] The total emissivity of calcium increases with flame temperature. However, the relative intensities of the molecular species versus atomic and ionic species shift away from the molecular systems at higher temperatures. The higher number of atomic species formed by dissociation at the higher temperatures creates a larger probability for atomic excitation and ionization.[15]

The large molecular bands produced by the dopant are shown in Figure 16. The calcium oxide (CaO) system a 547 to 560 nm is the tall and narrow system. The wider system from calcium hydroxide (CaOH) is seen from 580 to 650 nm. The band heads in this system appear at 606 and 622 nm as anticipated. The calcium line emission at 422 nm was collected separately (Figure 17). Unlike some metals in this study, the atomic line emission is within the 150 nm range of the narrow band emission at 554 nm. The two systems were collected in one scan. The narrow band emission is a common structure in both series of firings, which can be used to "calibrate" and compare one spectrum to the other.

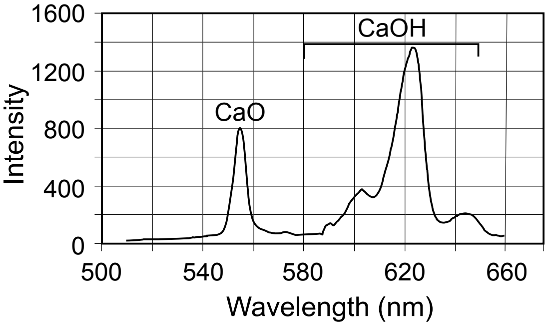


Figure 16. Calcium molecular band emission for 400 ppm Ca at 590 nm.

Calcium molecular band intensities versus concentration are plotted in Figure 18. The result is a linear relationship. In evaluating the trend in atomic line emission with increasing concentration, the atomic line emission was found to be relatively constant in intensity. The plot of atomic line intensity versus concentration (Figure 19) appears to have leveled off. It is suspected that at the high concentrations evaluated here, the atomic species are self-absorbing radiation while the analyte is preferentially forming molecular species.

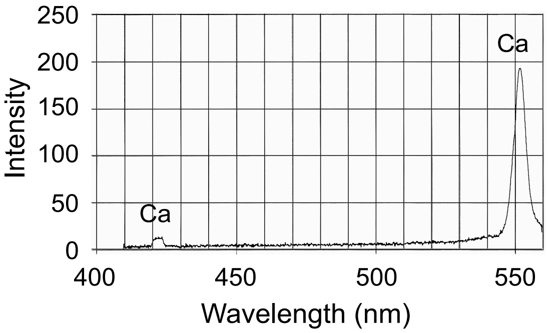


Figure 17. Calcium atomic line emission for 400 ppm Ca.

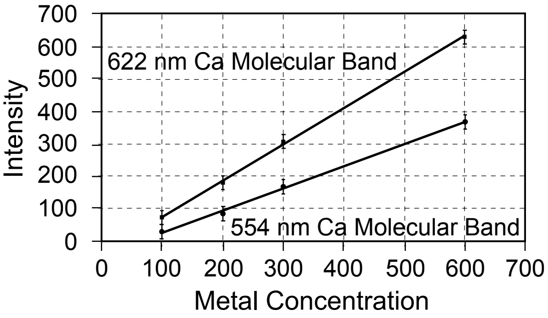


Figure 18. Calcium molecular band emissions versus metal concentration, 554 and 622 nm bands.

Barium

Barium produces a much less intense spectrum than other alkaline earth metals. The atomic resonance line arises at 553.6 nm between the barium oxide bands. When barium is ionized, a doublet appears at 455.4 and 493.4 nm. Unlike spectra from other alkaline earth metals, the molecular systems directly surround the atomic line emissions. Barium monohydroxide (BaOH) produces relatively strong molecular bands at 487, 515, and 527 nm. Weak bands arising from barium oxide (BaO) stretch from 530 to 630 nm.

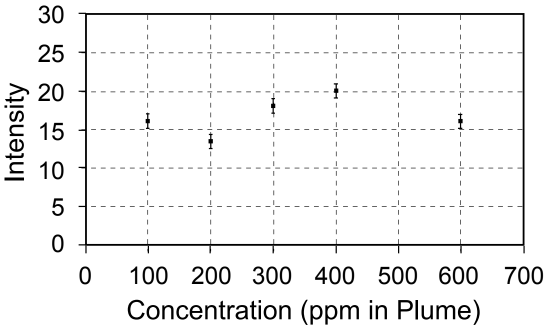


Figure 19. Calcium atomic line emission versus metal concentration.

Experimentally, the molecular bands and the atomic line emissions for barium are produced in the same data collection scan. Figure 20 illustrates the barium spectrum. The atomic resonance line at 553.6 nm is prominent among the barium oxide bands that range from 530 to 575 nm. Barium monohydroxide (BaOH) bands also appear from 480 to 530 nm.

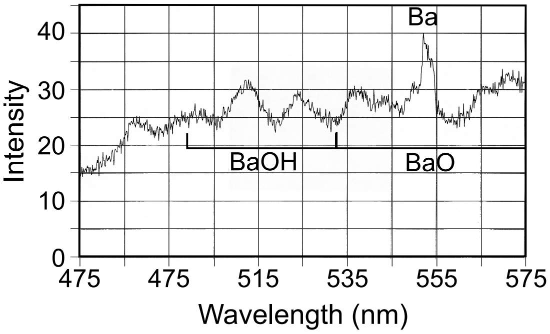


Figure 20. Barium atomic line and molecular band emissions for 525 nm.

The plot of barium emission intensities versus concentration appears as Figure 21. Both the atomic line and molecular band intensities produce a linear increase with concentration. Furthermore, the atomic line trend is almost parallel to the molecular band trend. This suggests that the atomic and the molecular species for barium exist in a definite proportionality during combustion.

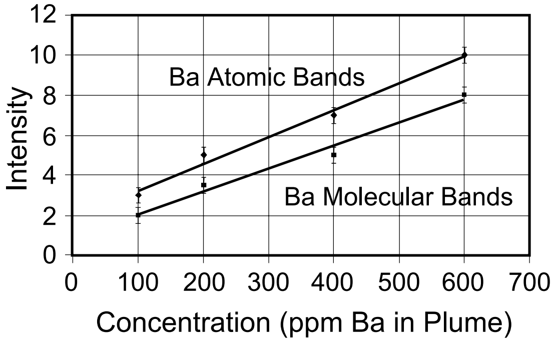


Figure 21. Barium atomic line and molecular band emission versus metal concentration.

The barium molecular emissions are of rather weak intensity when compared to other alkaline earth metals such as calcium and strontium. As a result, the atomic line emission seems to be of much higher proportionality. However, other metals do not produce molecular band emissions that spread across such a wide spectral region. This supports the tendency for alkaline earth metals to exist primarily in molecular form during combustion. Even at the high concentrations of analyte present in these studies, barium is not in high enough concentration elementally to show characteristics of self- absorption.

IV. Aluminum

Aluminum is known to produce several molecular band systems. Two in particular, arising from AlO^+, should be seen at 435–500 nm and 508–518 nm, the most intense emission centered at 484 nm. The atomic line emission of aluminum should occur at 396.2 nm when flame temperatures are hot enough to allow aluminum to exist in the atomic form. The relative intensities of the atomic line versus molecular bands will vary depending on flame temperature. Higher temperatures will produce more atomic species as the molecules are dissociated. The atomic line emission intensities should rise as the molecular band emissions decrease.[15,20]

Initial data collection of aluminum using 100–1000 ppm aluminum concentrations produced no indication of molecular band or atomic line emissions. Because aluminum has such a high tendency to oxidize, it is thought that the aluminum in the presence of the oxidizer flow goes straight to a blackbody particulate, aluminum oxide (Al_2O_3). No useable data were collected.

Aluminum is known to scavenge magnesium during combustion. By burning grains having a constant concentration of magnesium while increasing the aluminum concentration, the decrease in magnesium intensity should be observed. This would provide information on the combustion of aluminum. Attempts to observe the decreasing intensity of the magnesium molecular bands with increasing aluminum concentrations failed. There was no observable change. No background emission changes (i.e., blackbody emissions) were observed either. Aluminum emissions remain a mystery.

Note that there was a definite build-up of silvery material, perhaps aluminum metal, on the nozzle after these firings. This suggests that the metal partly exists in the elemental form at least in the chamber, but may not be excited, as the rocket combustion temperature is not hot enough. Transformation into the oxide after being forced through the nozzle may not actually occur until further into the length of the plume, due to possible after-burning of these particulates. It can be noted that aluminum oxide often coats the divergent side of a nozzle with a whitish and ragged coating.

Conclusions

Plumes containing high concentrations of metals were monitored for their emissions in this study. Most of the metals behaved generally as expected (i.e. a linear increase in molecular band emissions was found with increasing concentration). However, it appears that this behavior has many limitations. Self-absorption of emitting species appears to plays an important role in the characterization of these metals by molecular emission. Another important factor seems to be the molecular interactions among the metallic molecular species with increasing density in the plume. Together, these two limitations help to explain the unexpected behavior of the metals observed.

Manganese and magnesium exhibit an increase in fraction of molecular band emissions as metal concentration in the plume is increased. This may result from increased interactions among analyte species with flame gasses and each other.

Copper, magnesium and aluminum resonance line emissions were absent entirely. This was quite unexpected for the copper study, as copper is known to exist primarily in the free atomic form during combustion. It was not so unexpected for the magnesium and aluminum studies. Magnesium, an alkaline earth metal, is known to exist primarily in a molecular form in combustion. Aluminum, which also oxidizes readily in air, was expected to exist in the molecular form as well. Its molecular band emissions were not detected.

Alkaline earth metals exist primarily in the molecular form during combustion. Calcium and barium indicate a clear linear increase in molecular band intensity with increasing metal concentration. Strontium, on the other hand, exhibits characteristics of self-absorption for both the atomic and molecular species observed. The deviation from linearity occurs with a bend toward the concentration axis with increase in metal concentration.

The high concentrations evaluated for these metals resulted in unexpected intensity curves observed for atomic line and/or molecular band emissions. This is a safety concern for plume health monitoring. Unknown concentrations of metal, especially at higher concentrations, may provide misleading information of the amount of metal present in the plume. Therefore, the amount of component degradation for materials in the engine combustion path could be underestimated. The hybrid rocket proves to be a reasonable source for molecular emission quantitative studies. It allows for the development of techniques to evaluate metals and characterize their molecular formations during combustion. These results can be applied to larger hybrid rockets enabling the further generation of hybrids as possible flight propulsion systems.

Acknowledgements

The authors would like to thank the Arkansas Space Grant Consortium for partial support in this study and NASA Stennis Space Center for Ms. Maxwell's Graduate Student Research Fellowship No. NGTI3-52724. NASA Grants NCC-055 and NCC5-260 provided additional support. We also send thanks to Ken Kalb, Armand Tomany, Lize Wilcox and Yi Tang who helped with logistics and firing. Portions of this work were presented at the 36th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 16–19 July 2000, Huntsville, AL, USA (AIAA 2000-3887).

References

1) G. D. Tejwani, D. G. Gardner and D. J. Chenevert, "Approach to SSME Health Monitoring: Materials, Database and DTF Plume Seeding Experiments", *Proceedings from the First Annual Health Monitoring Conference for Space Propulsion Systems*, Cincinnati, OH, November 14–15, 1989.
2) G. D. Tejwani, J. A. Laboda, D. J. Gardner, D. B. Van Dyke, and D. J. Chenevert, "Spectral Studies of SSME Materials in a H_2-O_2 Exhaust Plume", NASA CP 3092, Vol. 1, *Advanced Earth-to-Orbit Propulsion Technology*, Huntsville, AL, May 15–17, 1990.
3) G. D. Tejwani, D. B. Van Dyke, F. E. Bircher and D. G. Gardner, "Spectroscopic Evaluation of Rocket Engine Materials in the Exhaust Plume Environment: Spectral Line Identifications of SSME Elements and Materials", NASA Contractor Report #4453, NAS12-290, July, 1992.
4) G. D. Tejwani, D. B. Van Dyke, F. E. Bircher, D. G. Gardner and D. J. Chenevert, "Emission Spectra of Selected SSME Elements and Materials", NASA Reference Publication 1286, December, 1992.
5) D. A. Skoog and D. M. West, *Principles of Instrumental Analysis*, Saunders College, Philadelphia, 1980, p 308.
6) R. B. Shanks and M. K. Hudson, "A Labscale Hybrid Rocket Motor for Instrumentation Studies", *Journal of Pyrotechnics*, No. 11, 2000, pp 1–10.
7) R. B. Shanks and M. K. Hudson, "The Design and Construction of a Labscale Hybrid Rocket Facility for Spectroscopy Studies", *A1AA* Paper No. 94-3016, June, 1994.
8) R. B. Shanks, "A Labscale Hybrid Rocket Motor and Facility for Plume Diagnostics and Combustion Studies", A Doctoral Dissertation, University of Arkansas at Little Rock, December, 1994.
9) M. K. Hudson, R. B. Shanks, D. H. Snider, D. M. Lindquist, C. Luchini, and S. Rooke, "UV, Visible, and Infrared Spectral Emissions in Hybrid Rocket Plumes", *Int. Journal/ Turbo and Jet Engines*, Vol. 15, 1998, pp 71–87.
10) K. L. Maxwell, "The Investigation of Metallic Molecular Bands in Hybrid Rocket Plumes", *A1AA* Paper No. 99-2137, June 1999.
11) K. L. Maxwell, "The investigation of Metallic Molecular Bands in Hybrid Rocket Plumes", A Master's Thesis, University of Arkansas at Little Rock, 2000.
12) D. H. Snider, "Evaluation of Photodiode Arrays for Use in Rocket Plume Monitoring and Diagnostics", A Masters Thesis, University of Arkansas at Little Rock, 1994.
13) R. B. Shanks, S. Rooke and M. K. Hudson, "Quantitation Study of Metals in the Hybrid Rocket Plume", *AIAA* Paper No. 95-2791, 1995.
14) D. Snider, R. B. Shanks, Reagan Cole, and M. Keith Hudson, "Inexpensive Photodiode Arrays for Use in Rocket Plume and Hot Source Monitoring and Diagnostics", *Meas. Sci. Technol.*, Vol. 14, 2003, pp 1725–1733.
15) .J. A. Dean, *Flame Photometry*, McGraw-Hill Book Co., New York, 1960.
16) Bill G. Hood, WPLOT Version 3.3.2, University of Arkansas, Little Rock, 1998.
17) James D. Ingle, Jr. and Stanley R. Crouch, *Spectrochemical Analysis*, Prentice Hall, Englewood Cliffs, New Jersey, 1988.
18) A. G. Gaydon, *Spectroscopy of Flames*, John Wiley & Sons, Inc., New York, 1957.
19) C. G. James, and T. M. Sugden, "A New Identification of the Flame Spectra of the Alkaline Earth Metals", *Nature*, Vol. 175, 1955, pp 333–334.
20) H. C. Eshman, J. A. Dean, O. Menis and T. C. Rains, "Extraction and Flame Spectrophotometric Determination of Aluminum", *Analytical Chemistry*, Vol. 31, 1959, pp 183–187.

Guide for Authors

Style Guide

The *Journal of Pyrotechnics* has adopted the *ACS Style Guide* [ISBN 0-8412-3462-0]. It is not necessary that authors have a copy; however, a copy can be ordered through a local bookstore.

Subject Areas

Fireworks, pyrotechnic special effects, propellants, rocketry and civilian pyrotechnics

Manner of Submission

Submissions should be made directly to the publisher at the address at bottom of page. Upon receipt of an article, the author will be sent an acknowledgment and a tentative publication date. For specific requests regarding editors, etc. please include a note with that information. Preferably the text and graphics will be submitted electronically or on a 3-1/2" diskette or CD in IBM format with a print copy as backup. The Journal is currently using Microsoft Word, which allows for the import of several text formats. Graphics can also be accepted in several formats. Please also inform us if any materials need to be returned to the author.

General Writing Style

- The first time a symbol is used, it is preferred to write it out in full to define it [e.g., heat of reaction (ΔH_r) or potassium nitrate (KNO_3)].
- Avoid slang, jargon, and contractions.
- Use the active voice whenever possible.
- The use of third person is preferred; however, first person is acceptable where it helps keep the meaning clear.

Format

In addition to the authors' names, please include an affiliation for each author and an address for at least the first author.

A short abstract is needed. (An abstract is a brief summary of the article, not a listing of areas to be addressed.)

Include 7 to 10 keywords to be used in a reference database: However, multi-word names and phrases constitute only one keyword (e.g., "potassium nitrate" and "heat of reaction" are each one word).

Use of SI units is preferred. If English units are used, please provide conversions to SI units.

Figures, Photos, and Tables are numbered consecutively. For submission, place them at the end of the text or as separate files. During page composition, they will be inserted into the text as appropriate. For graphs, please also submit "raw" X–Y data.

References cited in the text are referred to by number (i.e., "Smith[1] states"; or "the research[2,3] shows ..."). In the reference section, they will be ordered by usage and not alphabetically. It is preferred that a full citation, including author, title, book or journal, publisher for books, and volume and pages for journals, etc. be provided. Examples:

1) A. E. Smith, *Pyrotechnic Book of Chemistry*, XYZ Publishers, 1993, [p nn–nn (optional)].
2) A. E. Smith and R. R. Jones, "An Important Pyrotechnic Article," *Pyrotechnic Periodical*, Vol. 22, No. 3, 1994, [p n–n, (optional)].

Editing

The *Journal of Pyrotechnics* is refereed. However, the editing style is friendly, and the author makes the final decision regarding what editing suggestions are accepted.

More Information

Contact:
Bonnie Kosanke, Publisher,
Journal of Pyrotechnics, Inc.
1775 Blair Road
Whitewater, CO 81527, USA. or
email: bonnie@jpyro.com

OR

Tom Smith, Managing Editor
8 Aragon Place
Kimbolton, Huntingdon
Cambs, UK PE28 0JD
email: toms@davas.co.uk

Communications

Brief technical articles, comments on prior articles and book reviews

Note on "Metal Monochloride Emitters in Pyrotechnic Flames – Ions or Neutrals?"

Barry Sturman

6 Corowa Ct, Mount Waverley, VIC 3149, Australia

As pointed out in the subject paper,[1] several writers have erroneously attributed the molecular band spectra that produce the characteristic colours of flames containing various metals M, (M = Ca, Sr, Ba or Cu) and Cl to the singly-charged ions MCl^+.

A copy of a reference that the author had not seen at the time of writing was made available by the kind courtesy of Rutger Webb. This reference, mentioned by Shidlovskiy,[2] is a report on German signal flare compositions by H. J. Eppig[3] that describes research on colored signal lights at nine institutions involved with the research, testing and manufacture of military pyrotechnics in Germany during the Second World War. According to the report

> Very little fundamental research was done on the problem of the radiation emitted by pyrotechnic signal lights. Only small, direct-vision spectroscopes had been used in three of the pyrotechnic manufacturing plants… Nevertheless, it was known that blue lights were caused by radiation emitted by the bands in the molecular spectrum of copper chloride, green lights by the bands of the molecular spectrum of barium chloride and red lights by molecular bands due to strontium chloride.

This is the extent of the directly relevant information. The 29-page report contains some interesting information and formulas, and deserves to be more widely known. The title was slightly misquoted by Shidlovskiy (or his translator) as *The Chemical Composition of German Pyrotechnic Colored Signal Lights.*

The author has recently found a very early reference[4] by one of the founders of molecular orbital theory that is highly relevant to the "ions or neutrals?" issue.

As long ago as 1925, Robert S. Mulliken wrote:

> It is suggested that the absence of electronic band spectra for the hydrogen, silver and alkali halides may be associated with the non-occurrence of higher valence compounds of the type $NaCl_2$, and that the emission of any one of the CuX band spectra follows the transfer of a Cu^+ electron in the polar Cu^+X^- molecule from its normal state to one of a group of low-lying excited states, whose existence can be correlated with the occurrence of the compounds CuX_2, such easily excited electrons being absent in ions such as Na^+. The above relation may be accounted for by supposing that polar molecules cannot carry electronic energy in excess of their heat of dissociation into atoms. By analogy with the observed absence of electronic band spectra for compounds of the NaCl type, the band spectra of the alkaline earth halides should not be due to compounds MeX_2, since the Me^{++} ion contains no easily excited electron. The real emitter is probably MeX, which must contain a loosely bound valence electron like that in Me^+ or Na.

This is taken directly from the Abstract; more detail is provided in the text.

As pointed out previously,[1] a singly charged ion MCl^+ is "of the NaCl type" and does not have a loosely bound valence electron. Metal monochloride ions, therefore, cannot be the emitters of the band spectra responsible for the colours of pyrotechnic flames.

It is noteworthy that Mulliken's description of the origin of the CuX band spectra, written 80 years ago, is completely consistent with current ideas on the subject as outlined by Parekunnel et al.[5] in 2001.

Mulliken (1896–1986) was awarded the Nobel Prize for chemistry in 1966 "for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular-orbital method". His Nobel Lecture[6] provides a brilliant introduction to molecular orbital theory and its history.

References:

1) B. T. Sturman, "Metal Monochloride Emitters in Pyrotechnic Flames – Ions or Neutrals?" *Journal of Pyrotechnics*, No. 19, 2004, pp 1–13.
2) A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Mashinostoyeniye Press, Moscow, 1964, translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974, pp 182–186.
3) H. J. Eppig, *The Chemical Composition of German Pyrotechnic Colored Signal Items*, Combined Intelligence Objectives Sub Committee, H. M. Stationery Office, London, 1945, p 5.
4) R. S. Mulliken, "The Isotope Effect in Band Spectra. III. The Spectrum of Copper Iodide as Excited by Active Nitrogen", *The Physical Review*, Vol. 26, 1925, pp 1–32.
5) T. Parekunnel, L. C. O'Brien, T. L. Kellerman, T. Hirao, M. Elahine and P. F. Bernath, "Fourier Transform Emission Spectroscopy of CuCl", *Journal of Molecular Spectroscopy*, Vol. 206, 2001, pp 27–32.
6) R. S. Mulliken, *Spectroscopy, Molecular Orbitals and Chemical bonding*, Nobel Lecture, December 12, 1966, in *Nobel Lectures, Chemistry 1963–1970*, Elsevier Publishing Company, Amsterdam, 1972. Available at http://nobelprize.org/chemistry/laureates/1966/mulliken-lecture.html

---

Review of:

The Chemistry of Explosives

Jacqueline Akhavan

RCS Paperbacks [ISBN 0854046402] 2004

F. J. Feher

formerly Professor of Chemistry,
University of California, Irvine, CA 92697 USA
current: 4305 Sierra Drive, Copley, OH 44321 USA

Authors of introductory-level books in technical fields face a formidable challenge: they must strike an appropriate compromise between the needs of relatively uninformed students and the expectations of experts in the field. For subject matter as broad and complex as chemistry or explosives, it is practically impossible to satisfy both students and experts with a 170-page paperback book. This is the challenge facing Jacqueline Akhavan and the second edition of her book *The Chemistry of Explosives*, which is part of the RSC (i.e., Royal Society of Chemistry) Paperback series of inexpensive introductory-level texts for selected topics in chemistry. It therefore is not surprising that Akhavan's *The Chemistry of Explosives* fails to meet the challenge. What is surprising is that the author made only trivial changes in the second edition and that clear errors pointed out by reviewers of the book's first edition were addressed superficially or not at all. Although I have to acknowledge that the book probably provides much of what the author and publisher intend to provide – i.e., a clear, readable introduction to a selected topic in chemistry that should appeal to the general chemist – the persistence of known errors is disturbing and I would not recommend this book to people who want a technically accurate introduction to the subject.

There is very little difference between the first and second editions of this book. In fact, most pages are completely unchanged, and it is possible to spot most changes by doing page-by-page comparisons of the two editions. The first edition has 158 pages, not counting bibliography and index. The second edition has 164 pages.

Three of the additional pages (pages 15–17) were used in Chapter 1 for a small section entitled "Recent Developments" and two more (pages 45–46) appear in Chapter 2. These five pages describe a small number of newer explosives (e.g., NTO, TNAZ, nitrocubanes) and very briefly mention the topics "Insensitive Munitions" and "Pollution Prevention". The final new page was added to Chapter 5 as part of an effort to correct the discussion about "Force and Pressure of Explosion" (pages 100–102).

The first edition of this book was reviewed in the *Journal of Pyrotechnics* (No. 10, Winter 1999) by Ken Kosanke and Barry Sturman. Both reviewers, who are well respected for their broad knowledge of pyrotechnics, chemistry and physics, identified a number of technical errors. The author was made aware of these errors by the Journal of Pyrotechnics Editor. A few of the errors were corrected. Efforts were made to correct a few other errors, but these efforts weren't always successful. Two errors were addressed by adding superficial parenthetical remarks or footnotes, but most of the errors were not corrected. For example:

Page 1 still perpetuates the legend of Berthold Schwartz, who is credited with playing a major role in the adoption of Black Powder in Europe. The parenthetical comment that "many dispute his existence" only superficially addresses the comments in Sturman's review of the first edition. Why didn't Akhavan use the information provided by Sturman as an opportunity to develop a more accurate (and more interesting!) story about the adoption of gunpowder in Europe?

Page 51 now uses a value for atmospheric pressure (Equation 3.2 on page 51) that is more reasonable (9.869×10^{-2} N mm^{-2}), but it still is not the universally accepted pressure for 1 atm: 10.13×10^{-2} N mm^{-2} (i.e., 101.325 kPa).

Page 61, Table 3.3, line 9 still indicates that deflagrating explosives are "not affected by strength of container". This is incorrect and should be obvious in light of line 8, which states that "rate of burning increases with increasing ambient pressure". Moreover, isn't confinement in a strong container one of the ways deflagration can convert to detonation (line 11)?

Page 64, Figure 4.1 still incorrectly identifies the thermal run-away (or critical) temperature as the ignition temperature of a pyrotechnic material.

Page 70 still states "Almost all explosive trains contain a primary explosive as the first component". This is surprising in light of Kosanke's reminder that the blasting cap, which is one of the most common explosive trains in use, typically contains an ignition and/or delay charge before the primary explosive component.

Page 73 still states "The amount of chemical energy *H* generated by the decomposition of an explosive will give information on the sensitivity of the explosive... a high value of *H* will result in a more sensitive explosive." This is incorrect, and it should be obvious from Table 5.12 (page 87). No correction was made, even though this inconsistency was explicitly pointed out in Kosanke's review of the first edition.

Page 81 still states that the "heats of formation for a reaction containing explosive chemicals can be described as the total heat evolved when a given quantity of a substance is completely oxidized in excess amount of oxygen…" This is not true.

Page 100–102 contains a revised discussion of "Force and Pressure of Explosion". Although the discussion was expanded by nearly a page, it still appears to equate F to both PV and nRT, which should be familiar to all readers as parts of the ideal gas equation. Akhavan also calls F the "force constant". Many chemistry and physics students (as well as their teachers) will be confused by this section because both PV and nRT have units of "work" (i.e., force times distance) or "energy" (e.g., Joules). And force constants normally are associated with Hooke's law, not the PV term from the ideal gas law. Rather than using the term 'force' to describe F, it would have been better to use another term. Rudolf Meyer's book *Explosives* (3rd Ed, VCH, 1987, page 316) uses the term "specific energy", which for explosives is "defined as its working performance per kg, theoretically calculated from the general equation of state for gases: $f = pV = nRT$, where p is the pressure, V is the volume, n is the number of moles of the explosion gases per kg, R is the ideal gas constant, and T is the absolute temperature of the explosion". If the terms 'force' and 'specific energy' are used interchangeably by experts in the field (which appears to be the case from both Meyer's book and Akhavan's book), it should be explained why explosives experts use the term 'force' differently than most chemists and physicists.

Page 161, Table 8.7 still lists silicon tetrachloride and ammonia vapor as a pyrotechnic composition. Why? Pyrotechnic compositions are fuel-oxidizer mixtures, which give off light, evolve heat, produce fogs or smoke, or give acoustic effects. The reaction of silicon tetrachloride with ammonia is not a redox reaction. The mixture therefore is not a pyrotechnic composition, even though the reaction is capable of generating lots of heat and smoke.

Page 162 still states that $SrCl^+$, $BaCl^+$ and $CuCl^+$ are the light emitters generated by pyrotechnic mixtures, even though it is widely accepted that the light emitters are neutral molecules. The footnote at the bottom of page 162, which states "other researchers believe that there is no charge on these molecules", may be a response to comments in Sturman's review. Whatever the case, it's both surprising and unfortunate that Akhavan did not use the information provided by Sturman to research and provide a more accurate description of colored light-generation by pyrotechnic compositions.

Other areas for improvement:

There is no mention of recent efforts to develop nitrogen-rich or solid all-nitrogen compounds as explosives. Karl Christe's recent work is particularly elegant and simple. It could be used to illustrate and explain many points, and the fact that it still is a "work in progress" should be interesting to most students.

The line formula for lead azide is $Pb(N_3)_2$, not PbN_6 (page 22).

Page 26 states "the molecular structure (of RDX) breaks down on explosion leaving momentarily, a disorganized mass of atoms. These recombine…" At one time, this mechanism was widely accepted, and it might still be believed by some people in the field. However, enough is now known about rapid chemical reactions to conclude that explosives probably don't just make a mass of atoms that then recombine.

Page 24, reactions 2.2 and 2.3, describe reaction schemes for decomposition of lead azide. These reactions are pure speculation by the author and they don't belong in the book. (Decomposition of a neutral solid into ions?)

The organic chemistry in this book is very weak. The author should have consulted with an organic chemist regarding mechanisms for organic transformations. Did an organic chemist proof-read the book? Reaction 7.6 (page 125) has some unreasonable intermediates. Reaction 7.21 (page 140) invokes the "lasso mechanism", which most organic chemistry students are discouraged from using.

A Review of:

Color, An Introduction to Practice and Principles

Rolf G Kuehni

Wiley-Interscience [ISBN 047166006X] 2004

K. L. Kosanke
PyroLabs, Whitewater, CO, USA

Rolf G. Kuehni's book *Color, an Introduction to Practice and Principles* (published by Wiley-Interscience) is for the most part a delightful little book (199 pages in 12 chapters, approximately 6 by 9 inches, price $89.95) on the subject of color.

In one sense the book is rather complete, presenting a wide range of chapters covering some of the historical perspectives of color, the physiological and psychological aspects of color perception, the defining and measurement of color, and even the application of color theory to art. However, if the world of color is divided into what might be called reflected color (the color of objects) and emitted color (the color of light sources), then the emphasis is heavy on the reflected color side. While this will be disappointing from the point of view of practicing pyrotechnists, there is still much useful information that can be abstracted from this text, although that is mostly in the area of general information as opposed to information specifically applicable to pyrotechnic flames. Pyrotechnic researchers will also find the book lacking somewhat from a mathematical or quantitative perspective.

For readers wishing to expand their general understanding and appreciation of color and its perception, this is a fine book. However, pyrotechnists needing to learn and be able to directly apply the science of color perception in their research are likely to be somewhat disappointed.

Preface to Three Reviews of *Pyrotechnic Chemistry* published by the Journal of Pyrotechnics

On occasion, when a book to be reviewed has special significance, we have included more than one reviewer's comments about it. In the present case we are including three reviews by authors with differing backgrounds, and thus viewing the book from differing perspectives. The first short review was written by a past president of the Pyrotechnics Guild International, an organization with a close association with fireworks. The second and third short reviews were written by past presidents in the International Pyrotechnics Society, both of whom have extensive experience in military pyrotechnics, and one of whom has extensive experience in fireworks as well.

Review of:

Pyrotechnic Chemistry

Journal of Pyrotechnics [ISBN 1-889526-15-0] 2004

John R. Steinberg, M. D.
3944 Carthage Rd, Randallstown, MD 21133, USA

This is a collaborative work by many authors, resulting in many distinct writing styles between the various chapters; nevertheless the book provides a superb overview of the chemistry of pyrotechnics and various tangentially related topics. Given the stellar curricula vitae of the contributors, it is no surprise that this work is both technically excellent and extremely interesting to anyone with any degree of curiosity regarding pyrotechnic chemistry. While the preface discloses that this text is written at "an introductory to intermediate level" the more extensive one's background in the field, the greater the appreciation for the material will be. It is, indeed, as promised, accessible to both novices and appreciated by fairly advanced students of this subject. The book consists of nineteen chapters and is extensively, if not exhaustively referenced, providing a guide to further source material for those readers desirous of more advanced treatments of the various topics discussed in each chapter.

The first chapter, an Introduction, by David Dillehay, provides a brief history of both pyrotechnics and other energetic materials. It offers both background information and definitions. The eminent Takeo Shimizu wrote the second chapter, which discusses the Chemical Components of fireworks. More than simply a list, Shimizu provides a practically focused "chemical handbook" of the compounds' chemical and physical properties, the history of their use and the applications for each, as well as a brief introduction to the types of chemical reactions in which these materials are used. The compounds are reviewed by classes, according to function: oxidizers, coloring agents, fuels, dyes, other agents, and binding agents. I particularly enjoyed the discussions of organic fuels and charcoals.

Barry Sturman, in Chapter Three, provides an Introduction to Chemical Thermodynamics. This chapter is, of necessity, more technical, though the author successfully avoids making the material so abstruse as to be useful to only the expert. The physics naturally leads into a basic approach to classic pyrotechnic reactions and an introduction to chemical stoichiometry. The tendencies of pyrotechnic reactions to proceed are approached through a very well written discussion of the concepts of enthalpy and entropy as the first law of thermodynamics is explained. The second and third laws follow. Then, in a most lucid summary, the application of the laws of thermodynamics to pyrotechnics is provided. I compliment the author on one of the most useful explanations of the basic processes of physical chemistry that underlie all that we do in pyrotechnic chemistry. This reviewer would advise the novice reader to explore further source material as needed, should this somewhat more technical chapter be found challenging. If read for concept, rather than detail, however, it helps ground the novice reader in these most essential concepts.

Ken and Bonnie Kosanke contribute the Fourth Chapter on Pyrotechnic Ignition and Propagation and Chapter Five on Control of Pyrotechnic Burn Rate. The fourth chapter is a very interesting treatment of a topic more often assumed to be understood than *actually* understood. The authors are to be commended for including this material. The fifth chapter provides a very practical approach to pyrotechnic problem solving and explains why compositions behave in the manner that they do. Both compounding and particle size are discussed.

Ian von Maltitz, who has, in addition, written a superb textbook on the subject, contributes Chapter Six on Black Powder. No discussion of pyrotechnic chemistry could be considered complete without addressing, in detail, this most seminal pyrotechnic composition. Having had the advantage of reading the full textbook, the reviewer finds that the distilled discussion in this textbook more than meets the needs for a pyrotechnic chemistry book. Again, the reader desiring more detailed information would be well served by reading von Maltitz' full length book on this subject.

Chapter Seven, by the Kosankes, discusses Pyrotechnic Primes and Priming. Many an excellent star has been "blown blind" for failure to provide an adequate prime. Also, the use of dark primes in color changing stars is discussed. Both technical and practical information is provided.

Mike Wilson and Ron Hancox contributed Chapter Eight on Pyrotechnic Delays and Thermal Sources. This technical material may be of less direct use to most pyrotechnists, but, the discussion of this topic is both well written and serves to expand the reader's knowledge of this subject. It affords the reader a good understanding of basic behaviors of these pyrotechnic systems and compositions.

More in keeping with perhaps the most crucial element of pyrotechnic chemistry after Black Powder, The Chemistry of Colored Flames, Chapter Nine, is written by the Kosankes. This critically useful material begins with a brief discussion of the physics of visible light and proceeds to apply this basic material to a very detailed and cogent discussion of the basics of producing pyrotechnic colored flames. Emitter species, chlorine donors, the role of flame temperature, and the use of various fuels are reviewed. This is simply a superb contribution to this extremely broad field of pyrotechnic chemistry. It is a most useful chapter and greatly enhances the value of this textbook.

Chapter Ten on Illuminants, by Dillehay, naturally follows. Again, this material is of less direct application for many pyrotechnists, but nevertheless provides a useful treatment of the subject of pyrotechnic flashes, flares, and illuminants, often used to good effect in displays.

Propellant Chemistry by Naminosuke Kubota is the subject of Chapter Eleven. Composite propellants and Black Powder propellants are discussed. Combustion kinetics and chemistry are then reviewed.

Kubota's Chapter Twelve, Principles of Solid Rocket Motor Design, is, in and of itself, practically a monograph on this subject. This chapter can be read at either of two levels: the reader conversant with physics will be provided sufficiently detailed technical information to apply the material provided to designs of independently conceived rocket motor systems, while the amateur will still be able to read the chapter to gain an understanding of exactly how rocket motors are designed and how they function. Detailed discussions of exhaust gas momentum and aerodynamics lead to a discussion of the thermodynamics of thrust generation. Mass balance, thrust, specific impulse and topics related to the pressure sensitivity of burn rates and motor function are discussed. Propellant grain variants are reviewed and the effects of various grain designs on thrust generation are covered in a very practical manner, with superb accompanying illustrations. Propellant selection and the effects of reaction products are briefly addressed. Motor case and nozzle design are presented in a fairly lucid, though brief discussion. Igniter design and selection of materials are reviewed. This critical issue has not been as well addressed in other solid rocket motor articles and its inclusion is a welcome addition. Motor combustion phenomena are reviewed. The chapter concludes with a practical exercise: the application of the various principles previously discussed to the construction of a two-stage motor. Overall, this is a superbly well-written chapter. It makes some very abstruse material understandable to a wide range of readers. The author has done an exemplary job in writing the most complete though concise presentation of solid rocket motor design that this reviewer has seen.

Chapter Thirteen, by the Kosankes and by Clive Jennings-White, on Pyrotechnic Spark Generation provides an articulate discussion of a topic as important as colored flames. Indeed, the production of gold and silver sparks and their variations constitute an effect as responsible for the "oohs and aahs" uttered by the spectators at displays as any effect achieved. Both charcoal and metal spark effects are reviewed. Jennings-White follows in Chapter Fourteen with a discussion of Glitter Chemistry. While this is an easy effect to appreciate, the chemistry behind glitter is the subject of much debate and is extraordinarily complex. The author provides a rational discussion of the leading theories put forward by various proponents as to the nature of the chemistry behind the glitter effect so many of us enjoy. Colored glitters are also briefly discussed. Together, these two chapters afford one of the best reviews of these related topics that I have read.

Strobe Chemistry is the subject of Chapter Fifteen, also by Jennings-White. Again, this is an easy effect to compound and to produce and a rather difficult topic to understand in detail. A simplification of light and dark phase reactions more than adequately makes this topic accessible to readers of any and all levels of chemistry knowledge. While an expanded discussion of colored strobe effects and chemistry would have been appreciated in this textbook, the references noted in the bibliography offer access to this related topic. Overall, this discussion, while brief, is both fascinating and important.

Whistle Devices provide the topic for discussion in Chapter Sixteen, by Mike Podlesak and Mike Wilson. Whistles are ubiquitous in pyrotechnics: in drivers, ground devices, consumer and display items, and in rockets. A discussion of the fuels so crucial to providing these oscillating reactions and their use in pyrotechnics is offered. Whistle combustion chemistry is reviewed in a manner at once extremely technical and fascinating to almost any reader. Additional discussion regarding the use of these compositions in pyrotechnic rockets would be useful, but the basics of whistle compositions suffice for the purposes of this textbook.

From a safety perspective, there is, perhaps no more vital topic than that discussed by Dave Chapman in Chapter Seventeen: the Sensitiveness of Pyrotechnic Compositions. Tests for sensitivity and a discussion of the different nature of friction, impact, and temperature sensitivity are discussed. Implications for transportation are provided. A few specific compositions and related accidents are also discussed. This is a very practical chapter and the authors are to be commended for its inclusion.

Clive Jennings-White and Ken Kosanke review Hazardous Chemical Combinations in Chapter Eighteen. The authors provide a detailed discussion of dangerous chemical combinations, discussions of the hazards produced, and a basic chemical rationale for why these particular compositions are so hazardous. Chlorates and powdered metals (aluminum, magnesium, zinc, and magnalium) are reviewed in detail. The reviewer suggests that inclusion of phosphorus related compositions would be useful in a future edition, as would a more focused discussion of the hazards associated with various specific flash compositions. Nevertheless, the information provided in this chapter is most useful.

Tom Smith's concluding Chapter Nineteen, on Assessing the Risks, provides a safety-oriented and practical approach to those contemplating working with pyrotechnic compositions and devices. It is a well-written and most suitable conclusion to this text. The basic statistics of risk assessment are provided, so that the reader may make more mathematically informed and rational decisions. Both qualitative and quantitative risk assessments are addressed.

Overall, this is a most satisfactory endeavor. The Pyrotechnic Chemistry textbook offered by these authors through the Journal of Pyrotechnics is at once useful and fascinating. Its various topics differ in degree of complexity and will appeal to a wide range of readers. While no single textbook can completely cover this broad range of associated and collected topics, this reviewer feels that the Pyrotechnic Chemistry book is an excellent basic and reference text (thanks to its exhaustive bibliography) and is worthy of inclusion in any reader's pyrotechnic library. I enthusiastically recommend this book and offer my congratulations to its contributing authors and editors on a job well done.

Review of: Pyrotechnic Chemistry

Journal of Pyrotechnics [ISBN 1-889526-15-0] 2004

Bernard E. Douda
Naval Surface Warfare Center, Crane, IN, USA

Pyrotechnic Chemistry is the fourth in the Pyrotechnic Reference Series produced by the publisher of the *Journal of Pyrotechnics*. It is composed of nineteen stand-alone presentations each authored by pyrotechnic experts in their specialty area.

There are chapters dealing with pyrotechnic materials, thermodynamics, ignition and propagation, burning rate control, black powder, primes and priming, delays and thermal sources, illuminants, solid rocket motor design, spark generation, whistle devices, and the chemistry of colored flames, propellants, glitter, and strobes. Safety aspects are addressed in chapters discussing composition sensitiveness, hazardous chemical compositions, and risk assessment.

One advantage of a compilation of this sort is that it makes it convenient for the reader to find information across a wide range of pyrotechnic topics. The extensive Table of Contents makes this possible. The book contains a large number of figures and tables to support the text material. There are many examples of application of the information to pyrotechnic practical situations. For the most part, this book addresses the topics thoroughly but perhaps in some cases not to the degree that one would find in a textbook.

The compilation format provided the opportunity for each of the authors to address their topic to a degree sufficient to relate all aspects of their topic to practical pyrotechnics. They accomplished this by providing the underlying theory, the relevant equations, illustrative figures, and tables of supporting data. The result of this is that some chapters are much larger than others.

Another important characteristic of this book is that it addresses many pyrotechnic safety issues in chapters dedicated to this purpose. Not only were the authors able to point out safety concerns with material incompatibilities throughout their individual topics but also they prepared three chapters dedicated to sensitivity of pyrotechnic compositions, hazardous chemical combinations, and risk assessment.

Each chapter includes a set of its own references. These will be valuable to those wishing to explore a subject further. The book is easy to read. The topics are presented in an informative and educational manner. This book not only addresses topics related to fireworks but also addresses topics relevant to military pyrotechnics. It complements other pyrotechnic reference books and will serve as a valuable addition to one's library.

Review of:
Pyrotechnic Chemistry

Journal of Pyrotechnics [ISBN 1-889526-15-0] 2004

Tony Cardell
Edenbridge, Kent, UK

Having spent more than 42 very enjoyable years working with energetic materials, particularly in the areas of military pyrotechnics and fireworks, I know the frustration faced by so many workers, both new and experienced, with the almost impossible task of finding useful reference books on these very specialized subjects. Also, as the total international experience in pyrotechnics and other energetic materials appears to be constantly reducing, it is essential for newcomers (and those not so new!) to be able to find good quality publications which give the widest picture in terms of in-depth technical content and practical examples. I believe that the book "*Pyrotechnic Chemistry*" published by the Journal of Pyrotechnics Inc. goes a long way to achieving this aim. The breadth of pyrotechnic related subjects covered by this publication is very wide as it is a compilation of papers (many previously published, but now updated), forming 19 chapters by 13 authors, who are well known and highly experienced in their respective fields.

Based upon my own favourite topics it is always pleasing to find a new book which covers aspects of military pyrotechnics, fireworks and related safety considerations. Chapters describing *Pyrotechnic Delays* and *Thermal Sources*, *Illumination and Illuminant Research*, *Propellant Chemistry* and *Rocket Motor Design* provide interesting reading for the military researchers whereas the papers on *Chemical Components of Firework Compositions*, *Pyrotechnic Spark Generation, Glitter Chemistry* and *Strobe Chemistry* will be extremely useful to those working with fireworks and theatrical pyrotechnics.

Linking the technologies of all of the above subjects are chapters on *Pyrotechnic Chemistry*, *Chemical Thermodynamics, Pyrotechnic Ignition and Propagation, Control of Pyrotechnic Burn Rate, Primes and Priming, Chemistry of Coloured Flames, Chemistry of Black Powder* and *A Study of the Combustion Behaviour of Pyrotechnic Whistles.*

There are also important safety related chapters which include *Sensitiveness of Pyrotechnic Compositions, Hazardous Chemical Combinations* and *Assessing the Risks.* These chapters complement and reinforce the safety issues discussed elsewhere in the book.

I enjoyed the "easy to navigate" lay-out of *Pyrotechnic Chemistry* as each chapter is presented as a stand-alone paper, along similar lines to the format of a scientific seminar or conference proceedings. However, without an overall book index it does take time to 'sieve out' all the information on any specific subject. Each chapter gives many useful references adding up to a total of about 400.

This is one of my 'A-list' volumes that should be on the bookshelf of all those requiring an 'in-depth' introduction to these areas of pyrotechnics, however I am also certain that it will be a very useful reference source for the more experienced people working in this technical field.

Overall, all the authors have done an excellent job in compiling this fascinating and important pyrotechnic reference book.

Journal Sponsors

Journal of Pyrotechnics **wishes to thank the following Sponsors for their support.**

Individual Sponsors:

Ed Brown
PO Box 177
Rockvale, CO 81244, USA
Phone: 719-784-4226
email: edwinde@peoplepc.com

Gerald Laib
17611 Longview Lane
Olney, MD 20832, USA
Phone: 301-744-4358
FAX: 301-744-6406

Corporate Sponsors:

Allied Specialty Insurance
Mary Chris Smith
10451 Gulf Blvd
Treasure Island, FL 33706, USA
Phone: 800-237-3355
FAX: 727-367-1407
email: info@alliedspecialty.com
web: www.alliedspecialty.com

American Fireworks News
Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: 570-828-8417
FAX: 570-828-8695
email: afn@fireworksnews.com
web: www.fireworksnews.com

American Pyrotechnics Association
Julie Heckman
7910 Woodmont Ave, Ste. 1220
Bethesda, MD 20814, USA
Phone: 301-907-8181
FAX: 301-907-9148
email: jheckman@americanpyro.com
web: www.americanpyro.com

Astro Pyrotechnics
Leo Autote
2298 W. Stonehurst
Rialto, CA 92377, USA
Phone: 909-822-6389
FAX: 909-854-4749
web: www.astropyro.com

Brooke * Mawhorr, PC
Douglas K Mawhorr
112 East Gilbert St, PO Box 1071
Muncie, IN 47305, USA
Phone: 765-741-1375
FAX: 765-288-7763
email: dmawhorr@brookemawhorr.com

Canadian Explosives Research Laboratory
Dr. Phil Lightfoot, Manager
CANMET - 555 Booth St
Ottawa, ON, K1A 0G1, Canada
Phone: 613-947-7534
FAX: 613-995-1230
email: plightfo@nrcan.gc.ca
web: www.nrcan.gc.ca/mms/cerl

Combined Specialties International. Inc.
John and Alice Allen
8362 Tamarack Village, Ste. 119
Woodbury, MN 55125, USA
Phone: 651-855-0091
FAX: 651-855-0088
email: jallen@combinedspecialties.com

Davas Ltd
Tom Smith
8 Aragon Place
Kimbolton, Huntingdon
Cambs, UK PE28 0JD
Phone: +44-1480-860124
FAX: +44-1480-861108
email: toms@davas.co.uk
web: www.davas.co.uk

Daveyfire, Inc.
Alan Broca
2121 N California Blvd. Ste. 290
Walnut Creek, CA 94596, USA
Phone: 925-926-6414
FAX: 925-926-6439
email: info@daveyfire.com

Delcor Industries Inc.
Sam Bases
19 Standish Ave.
Yonkers, NY 10710, USA
Phone: 914-779-6425
FAX: 914-779-6463
email: delcor@hotmail.com
web: www.delcorind.com

European Pyrotechnic Arts News
Rob Driessen
Grenadiersweg 55
Riemst, B 3770, Belgium
Phone: +32-12-210-630
FAX: +32-12-210-630
email: epan@pandora.be
web: http://users.pandora.be/epan

Fawkes Fireworks
Tony Cardell and David Watts
89 Lingfield Road
Edenbridge, Kent TN8 5DY, UK
Phone: 44-1732-862-862
FAX: 44-1342-317-818
email: Tony@fawkes.co.uk

Fire One
Dan Barker
863 Benner Pike
State College, PA 16801, USA
Phone: 814-238-5334
FAX: 814-231-0799
email: info@fireone.com
web: www.fireone.com

Firefox Enterprises Inc.
Gary Purrington
11612 N Nelson
Pocatello, ID 83202, USA
Phone: 208-237-1976
FAX: 208-237-1976
email: custserv@firefox-fx.com
web: www.firefox-fx.com

Firework Professionals
Anthony Lealand
PO Box 19-912
Christchurch, 8030, New Zealand
Phone: 64-3-982-3473
FAX: 64-3-982-3474
email: firework@firework.co.nz
web: www.firework.co.nz

Fireworks
PO Box 40
Bexhill, TN40 1GX, England
Phone: 44-1424-733-050
FAX: 44-1424-733-050
email: editor@fireworks-mag.org
web: www.fireworks-mag.org

Fireworks and Stage FX America
Kevin Brueckner
PO Box 488
Lakeside, CA 92040, USA
Phone: 619-938-8277
FAX: 619-938-8273
email: info@fireworksamerica.com
web: www.fireworksamerica.com

Fireworks Business
Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: 717-828-8417
FAX: 717-828-8695
email: afn@fireworksnews.com
web: www.fireworksnews.com

Fireworks by Grucci, Inc.
Phil Grucci
1 Grucci Lane
Brookhaven, NY 11719, USA
Phone: 631-286-0088
FAX: 631-286-9036
email: philgrucci@aol.com
web: www.grucci.com

Fullam's Fireworks, Inc.
Rick Fullam
P.O. Box 1808 CVSR
Moab, UT 84532, USA
Phone: 435-259-2666
email: Rfullam_3@yahoo.com

Goex, Inc.
Mick Fahringer
PO Box 659
Doyline, LA 71023, USA
Phone: 318-382-9300
FAX: 318-382-9303
email: email@goexpowder.com
web: www.goexpowder.com

High Power Rocketry
Bruce Kelly
PO Box 970009
Orem, UT 84097, USA
Phone: 801-225-3250
FAX: 801-225-9307
email: tra00015@aol.com
web: www.tripoli.org

IPON srl
Pagano Benito
Via Trofa
Ottaviano, Napoli 80044, Italy
Phone: +39-81-827-0934
FAX: +39-81-827-0026
email: info@ipon.it
web: www.ipon.it

Island Fireworks Co. Inc.
Charles Gardas
N735 825th St
Hager City, WI 54014, USA
Phone: 715-792-2283
FAX: 715-792-2640
email: islndfwk@pressenter.com
web: www.island-fireworks.com

Lantis Fireworks & Lasers
Ken Lantis
PO Box 491
Draper, UT 84020, USA
Phone: 801-768-2255
FAX: 801-768-2433
email: info@fireworks-lasers.com
web: www.fireworks-lasers.com

MagicFire, Inc.
Paul McKinley
PO Box 896
Natick, MA 01760, USA
Phone: 508-647-9645
FAX: 508-647-9646
email: pyrotech@magicfire.com
web: www.magicfire.com

Marutamaya Ogatsu Fireworks Co., Ltd.
1-35-35 Oshitate Fuchu
Tokyo, 183-0012, Japan
Phone: 81-42-363-6251
FAX: 81-42-363-6252
email: hanabi@mof.co.jp
web: www.mof.co.jp

Mighty Mite Marketing
Charlie Weeth
122 S 17th St
LaCrosse, WI 54601, USA
Phone: 608-784-3212
FAX: 608-782-2822
email: chzweeth@pyro-pages.com
web: www.pyro-pages.com

MP Associates Inc.
P.O. Box 546
Ione, CA 94640, USA
Phone: 209-274-4715
FAX: 209-274-4843

Nitrotech Australia Pty Ltd
Chris Larkin
PO Box 349, Mount Isa
QLD 4825, Australia
Phone: +617-47-44-2290
FAX: +617-47-44-3998
email: nitrotech@smartchat.net.au

Precocious Pyrotechnics, Inc.
Garry Hanson
4420 278th Ave NW
Belgrade, MN 56312, USA
Phone: 320-346-2201
FAX: 320-346-2403
email: ppinc@tds.net
web: www.pyro-pro.com

Pyro Shows, Inc.
Lansden Hill
P.O. Box 1406
LaFollette, TN 37766, USA
Phone: 800-662-1331
FAX: 423-562-9171
email: info@pyroshowsusa.com
web: www.pyroshowsusa.com

Pyrodigital Consultants
Ken Nixon
1074 Wranglers Trail
Pebble Beach, CA 93953, USA
Phone: 831-375-9489
FAX: 831-375-5225
email: pyrodig@aol.com
web: www.infinityvisions.com/pyrodigital

PyroLabs, Inc.
Ken Kosanke
1775 Blair Road
Whitewater, CO 81527, USA
Phone: 970-245-0692
FAX: 970-245-0692
email: ken@jpyro.com

RCS Rocket Motor Components, Inc.
Gary Rosenfield
2113 W 850 N St
Cedar City, UT 84720, USA
Phone: 435-865-7100
FAX: 435-865-7120
email: garyr@powernet.net
web: www.rocketmotorparts.com

RES Specialty Pyrotechnics
Steve Coman
21595 286th St
Belle Plaine, MN 56011, USA
Phone: 952-873-3113
FAX: 952-873-2859
email: respyro@earthlink.net
web: www.respyro.com

Rozzi Famous Fireworks
Arthur Rozzi
PO Box 5
Loveland, OH 45140, USA
Phone: 513-683-0620
FAX: 513-683-2043
email: art@rozzifireworks.com
web: rozzifireworks.com

Service Chemical, Inc.
Ben Cutler
2651 Penn Avenue
Hatfield, PA 19440, USA
Phone: 215-362-0411
FAX: 215-362-2578
email: ben@servicechemical.com
web: www.servicechemical.com

Skylighter, Inc.
Harry Gilliam
PO Box 480
Round Hill, VA 20142, USA
Phone: 540-338-3877
FAX: 540-338-0968
email: orders@skylighter.com
web: www.skylighter.com

Spirit of 76 Fireworks
John Bechtold
6401 West Highway 40
Columbia, MO 65202, USA
Phone: 573-477-1776
FAX: 573-477-1786
email: marketing@76wholesale.com
web: www.76wholesale.com

Starburst Pyrotechnics & Fireworks Displays Ltd
Bonnie Pon
2nd Fl-Sui Hing Hong Bldg - 17 Commissioner St
Johannesburg, Gauteng 2000, South Africa
Phone: 27-11-838-7705
FAX: 27-11-836-6836
email: info@starburstpyro.co.za
web: www.starburstpyro.co.za

Swedish Chemistry
Hans nilsson
Box 130
S0372 22, Ronneby, Sweden
FAX: +46-457-156-01
email: hanskemi@post.utfors.se

Western Pyrotechnics, Inc.
Rudy Schaffner
PO Box 176
Holtville, CA 92250, USA
Phone: 760-356-5679
FAX: 760-356-2155
email: rudys@holtville.net

Sponsorships

No advertising as such is printed in the *Journal of Pyrotechnics*. However, a limited number of sponsors have been sought so that the selling price of the Journal can be reduced from the listed cover price. The cost of helping sponsor an issue of the *Journal of Pyrotechnics* is $70 per issue for businesses and organizations. Individuals can sponsor a single issue of the Journal for $35 per issue. In addition to a listing in the Sponsor section of the Journal, full sponsors receive two free copies of the sponsored Journal. Individual sponsors only receive one copy of the Journal. Both sponsors receive a brief listing on a flyer inserted under the transparent cover of the Journal.

Additionally, if you so desire, we can provide a link from the Journal of Pyrotechnics Web Site to your web site, e-mail address or simply a company name, address and phone information listing. If you would like to be a sponsor contact the publisher.