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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.

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Evaluation of the Hazards Posed by High Energy Bangers
Part 1. Noise, Overpressure and TNT Equivalence

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ABSTRACT

The work reported in this paper was undertaken to determine the hazards posed by certain types of European bangers (firecrackers) that use flash composition. Experiments were done to evaluate the overpressures and noise levels close to such fireworks when they function.

The results indicate that powerful flashbangers could cause hearing damage to those in their immediate vicinity.

The TNT equivalences derived from overpressure for the barium nitrate and potassium perchlorate flashbangers tested were found to be 25 and 57%, respectively.

Keywords: noise, overpressure, TNT equivalence, flash composition, bangers, firecrackers

Introduction

The 1988 British Standard BS7114[1] defined the types of fireworks that could be sold to the general public in the United Kingdom (UK). Category 2 bangers could contain up to 1.6 g of gunpowder (blackpowder) as the explosive charge and should not cause injury to a person 5 m away, while Category 3 bangers could contain up to 10 g of an unspecified explosive composition and should not cause injury to a person at a distance of 25 m from the firework.

The sale of bangers was banned in the UK in 1997 on safety grounds. Prior to this, flashbangers had been classed as Category 3 items.

Work is currently underway to produce a European (CEN)[2] Standard for Fireworks,[3] Table 1 gives details of the net explosive content of the proposed categories for flashbangers.

Additionally, the CEN standard sets maximum sound level requirements of 120 dB (AI_{max}) at 1, 8 and 15 m for Category 1, 2 and 3 bangers, respectively.

Typical flash compositions used in fireworks contain mixtures of either barium nitrate or potassium perchlorate with a metal powder.

The programme of work undertaken to quantify the hazards from energetic bangers was composed of two parts. The first study, which is reported in this paper, involved examination of the near field blast and medium range noise effects produced by the initiation of flashbangers containing the two types of composition under consideration by the CEN committee.

The second component of the study involved qualitative experiments to simulate and record the effects produced by different flashbangers when they function while being held. This work will be reported separately.[4]

Table 1. Net Explosive Content Proposed by CEN Committee CEN/TC212 for Flashbangers.

Banger Type	Net Explosive Content (g)		
	Category 1	Category 2	Category 3
Friction ignited flashbangers	—	1.0 nitrate based 0.5 perchlorate based	6.0 nitrate based 3.0 perchlorate based
Flashbangers	0.3 nitrate based 0.2 perchlorate based	1.0 nitrate based 0.5 perchlorate based	10.0 nitrate based 5.0 perchlorate based

Manufacture of Bangers

To simplify the experiments, the bangers for the tests were made with an electrical ignition system, rather than a manually lit fuse, and no work was undertaken with friction ignited flashbangers. The bangers were specially manufactured by Standard Fireworks (now Black Cat Fireworks) of Huddersfield, UK.

The pyrotechnic materials chosen for the test programme were:

1) barium nitrate / aluminium powder

2) potassium perchlorate / aluminium powder

Since various types of cardboard tube can be employed in making bangers, it was decided that each firework would be produced in three tube types (i.e., weak, medium and strong). Also, since closures can be made of either paper or clay, each type was produced with two types of end plug. Different strengths of tubing were achieved by using rolled cardstock with different degrees of perforations. This is a common industry practice for banger construction as it introduces points of preferential weakness.

End plugs were either a standard clay type or a paper end-disc glued in place and then sealed with a layer of hot glue melt. Ignition in all instances was achieved by initiating an electrical fusehead (electric match) that had been incorporated beneath a tapered plug at the top of the firework.

Table 2. Type of Composition and Net Explosive Content Used in the Bangers.

Pyrotechnic Composition	Net Explosive Content (g)		
	Cat. 2	Cat. 3	
Potassium perchlorate / aluminium powder	0.5	3*	5
Barium nitrate / aluminium powder	1	6*	10

* These values would apply to friction ignited flashbangers.

Details of the net explosive content of the manufactured bangers are given in Table 2.

Physical measurements were made on randomly selected fireworks to check compliance with these requirements and the results are summarised in Tables 3 and 4.

All the bangers showed some variation in the amount of composition they contained, but this was typical of similar manufactured goods.

The oxidiser metal ion was measured by flame emission atomic spectroscopy: the barium nitrate bangers had a mean barium nitrate content of 64.6% compared with a specified level of 68%. Similarly, the potassium perchlorate bangers had a mean potassium perchlorate content of 68.8%, compared with the specified 71%. These minor deviations in chemical composi-

Table 3. Measurement of Barium Nitrate / Aluminium Bangers.

Type	Length (mm)	Tube Outside Diameter (mm)	Wall Thickness (mm)	Type of closure / tube	Mass of composition (g)
Small tube	69.60–70.20	10.90–11.10	2.10–2.30	clay / medium	1.01–1.25
Medium tube	107.70–107.85	23.30–23.50	5.45–5.55	cardboard / strong	5.84–6.71
Large tube	139.65–140.05	23.10–23.50	5.20–5.50	clay / strong	9.69–10.99

Table 4. Measurement of Potassium Perchlorate / Aluminium Bangers.

Type	Length (mm)	Tube Outside Diameter (mm)	Wall Thickness (mm)	Closure / Tube Type	Mass of Composition (g)
Small tube	69.90–70.50	10.80–10.90	2.40–2.45	clay / medium	0.53–0.61
Medium tube	107.20–107.60	17.85–17.95	2.60–2.65	clay / medium	2.37–2.91
Medium tube	107.75–107.95	17.70–17.85	2.45–2.50	cardboard / weak	4.63–5.22

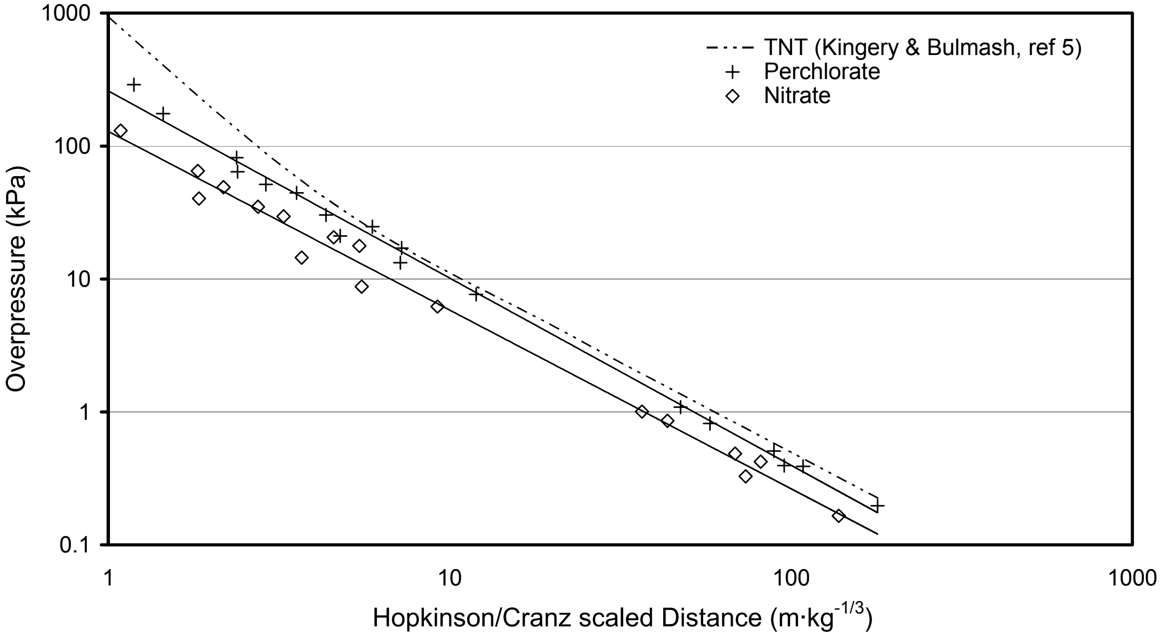

Figure 1. Measured overpressures from bangers containing barium nitrate and potassium perchlorate flash compositions.

tion were expected to have little effect on the overall performance of the bangers when compared with the effect of altering the masses of the compositions.

Experimental Programme

An experimental programme was undertaken to gain information on the blast and sound pressure levels generated by energetic bangers. Key elements of the programme were:

- All experiments (noise and blast measurements) were done outdoors.
- For each experiment, a record was taken of ambient temperature, ambient pressure, wind speed, and wind direction as well as the primary blast and noise data. Relative humidity was also recorded for each block of tests.
- Noise levels for each firework were measured at the proposed CEN Standard 'testing' distances of

Category 2	8 m
Category 3	15 m

- Pressures were monitored using four spear gauges (PCB type 137A23) mounted in a plane 1.5 m above ground and at distances of 0.2, 0.4, 0.6 and 1.0 m from the firework.
- Sound pressure levels (*SPL*) were measured using six calibrated recording instruments (CEL-414/3C) situated at distances of 1, 8 and 15 m from the functioning point and in two planes at right-angles to each other.
- Tests were undertaken with fireworks selected in a random order.
- Each firework type (i.e., net explosive content / tube / closure) was tested 5 times.

Blast Overpressures

The use of Hopkinson/Cranz scaling for distance permits experimental overpressure data to be used for estimating the overpressure of any mass / distance combination. Figure 1 illustrates the results from the tests with flashbangers and incorporates overpressures measured using the spear blast gauges and those derived from noise

Table 5. Constant Terms in the Relationship Linking the Decay of Mean Overpressure with Scaled Distance.

Pyrotechnic Composition	Constants		Correlation Coefficient (R^2)
	a	*b*	
Barium nitrate / aluminium	–1.344	2.110	0.991
Potassium perchlorate / aluminium	–1.408	2.415	0.996

measurements (converted to pressures from decibels). Mean values for a particular composition are shown, irrespective of tube type and closure since these parameters were found to exert little influence. In evaluating the results, the experimentally determined mean mass of composition was used to calculate the scaled distances.

The combined pressure and noise data were used to determine the dependence of the decay of overpressure with scaled distance (z) for each composition. The relationships are of the form

$$\text{Overpressure (mean)} = 10^{(a \log(z) + b)}$$

where z is the Hopkinson/Cranz scaled distance ($\text{m·kg}^{-1/3}$) and the constant terms are defined in Table 5.

The primary variables that affect the results are the net explosive content and the type of pyrotechnic composition used. As reported above, the effects of tube type and tube closure, though statistically measurable, were small compared to the effect of the pyrotechnic composition used. The effect of relative humidity was not statistically determinable for all banger types as it was subsumed within the random variability in the pressure and noise readings. A slight, statistically relevant, effect of wind speed on the noise measurements from potassium perchlorate / aluminium bangers was noticed, but the effect was so small that it can be ignored in any calculations to determine the pressure / distance relationship.

TNT Equivalence

It is common for the blast effects from explosions to be presented using a TNT-equivalence (TNT_e),[6] and compositions containing mixtures of aluminium and potassium perchlorate (such as are used for producing light and sound effects) are known[7] to generate blast waves similar to TNT when they explode. In general, lower energy pyrotechnics that deflagrate react much more slowly than conventional high explosives. As a result, the corresponding pressure wave is usually of much lower amplitude initially and of much longer duration. Even though information on the blast parameters from pyrotechnic compositions is somewhat limited, and the ability of pyrotechnics to cause blast damage is different to TNT-type explosions, it is still usual and convenient to equate them all to TNT.

There is a considerable amount of published work relating to the estimation of blast effects (blast scaling), although the majority of the studies have little application to relatively small distances from the explosion source. However, Yallop[8] has given the pressure at 1 m from 100 g of TNT derived from Cook's equation,[9] and De Yong and Campanella[10] have published data for the blast wave characteristics from 200 to 1000 mg quantities of pyrotechnics measured at 1 m.

The difficulty with theoretical estimation of blast damage from bangers is that the effect of the confinement of the tube on the blast characteristics (i.e., on TNT_e) is not known. However, De Yong and Campanella[10] have performed experiments with confined pyrotechnic powders that suggest that the TNT_e of MRL(X)210 (potassium perchlorate / aluminium / acroid resin in 59:40:1 proportions) is 60%.

A recent paper by Merrifield and coworkers[11] reported TNT_e values in the range of 40 to 130% for flash composition (30% aluminium / 70% potassium perchlorate) with the lower figure applicable to confinement in a firework. This lower value is broadly in keeping with the TNT_e values of 20 to 60% quoted by Contestabile and Augsten[12] for firework report shells.

Table 6. Values for the Constants *A* and *B* in the Equation $SPL = A\,D + B$ Used To Define the Dependence, at $D > 10$ m, of the Peak Sound Pressure Level (*SPL*) on Distance (*D*).

Firework	*A*	*B*	Correlation Coefficient (R^2)
Barium nitrate / aluminium banger (1g)	–0.59	147.5	0.978
Barium nitrate / aluminium banger (6g)	–0.77	156.2	0.951
Barium nitrate / aluminium banger (10g)	–0.63	157.4	0.975
Potassium perchlorate / aluminium banger (0.5g)	–0.63	149.3	0.978
Potassium perchlorate / aluminium banger (3g)	–0.65	155.5	0.978
Potassium perchlorate / aluminium banger (5g)	–0.67	157.0	0.978

Table 7. Values for the Constants *A* and *B* in the Equation $SPL = A\ln(D) + B$ Used To Define the Dependence of Peak Sound Pressure Level (*SPL*, dB(*C*)) on Distance (*D*, m).

Firework	*A*	*B*	Correlation Coefficient (R^2)
Barium nitrate / aluminium banger (1g)	–11.05	170.0	0.997
Barium nitrate / aluminium banger (6g)	–11.64	177.6	0.998
Barium nitrate / aluminium banger (10g)	–11.82	179.3	0.999
Potassium perchlorate / aluminium banger (0.5g)	–11.62	170.8	0.978
Potassium perchlorate / aluminium banger (3g)	–12.17	178.1	0.978
Potassium perchlorate / aluminium banger (5g)	–12.44	180.1	0.978

Using published methods[13] and the data presented in Figure 1, it is possible to calculate TNT_e values of 57.3 and 24.9% for potassium perchlorate / aluminium and barium nitrate / aluminium compositions, respectively. The results are in keeping with relative magnitudes of the peak overpressure data for perchlorate and nitrate flash salutes reported by Kosanke and Kosanke[14] and with the literature values for the TNT_e of pyrotechnics given above.

Noise

From the sound pressure level (*SPL)* results it is possible to evaluate equations for the relationships between *SPL* and linear distance (*D*, in metres).

Earlier studies[15,16] have reported that a simple linear relationship of the form

$$SPL = A\,D + B$$

where *A* and *B* are constants, adequately represents the dependence. For values of $D > 10$ m and with *SPL* measured in units of dB(C),* this was again found to be the case. To enable comparison with previous work, Table 6 gives the values of the constant terms.

However, it was found that inclusion of near field data at $D < 10$ m introduced some curvature, and in these instances the results were better represented by the logarithmic equation

$$SPL = A\ln(D) + B$$

The use of this equation produced a better overall fit to the total data, yielding improved correlation coefficients, Table 7.

The CEN fireworks committee has selected 120 dB (Al_{max}) as the noise level to be cited in

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* There are a number of different measures of sound using dB scales. A-weighted (dB(A)) and C-weighted (dB(C)) are commonly used. They differ in the weighting given to different frequencies. The C-weighted scale approximates to a flat response while the A-weighting "corrects" the values at different frequencies to reflect the response of the ear. For further reading on sound measurement see:
A. Barber, *Handbook of Noise and Vibration Control,* Elsevier Science Publ. Ltd, Oxford (1992) pp 18–21.

D. A. Bies and C. H. Hanson, *Engineering Noise Control, Theory and Practice*, E & FN Spon, London (1988) pp 72–76

K. D. Kryter, *The Effects of Noise on Man,* Academic Press, Inc. Orlando (1989) pp 10–14.

Table 8. Distances for 140 dB(C) Derived from the Logarithmic Relationship and Mean Mass Data and also from the Overpressure / Scaled Distance Equation.

Composition	CEN Category	CEN Net Explosive Content (g)	Mean Mass of Composition in this Study (g)	CEN 'testing' Distance (m)	Distance for 140 dB(C) Evaluated from log Relationship (m)	Distance for 140 dB(C) Evaluated from Scaled Distance Equation (m)
Barium nitrate / aluminium	2	1	1.3	8	12.6	12.3
	3	6	6.2	8	25.4	23.4
	3	10	10.1	15	27.8	26.5
Potassium perchlorate / aluminium	2	0.5	0.6	8	14.2	12.9
	3	3	2.6	8	22.9	23.4
	3	5	4.8	15	25.0	27.8

the draft standards at various specified (testing) distances. From published work[16] this equates to approximately 140 dB(C), and this value can be substituted into the above equation to yield values of D using the constant terms derived for the various fireworks.

Table 8 summarises the results and indicates that, at the proposed CEN 'testing' distances of 1, 8 and 15 m, the sound levels for the flash compositions examined in this study will exceed 120 dB(Al_{max}) in all cases.

However, since the mean mass of composition contained in the various fireworks varied from the CEN notional masses, a more accurate means of calculation involves use of the overpressure / scaled distance relationship to calculate overpressure (and hence noise) at the flashbanger masses specified in the draft CEN standards. These results are also presented in Table 8.

An equivalent treatment for Category 1 flashbangers produces distances for 140 dB(C) of 8.2 and 9.5 m for the barium nitrate (0.3 g) and potassium perchlorate (0.2 g) compositions, respectively, when the CEN 'testing' distance is 1 m. Figure 2, derived from the overpressure / scaled distance relationship, illustrates the distances from high energy bangers required for the noise to have reduced to 140 dB(C).

Previously published data[16] on the noise levels produced at the CEN testing distance of 15 m by commercially available Category 3 bangers using nitrate and perchlorate compositions have indicated that the perchlorate bangers should be ranked above the nitrate bangers in terms of potential noise hazards. However, for the Category 3 fireworks manufactured specifically for this study, the difference in performance of the two compositions is largely accounted for by the different net explosive content prescribed for each type.

The British Standard for Fireworks[1] states that BS Category 3 fireworks are for use in large open spaces and should not cause injury to people standing 25 m away. Advice is also given that people lighting these fireworks should wear suitable personal protection. It is noted from Table 8 that noise levels in excess of 140 dB(C) will occur at distances greater than 25 m from the firework for barium nitrate / aluminium bangers with 10 g of composition and for potassium perchlorate / aluminium bangers with 5 g of composition.

Conclusions

From this study, it is apparent that both CEN Category 2 and Category 3 bangers containing flash compositions are a major hazard if misused. Hearing damage to the user from these bangers could be severe, and noise hazards to bystanders could become unacceptable.

The noise generated by the two types of banger compositions investigated in this study has been found to be greater in the perchlorate bangers than the nitrate ones for flashbangers of equal net explosive content, but at the proposed

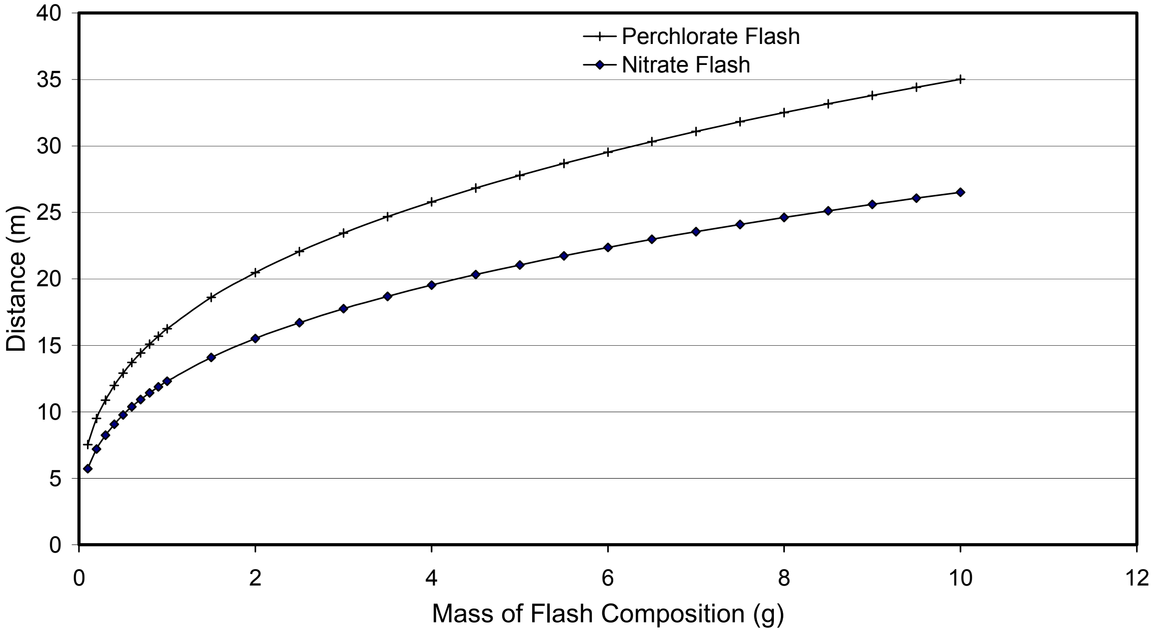

Figure 2. Distance required for the banger noise level to reduce to 140 dB(C).

CEN Standard net explosive contents for Category 2 and Category 3 bangers, the fireworks produce similar sound levels.

Acknowledgements

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References

1) "British Standard, Fireworks, Part 1. Classification of Fireworks", BS7114: Part 1: 1988, British Standards Institution.

2) CEN is the Comité Européen de Normalisation.

3) R. J. Rapley, "European Standardisation of Fireworks CEN/TC/212, A Review of the Position as at June 1994", *Proc. 2nd Intl. Symp. on Fireworks*, October 24–28, 1994, Vancouver, Canada, pp 393–410.

4) R. K. Wharton and A. E. Jeffcock, "Evaluation of the Hazards Posed by High Energy Bangers. Part 2. Damage to Hand Simulants", accepted for publication in *J. Pyro.*

5) C. N. Kingery and G. Bulmash, "Airblast Parameters from TNT Spherical Air Burst and Hemispherical Surface Burst", ARBRL-TR-02555, US Army Armament Research and Development Center, BRL, Aberdeen Proving Ground, MD, USA, 1984

6) R. Merrifield, "Simplified Calculations of Blast Induced Injuries and Damage", Specialist Inspector Report No. 37, Health and Safety Executive, April 1993.

7) R. Wild, "Blast Waves Produced by a Pyrotechnic Flash Mixture Compared to those Produced by High Explosives", *18th Department of Defence Explosives Safety Seminar*, San Antonio, TX (1978) pp 727–739.

8) H. J. Yallop, "Explosion Investigation", *The Forensic Science Society*, Harrogate, England, 1980.

9) M. A. Cook, *The Science of High Explosives*, Robert E. Krieger Pub. Co. Inc., Huntington , NY, 1971.

10) L. V. De Yong, and G. Campanella, "A Study of Blast Characteristics of Several Primary Explosives and Pyrotechnic Compositions", *J. Haz. Mats*., Vol. 21 (1989) pp 125–133.

11) R. Merrifield, R. K. Wharton and S. A. Formby, "Potential Fire and Explosion Hazards of a Range of Loose Pyrotechnic Compositions", US Dept. of Defense, Explosives Safety Board, *27th Explosives Safety Seminar*, 20–22 August, 1996, Las Vegas.

12) E. Contestabile and R. A. Augsten, "Blast Pressure from Exploding Firework Mortars", *Proc. 19th Int'l Pyrotechnic Seminar,* Christchurch, New Zealand (1994) pp 135–152.

13) S. A. Formby and R. K. Wharton, "Blast Characteristics and TNT Equivalence Values for Some Commercial Explosives Detonated at Ground Level", *J. Haz. Mats.*, Vol. 50 (1996) pp 183–198.

14) K. L. and B. J. Kosanke, "Flash Powder Output Testing: Weak Confinement", *J. Pyro.,* No. 4 (1996) pp 5–14.

15) R. K. Wharton, P. M. Pitts and B. J. Thomson, "Measurement and Interpretation of the Peak Noise Levels Produced by a Range of Fireworks", *Proc. 19th Int'l Pyrotechnic Seminar*, Christchurch, New Zealand (1994) pp 483–500.

16) R. K. Wharton and H. J. Slater, "Further Studies of the Noise Levels Produced by Fireworks", *Pyrotechnica XVI*, (1995) pp 20–29.

Errata

***Issue 14, Winter 2001*, page 66, left column.**

Do the Polysulfides Really Form as Intermediates?

In an attempt to produce one or more polysulfides, a mixture of potassium carbonate and sulfur were reacted; 0.30 g of [*potassium nitrate* should have been ***sulfur***] and 0.20 g of anhydrous potassium carbonate were mixed together. Approximately 0.1 g of this mixture was placed on a metal spatula and heated gently with a propane torch. During the heating process, the melted mixture bubbled (probably CO_2 and trace amounts of other side reaction gases were produced) then the material turned reddish brown and crumbly when cooled. Upon referencing the *Merck Index*[6] and the *CRC Handbook of Chemistry and Physics*,[7] it seems most likely that the reddish brown solids were a mixture of K_2S_4 and K_2S_5. Thus, it was concluded that polysulfides form when potassium carbonate is heated with sulfur.

Special Materials in Pyrotechnics Part 2.[55] — Application of Cæsium and Rubidium Compounds in Pyrotechnics

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ABSTRACT

The application and thermochemical behavior of pyrotechnics based on rubidium and cæsium compounds are reviewed.

Keywords: alkali metal, cæsium, pyrotechnics, rubidium

Introduction

The application of the salts of sodium and potassium in pyrotechnics has a long tradition, but there is little information available on the application of the salts of the heavier alkali metals: rubidium (Rb) and cæsium (Cs). Although they are not used in civilian fireworks, compounds of these two elements do find application in technical and military pyrotechnics.

Application in Fireworks

a) Flame Color

The testing of both cæsium and rubidium salts for firework applications stems from the fact that alkali metals in general yield intense visible emission due to radiative transitions of the s^1-electrons. In addition, the names "cæsium" (derived from Latin "cæsius" ≡ sky blue) and "rubidium"(derived from Latin "rubidus" ≡ dark red) may imply that these elements impart sky blue and dark red color to flames. Unfortunately these incorrect suppositions have found their way into such fundamental pyrotechnic literature such as Douda's "Theory of Colored Flame Production"[1] and Ellern's *Military and Civilian Pyrotechnics.*[2] Actually the names originated with Kirchhoff and Bunsen, who discovered both elements in the spa of Bad Dürkheim, Germany, and they based the names on the sky-blue spectral lines of cæsium [455.5 and 459.3 nm] and the dark red spectral lines of rubidium [780.0 and 794.8 nm], respectively.[3a] Nevertheless, from the literature it is known that both elements when applied to the laboratory burner flame yield colors similar as potassium.[4] This is because the prominent color lines from which rubidium and cæsium were given their names are not the only features in the visible spectra of flames containing these elements. As well as its two deep red lines from the

$$5p^2P_{1/2,3/2} \rightarrow 5s^2S_{1/2}$$

transition, the spectrum of rubidium has two blue-violet lines [421.6 and 420.2 nm] that come from the

$$6p^2P_{1/2,3/2} \rightarrow 5s^2S_{1/2}$$

transition, which is analogous to the

$$7p^2P_{1/2,3/2} \rightarrow 6s^2S_{1/2}$$

transition that produces the two sky blue lines in the spectrum of cæsium. The spectra of both elements also have lines in the red, orange, yellow and green regions that arise from electronic transitions between the excited states. In addition, the spectra also display continuous emissions, which have been attributed to several different processes described below:

The ease of ionization of both Rb and Cs gives rise to M^+ and e^- species yielding continuum radiation upon recombination (eq 1)

$$M^+ + e^- \rightarrow M + h \cdot \nu \qquad (1)$$

where M is Rb or Cs, h is Planck's constant [6.626×10^{-34} J·s^{-1}], and ν is the frequency [s^{-1}].

Furthermore, it is assumed that thermal line broadening of the minor series lines[5a] provides a quasi continuous spectrum, and finally the known reaction

$$M + \mathrm{OH} \rightarrow M\mathrm{OH} + h \cdot \nu \qquad (2)$$

Table 1. Thermochemical Properties of Alkali Metal Sulfides and Sulfates.

	K_2S	K_2SO_4	Rb_2S	Rb_2SO_4	Cs_2S	Cs_2SO_4
CAS-Nr.	1312-73-8	7778-80-5	31083-74-6	7488-54-2	12214-16-3	10294-54-9
m_r [g·mol^{-1}]	110.263	174.261	203.002	267.00	297,877	361.875
mp [°C]	948	1069	425	1050	515	1005

where M is Rb or Cs and is also assumed to contribute to the continuous radiation.[6] Thus atomic emission of cæsium or rubidium with traditionally composed pyrotechnics cannot yield distinct colors other than whitish pink to violet. In terms of suppressing the minor line radiative transitions it is known that a cooler flame or generally speaking an excitation at lower temperature may help to suppress radiative transitions between higher quantum levels.[7] This is in accord with Boltzmann's equation (eq 3), which calls for a higher number of atoms in the excited state with rising temperature. That is,

$$\frac{N_e}{N_g} = \frac{P_e}{P_g} \cdot e^{\left(-\frac{E_e}{kT}\right)} \tag{3}$$

where N_e and N_g designate numbers of atoms in either excited or ground state, P_e and P_g designate statistical factors that are derived from the number of states energetically equivalent at a given quantum level, E_g designates the energy difference between the ground and excited state in Joules, k is Boltzmann's constant [$1.38 \cdot 10^{-23}$ J·K^{-1}], and T designates the absolute temperature in Kelvin. Indeed, references 5 and 8 both state that with rising flame temperature the metal spectra become more brilliant and display more lines than at lower temperatures.

Weingart[9] confirms that lowering the flame temperature may be a feasible approach to reduce unwanted radiative transitions. He proposes that simple blue colors can be made by dissolving cæsium carbonate in ethanol and then burning it with a cotton wick. Although this experiment yields a gray-blue colour at the side of the flame, the top of the flame, which is known to be the hottest part of the flame, still yields a whitish pink flame.[4]

Jennings-White[10] applied both nitrates and perchlorates of rubidium and cæsium in pyrotechnic formulations. In these experiments the flame color was always white or whitish pink-violet. Especially in the case of formulations containing halogens, this is not surprising since rubidium chloride (RbCl) as well as cæsium chloride (CsCl) are known to produce emissions exclusively in the UV.[11a,b]

Hiskey,[12] in his reply to a comment by Webb, states that he tried CsCl as a replacement for copper(I) chloride (CuCl) in high nitrogen containing pyrotechnics, but had no luck in obtaining a blue color.

b) Glitter Formulations

Verifying different theoretical approaches for glitter stars, Jennings-White[13] tested both cæsium nitrate ($CsNO_3$) and rubidium nitrate ($RbNO_3$) as substitutes for potassium nitrate (KNO_3) in glitter formulations. Oglesby's theory,[14] whereby the glitter effect is based on the intermediate formation of potassium sulfide (K_2S) that would be subsequently oxidized in air to potassium sulfate (K_2SO_4), was confirmed. Table 1 gives the melting points of the sulfides and sulfates of potassium, cæsium and rubidium. In addition, cæsium sulfide is known to oxidize easily in air when ignited with a propane flame.[5b] Jennings-White describes glitters with either $RbNO_3$ or $CsNO_3$ as showing bright silver and impressive terminal delayed flash. As expected, these formulations did not impart any color to the flame.

Table 2 lists formulations with both nitrates and perchlorates of Rb and Cs tested by the author[4] and Jennings-White.[10,13] None of these formulations provided a distinct color.

No successful experiments have been reported in the literature to produce colored flames with either rubidium or cæsium salts.

Table 2. Formulations with Nitrates and Perchlorates of Rb and Cs.

	1	2	3	4	5	6	7	8	9	10	11
$RbNO_3$								~80		55	
$RbClO_4$									~80		
$CsNO_3$	90.93	81.1			70		~80				55
$CsClO_4$				83		80					
Cs_2SO_4			17								
$KClO_4$			8								
Guanidine nitrate			42								
Nitrocellulose	1.17		4								
Tetrachloro-phthalic acid anhydride $(C_6Cl_4)C_2O_3$			12								
Mg	7.90		17								
Mg / Al 50:50										10	10
Sb_2S_3										10	10
Si					20						
$CaSi_2$		18.9									
S_8										10	10
Charcoal										10	10
Dextrin										5	5
Shellac							~20	~20	~20		
Gum acca-roides											
Methaldehyde					10						
Hexamine				17							
$Zr(C_5H_7O_2)_4$ Zirconium(IV)-pentandionate						20					
Flame color	white	whitish blue	white	whitish pink	bluish cone	whitish pink	white	pale pink	?	bright silver	bright white
Effects		sparks	strobes	strobes	violet aureole					glitter	large glitter
Reference	4	4	4	4	4	4	10	10	10	13	13

Technical and Military Applications

Although of no practical use for fireworks, both rubidium and cæsium have been thoroughly investigated by technical researchers and have subsequently found application in military and technical pyrotechnics. Admittedly, rubidium compounds have found only very minor application, because there are no rubidium minerals and because rubidium compounds are available only as by-products of the extraction of lithium and cæsium.[3b] The interest in rubidium and cæsium is mainly due to their emissions in the far red (Rb) and the near infrared (Cs), and to the low ionization energy of both metals and the consequent ease of thermal electron emission, which gives rise to a number of interesting applications.

a) Devices Using Ionization of Cæsium and Rubidium

Ionization of chemical species in flames has long been known. As early as World War II German researchers, developing the A4 liquid propellant powered ballistic missile, found that the highly ionized plume (estimated ~10^6 ions

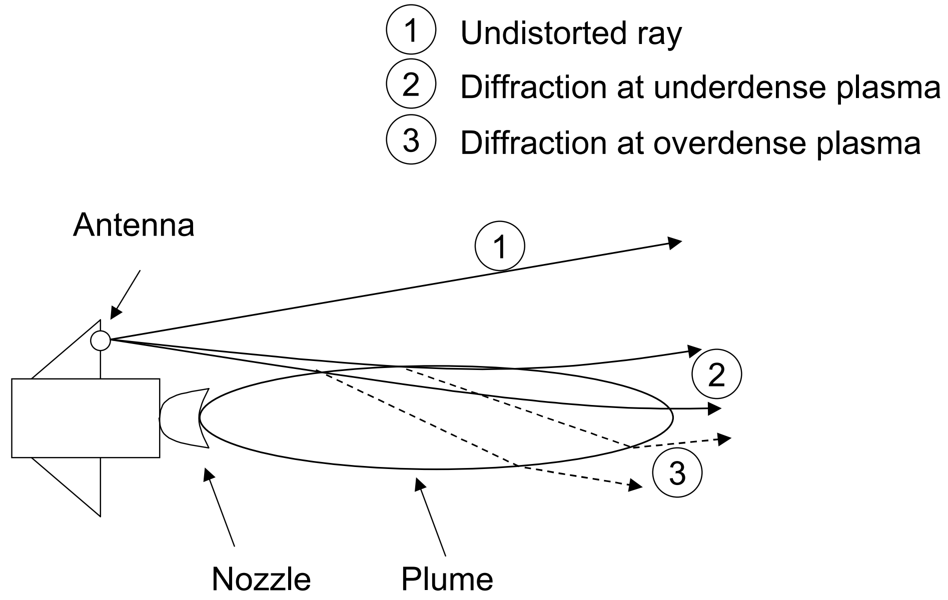


Figure 1. Antenna pattern in the wake of a missile with either an underdense or overdense plume.

per cubic centimeter) interfered severely with then applied 50 MHz radio guidance system.[15] In the 1950s to 1960s as missile development grew in the U.S. this problem was addressed by Balwanz.[16] He investigated the distortion of the antenna pattern of guided rockets from the effects of the plume (Figure 1).

This interaction between rocket plume and radio signals is due to thermal ionization of the main flame gas constituents and, in the case of composite propellants, due to thermoionic emission from either aluminum oxide and/or ionization of alkali metal impurities (Na, K, Cs) in the composite propellant. Flames possessing high electron densities may be considered as low temperature plasmas. The electrical properties of plasma may be described by the so-called plasma frequency $\omega_{p.}$

$$\omega_p = \sqrt{\left(\frac{4\pi e^2 n_e}{m_e}\right)} \tag{4}$$

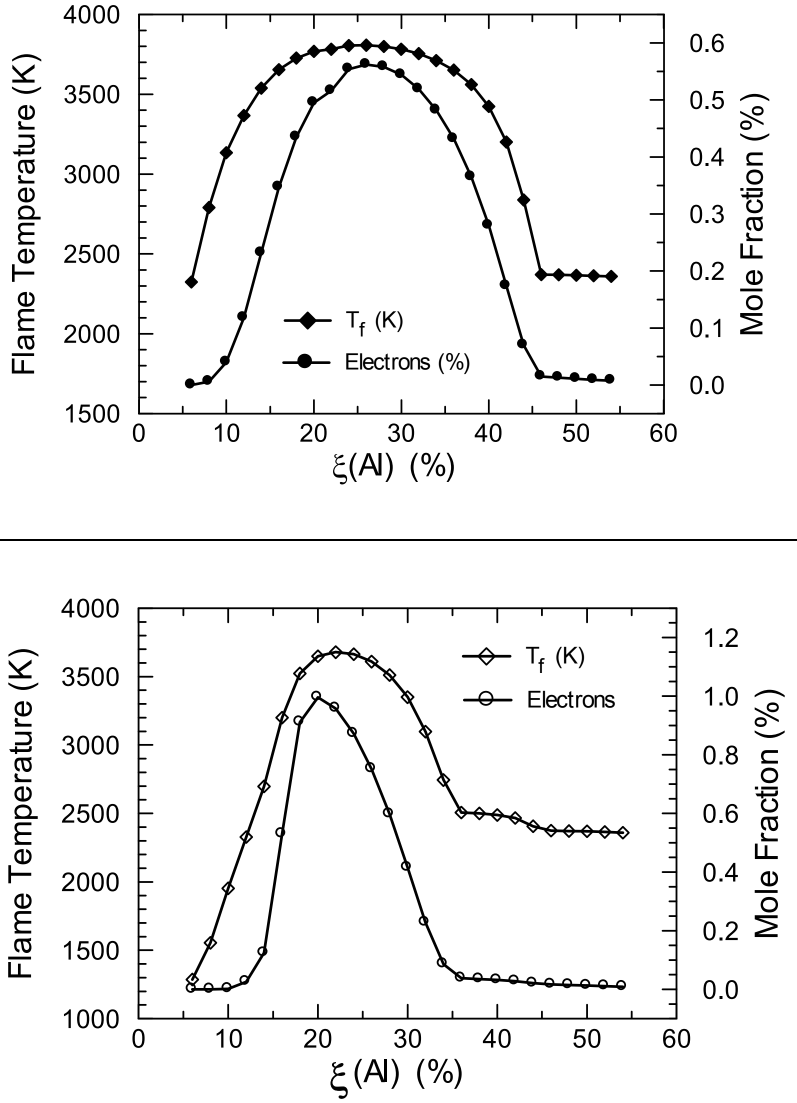
where e denotes the charge of the electron, n_e denotes the electron density and m_e denotes the mass of the electron.

In the interaction of an electromagnetic wave and plasma, if the plasma frequency ω_p is much larger than the angular frequency ν of the incident wave, the plasma may be considered a good reflector to the wave and is thus designated as "overdense" (Figure 1). As soon as this effect was recognized, it was studied primarily with the aim of finding ways of reducing it as has been done, for example, by Sukhia[17] who investigated the antenna pattern distortion of towed aerial targets by the burning of IR tracking flares.

The ease of ionization of the heavy alkali metals such as rubidium and cæsium in flames was envisioned as being useful for certain technical and military applications.

Shidlovsky as early as 1964 refers to the work of Fagg and Friedman producing cæsium plasma by combustion of cæsium perchlorate ($CsClO_4$)/aluminum (Al) mixtures.[18] Fagg also investigated $CsNO_3$/Al pyrotechnic mixtures for producing cæsium plasma in upper atmosphere electron diffusion studies.[19] In this work the electron density of both stoichiometric $CsClO_4$ and $CsNO_3$/Al plasmas was measured by determination of the half-widths of the 546.7, 550.4, 563.8 and 566.4 nm Cs lines and was compared to thermochemical calculations.

Figures 2a and 2b give the molar fraction of electrons and temperature in flames produced by $CsClO_4$/Al and $CsNO_3$/Al mixtures, calculated for a pressure of 0.1 MPa. Figures 3a and 3b give the respective values for the rubidium systems.



Figures 2a and 2b. The molar fraction of electrons as a function of ξ (Al) in $CsClO_4$/Al (upper) and $CsNO_3$/Al (lower) mixtures at 0.1 MPa pressure.[56]

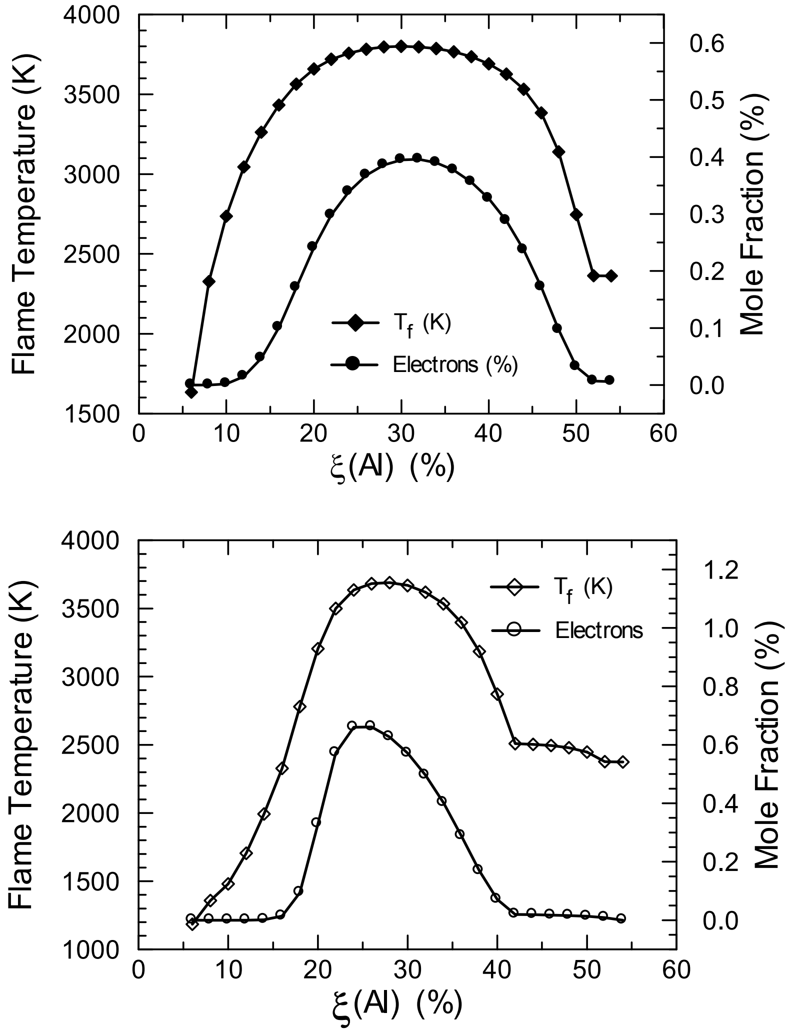
It can be seen that within a given chemical system that the electron fraction is mainly a function of the temperature of the system. The Saha-Eggert equation[20] [equation 5] gives the degree of ionization x_i of a given gaseous system.

$$\frac{x_I^2}{1-x_I^2} = 2\frac{Z_i}{Z_a}\left(\frac{2\pi m_e}{h^3}\right)^{\frac{3}{2}} \cdot \frac{E_I^{\frac{5}{2}}}{2p} \cdot \left(\frac{kT}{E_I}\right)^{\frac{5}{2}} \exp-\left(\frac{E_I}{kT}\right) \qquad (5)$$

In the case of alkali metals, the partition functions Z_i and Z_a for the ion and the atom are 1 and 2, respectively, thus simplifying the equation to give

$$\frac{x_i^2 P_M}{(1-x_i)} = \left(\frac{2\pi m_e}{h^2}\right)^{\frac{3}{2}} \cdot \left(kT\right)^{\frac{5}{2}} \exp-\left(\frac{E_i}{kT}\right) \qquad (6)$$

where h is Planck's constant [6.62608×10^{-34} J·s], E_I denotes the ionization energy of both Rb (4.177 eV) and Cs (3.894 eV), m_e denotes the mass of the electron [9.10939×10^{-31} kg], $P_M = p_a + p_i$, where p_a denotes the partial pressure of the atoms and where p_i denotes partial pressure of the ions, k denotes Boltzmann's constant



Figures 3a and 3b. The molar fraction of electrons as a function of ξ (Al) in $RbClO_4$/Al (upper) and $RbNO_3$/Al (lower) mixtures at 0.1 MPa pressure.[56]

$[1.38088 \times 10^{-23}\ J \cdot K^{-1}]$ and T denotes the absolute temperature of the system. Although T_f is higher for the $CsClO_4$/Al system (Figure 2a), the electron concentration is only about 50% of the $CsNO_3$/Al system (Figure 2b). This lower electron concentration is due to the formation of the Cl^- species, which scavenges the electrons in the case of the perchlorate system. In comparison, the rubidium systems, due to the higher ionization energy of Rb, yield lower electron concentrations but qualitatively show plots that are quite similar to the cæsium system.

Since cæsium plasmas have been considered as ideal working fluids for magnetohydrodynamic (MHD) electric power generation,[21] Flanagan[22] proposed to apply pyrotechnic compositions made of 65–75% dicæsium tetranitroethane $[(CsC(NO_2)_2)_2]$, 15–20% energetic binder (e.g., Glycidyl Azide Polymer (GAP)), 15–20% metallic fuels (e.g., zirconium (Zr)) and ~5% $CsNO_3$ to generate a cæsium-containing plasma yielding electron densities of up to 2.25×10^{16} $e^- \cdot cm^{-3}$. This composition looks quite similar to the system from Maček's older work[23] on energetics yielding high electron densities for seeding the upper atmosphere. Maček for this purpose applied stoichiometric compositions that were based on hexanitroethane ($C_2N_6O_{12}$), cæsium azide (CsN_3) and tetracyanoethylene

(C_6N_4). The equilibrium electron density was calculated as a function of $\xi(CsN_3)$ and was found to be maximum at the following stoichiometry:

$$5\ C_6N_4 + 3\ C_2N_6O_{12} + 2\ CsN_3$$

The composition was additionally investigated for thermal stability and was found to be stable when stored at a refrigerator temperature (+3 °C) and with exclusion of moisture. At ambient temperature and upon exposure to atmospheric moisture the composition would undergo rapid decomposition due to unstable hexanitroethane. Spontaneous ignition was found to occur between 100 and 110 °C. The stoichiometric mixture was calculated to burn at 3660 K. By the line-intensity-method, the combustion temperature was found be ~3520 K. The electron density was spectroscopically determined to be 6.5×10^{14} $e^{-} \cdot cm^{-3}$.

Similarly as in Maček's work, cæsium picrate ($CsO(C_6H_2N_3O_6)$) has been proposed as a monopropellant for MHD generators.[24]

Balwanz[25,26] investigated rocket exhaust plasmas based on combustion of stoichiometric $CsNO_3$/Al and KNO_3/Al with the aim of understanding radio diffraction effects at either 10, 23.5, 35 or 70 MHz in rocket motor plumes. He showed that the electron concentration in plumes generated by $CsNO_3$/Al payloads were depleted via electron attachment to aluminum oxide (Al_2O_3) particles, which is in accord with Maček's approach to exclude condensable species in a plasma generating mixture.

Another application using the ease of ionization of cæsium in pyrotechnic applications was given by Boettcher.[27] He proposed pyrotechnic compositions in the form of sheets that may be applied to the nose of missiles. Upon re-entry into the earth's atmosphere, these sheets would be ignited and would yield a high electron density. The sheets are composed of 19–38% cæsium chromate ($Cs_2Cr_2O_7$), 37–57% $CsNO_3$, 4–5% boron (B), 14–15% Al and ~5% binder. Other sheets in this invention comprise 50–82% $CsNO_3$, 14–47% Al, and 3–5% binder.

Chemical tracer experiments have been carried out recently to obtain insight into the distribution of rocket exhaust effluents in higher atmosphere regions from the standpoint of environmental chemistry.[28] Pyrotechnic payloads based on $CsNO_3$, Titanium (Ti) and B were used in these experiments. The chemicals in loose powder form were disseminated along the flight path of a missile. There again $CsNO_3$ served as both an oxidizer for Ti and B as well as an electron source.

For similar purposes, a pyrotechnic seeding pellet based on boron, nitrates, and magnesium aluminum alloy mixed with an unspecified cæsium source, was disclosed in reference 29. This pellet is supposed to be ejected in the wake of re-entering spacecraft to generate electrons for analytical purposes. In addition, the inventor claims this device also to be useful as a radar 'spoof' to decoy incoming radar-guided missiles.

As a combined distress signal Cornia[30] proposed a device to provide free electrons for detection by radar. This device employs a complex mixture of magnesium, ammonium perchlorate, cæsium nitrate, hexachlorobenzene, Viton and fluoroacrylic binder. Alternatively, cæsium perchlorate is proposed as a source of free electrons. The design of the device, which resembles a solid propellant rocket motor, provides oscillating combustion due to a pressure rise in the combustion chamber and the large pressure exponent of the composition. This in turn gives rise to a strobe-like behavior of the signals, which, in addition to the free electrons, provides smoke, and emissions in the visible and infrared region.[31]

Cohen[32] studied the velocity of ions present in plasma generated by a stoichiometric $CsNO_3$/Zr mixture ($3\ CsNO_3 + 2\ Zr$) ($T_f \sim 3300$ K) to provide insight into the electrical perturbations due to charge collection on the outside of spacecrafts. He found the ion velocity, mainly based on the Cs^{+}-ion, to be ~1148 $m \cdot s^{-1}$.

From Wilson's 1911 cloud chamber experiments, it is known that ions serve as condensation nuclei for aerosols. Today, ion-induced nucleation is investigated with the aim of understanding their mechanisms[33] as well as the environmental consequence (e.g., associated with release of easily ionizable material from nuclear power plants and nuclear reprocessing plants[34]). In view of this, Weber,[35] in 1982 developed a series of pyrotechnic smoke formulations based on either rubidium or cæsium compounds to be used in smoke pots, hand gre-

Table 3a. IR-Smoke Formulations with Rb and Cs Compounds.

Ingredient	1	1a	1b	2	2a	2b	3	3a	3b
NH_4ClO_4	34	31.48	31.48	—	—	—	—	—	—
ZnO	30	27.78	27.78	17.78	14.55	14.55	—	—	—
Polybutadiene	26	27.07	27.07	4.45	3.64	3.64	1.79	1.31	1.31
NH_4Cl	10	9.26	9.26	—	—	—	—	—	—
$CsNO_3$	—	7.41	—	—	18.18	—	—	26.32	—
$RbNO_3$	—	—	7.41	—	—	18.18	—	—	26.32
Al	—	—	—	6.67	5.46	5.46	13.39	9.87	9.87
Si	—	—	—	8.89	7.27	7.27	—	—	—
C_2Cl_6 (HC)	—	—	—	55.56	45.46	45.46	—	—	—
B	—	—	—	6.67	5.46	5.46	—	—	—
$P_{(red)}$	—	—	—	—	—	—	58.04	42.76	42.76
Fe_2O_3	—	—	—	—	—	—	13.39	9.87	9.87
Mg	—	—	—	—	—	—	13.39	9.87	9.87

nades, vehicle discharge grenades or projectiles. Weber succeeded in modifying a wide variety of existing visible smoke formulations to be used as effective screening agents in the thermal infrared (Tables 3a and 3b). The screening effectiveness of compositions was determined in field trials using three white plates heated to 40 °C. The plates where positioned in a row 10 m apart. The plates were observed with electro optical (EO) sensors at 0.6, 3.5 and 10.6 µm from a distance of 100 m. After determination of the undisturbed contrast value, the smoke charges were ignited ~50 m from both the plates and the EO equipment and the contrast was evaluated again. As a footnote to Table 3b, (++) refers to 95–100% change in contrast, (+) refers to 80–95% contrast change, (–) refers to 50–80% contrast change and (—) refers to change in contrast lower than 50%. In these smoke compositions, both Rb and Cs compounds become partially ionized and thus enhance the yield factor Y_f:

$$Y_f = \frac{m_s}{m_p} \tag{7}$$

where m_s is the mass of smoke and m_p is the mass of the device, by enhancing the number of nuclei formed from the smoke reaction, as has been confirmed by measurements at ERDEC.[36]

Table 3b. Performance of IR-Smoke Formulations.

Band	0.6 µm	3.5 µm	10 µm
1	+(*)	—	—
1a $CsNO_3$	++	+	+
1b $RbNO_3$	+	+	+
2	++	–	—
2a $CsNO_3$	++	++	++
2b $RbNO_3$	++	+	+
3	++	—	—
3a $CsNO_3$	++	++	++
3b $RbNO_3$	++	++	+

(*) for designation see text.

Today the author's company (DIEHL Munitionssysteme GmbH & Co KG) manufactures smoke ammunition based on $CsNO_3$, $P_{(red)}$ and Zr. In the case of red phosphorus ($P_{(red)}$) as an aerosol source, reactions in the smoke plume cause extremely intense broadband infrared emissions that are the result of exothermic acid-base processes between cæsium hydroxide (CsOH) and phosphoric acid (H_3PO_4).[37] These broadband emissions result in lowered contrast and thus improved screening in both the 3–5 and 8–14 µm regions.

b) Devices Applying Infrared Emission

The $6p^2P_{\frac{1}{2},\frac{3}{2}} \rightarrow 6s^2S_{\frac{1}{2}}$ transition in cæsium produces two intense but invisible lines in the near infrared [894.3 and 852.1 nm]. This has led to the application of cæsium compounds in

Table 4. Emission Lines from *M*NO_3/Mg Flares where *M* is Rb or Cs. [40]

$RbNO_3$ nm	Series	$CsNO_3$ nm	Series
421.5	Main	455.5	Main
564.8	I. minor	459.3	Main
572.4	I. minor	566.4	I. minor
620.6	I. minor	584.5	I. minor
629.8	I. minor	601.0	I. minor
728.0	II. minor	621.3	I. minor
740.8	II. minor	621.7	I. minor
780.0	Main	697.3	I. minor
794.7	Main	698.3	I. minor
		722.8	Bergmann
		728.0	Bergmann
		801.5	Bergmann
		807.9	Bergmann
		852.1	Main
		876.1	I. minor
		894.3	Main

pyrotechnic compositions to provide convenient sources of near-infrared radiation for night vision devices. Perhaps surprisingly, in view of the attempts discussed previously to use rubidium to make red flames, the deep red rubidium lines have also been investigated for this purpose.

Night vision devices are widely used as electro-optical equipment for surveillance, searching and tracking in the near infrared (NIR) region of the electromagnetic spectrum. Since these devices, when operated in a passive manner, require only a small number of photons from both the visible and the near infrared, additional illumination is required under certain conditions such as the new moon and clouded skies at night. Although conventional illuminating rounds would achieve enhancement of illumination in the NIR, military tactics require concealed illumination. Thus NIR-illuminating sources must not be detectable in the visible range.

Lohkamp[38,39] was the first to address the problem and to propose a “Black Nite Flare”, which combines both requirements such as illumination in the NIR as well as only slight emission in the visible. Lohkamp advises the use of flares based on either $CsNO_3$ or $RbNO_3$, hexamine, silicon and epoxy binder. This invention applies the strong emission behavior of both alkali metals in the NIR as has been measured by Douda.[40] Douda observed intense emission bands for $CsNO_3$ and $RbNO_3$ compositions ($\xi(Mg) = 45\%$ and 5% binder) as given in Table 4.

While yielding only 65 cd output in the visible range, Lohkamp’s compositions (see Table 5) provide 14 $W \cdot sr^{-1}$ of radiation in the 0.7 to 1.0-µm range with a 40 mm cartridge flare.

Table 5. IR Compositions Based on KNO_3, $RbNO_3$ or $CsNO_3$. [38]

Ingredient	1	2	3
KNO_3	70	—	—
$RbNO_3$	—	60.8	—
$CsNO_3$	—	—	78.7
Si	10	10	16.3
$C_6H_{12}N_4$	16	23.2	—
Epoxy binder	4	6	5
λ_{max} [nm]	760	790	800–900

Based on this knowledge, Nielson and Dillehay of Thiokol, improved these formulations, proposing either $CsNO_3/KNO_3$ blends[41] and $CsNO_3$/ammonium nitrate (NH_4NO_3) or $RbNO_3/NH_4NO_3$ blends.[42] In addition, in recent years much work has been done by Nielson in adaptation of these compositions to varying manufacturing processes such as casting[43] and pressing.[44]

Similar to these applications are small arms tracers, which can be tracked in the NIR with a suitable enhanced night vision device for special operations. Although NIR tracer compositions are known to use barium peroxide (BaO_2) as the oxidizer, because the gaseous combustion product barium oxide (BaO) provides intense emissions in the 800 to 900 nm range,[45] Nielson proposes the use of blends of both $CsNO_3$ and BaO_2 together with fuels such as boron and silicon with vinyl acetate-alcohol resins as non-sooting binders.[46] In addition, both the rubidium and cæsium salts of bitetrazole amines (BTA) are proposed as burn rate modifiers in these compositions. Unfortunately no information on performance is given.

Another application of both $CsNO_3$ and $RbNO_3$ to improve concealment in military applications is their use as muzzle flash suppressants as has been stated in reference 47a.

Similarly Vanpee[48] has investigated the inhibition of afterburning in rocket exhaust plumes by cæsium carbonate (Cs_2CO_3) and rubidium carbonate (Rb_2CO_3). Vanpee assumed that this inhibition is greatly dependent on the intermediate formation of the gaseous hydroxide of the respective metals in the combustion zone, which may suppress visible oxidative reactions via radical scavenging.

c) Miscellaneous Uses and Work

Aside from the above applications making use of inherent features of both cæsium and rubidium such as infrared emission and ionization, a series of other unspecific applications of both metals in pyrotechnics have been reported.

Spector[49] advises the use of cæsium nitrate among other oxidizers together with unspecified fuels in a "non-toxic smoke generator". Since the primary combustion products in this case are fed through a scrubber filled with unspecified coolant liquid, the ions, which contribute to the smoke performance in Weber's invention, may not account for the principle given here.

Burkardt[50] has proposed pyrotechnically generated nuclei based on mixed alkali-transition metal iodides as ice-forming agent for weather modification. He proposes compositions based on silver iodate ($AgIO_3$)/$M$$IO_3$/$NH_4NO_3$ and plasticized nitrocellulose (NC) where M = Li, Na, K, Rb, or Cs with stoichiometries of (5–15% /0.1–30%/5–45%/50–55%). Interestingly, Rb-based compositions provide higher nuclei yield than Cs-based compositions, the latter being even worse than pure silver iodide-based compositions. Contrary to Weber's findings mentioned above, the nucleus formation in this invention does not relate to ionization. The active species in causing ice formation are the microscopically dispersed complex iodides formed upon combustion.

In reference 47b, the $CsClO_4$/Al compositions are described as being suitable for incendiary payloads. In view of the flame temperatures in Figure 2a this is quite feasible but would make incendiaries much more expensive compared to those based on less expensive potassium perchlorate.

An application based on solid-state effects is mentioned in reference 51. According to this, $CsNO_3$ should be an effective phase stabilizer for ammonium nitrate, which is known to undergo phase changes at –170, –16, 32.1, 84.2 and 125.2 °C.

In addition, $CsNO_3$ and $RbNO_3$ are known to provide a series of low-melting eutectics with some alkali nitrates. $RbNO_3$ forms a double salt with $LiNO_3$. The eutectic mixture, which is 35 mol-% $RbNO_3$ + 65 mol-% $LiNO_3 \cdot RbNO_3$, melts at 179.5 °C. With $NaNO_3$, the eutectic mixture (178.5 °C) is found at 55 mol-% $RbNO_3$. With KNO_3, the eutectic mixture (291 °C) is found at 70 mol-% $RbNO_3$. The eutectic mixture of $CsNO_3$/$LiNO_3$ is at 43 mol-% $CsNO_3$ and melts at 174 °C. With KNO_3, the eutectic mixture (200 °C) is found between 50 and 67 mol-% $CsNO_3$. All information is from references 5 and 8.

Dodecahydrododecaborate methanolate $Cs_2(B_{12}H_{12} \cdot CH_3OH)$ has been described as an additive to propellants and pyrotechnics to enhance ignition and burning rate.[52] In addition, $Cs_2(B_{12}H_{12} \cdot CH_3OH)$ is proposed as fuel for a gas generant composition.[53]

Recently Berger[54] investigated $CsClO_4$/Ti compositions as possible sources for near infrared radiation. Although $CsClO_4$ compositions, as mentioned above, would certainly give rise to cæsium chloride (CsCl) formation which exclusively radiates in the UV,[9b] titanium might serve as a chlorine scavenger due to the higher bond dissociation energy of titanium chloride (TiCl) (494 $kJ \cdot mol^{-1}$) compared to CsCl (448 $kJ \cdot mol^{-1}$) as has been discussed recently for the lithium perchlorate ($LiClO_4$)/Al system.[55] Because the authors did not present thermochemical calculation on the investigated stoichiometries, this has now been done in Figure 4 for adiabatic flame temperature, electron, cæsium, and cæsium chloride concentrations.[56]

Since there is no advantage of the $CsClO_4$/Ti compositions over existing "concealed" NIR payloads because of the intense visible emission of TiO as has been shown in reference 57,

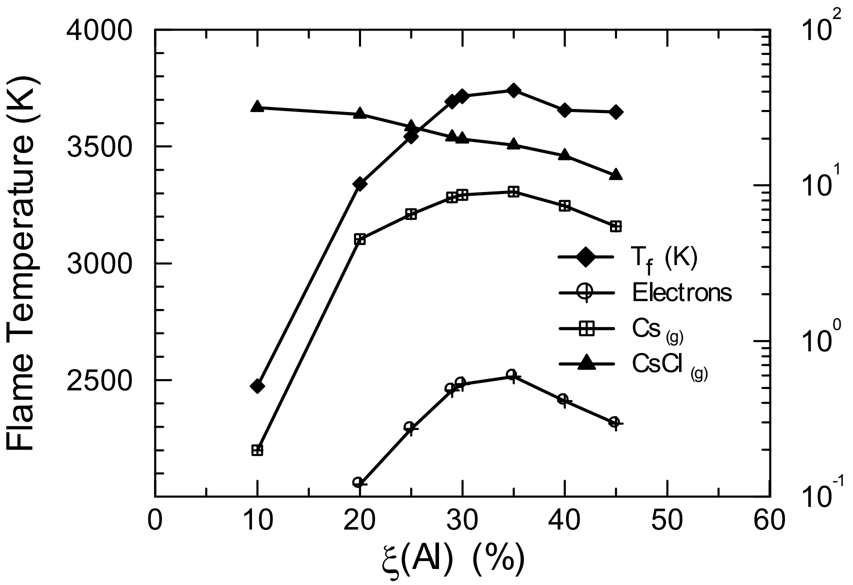


Figure 4. Molar fraction of electrons, Cs and CsCl as function of ξ(Ti) in $CsClO_4$/Ti at 0.1 MPa.

it seems that these payloads may be more suitable for tracking flares in either surface-to-air or anti-tank missiles.

Berger's work also provides details of the combustion mechanism, burn rate and heat of combustion as well as safety information on the $CsClO_4$/Ti mixtures. It was observed by differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TGA) measurements that $CsClO_4$ forms an eutectic mixture with the primary decomposition product CsCl at ~400–500 °C wherein oxidation of the solid Ti particles occurs. The burn rate u increases almost linearly between ξ(Ti) 20 and 60% from 3 to 127 $cm \cdot s^{-1}$, whereas the highest heat of combustion (5080 $J \cdot g^{-1}$) is attained at ξ(Ti) of 40%. The highest sensitivity towards electrostatic discharges occurs at ξ(Ti) > 40% with ignition energy values ranging from 0.56 to 1 mJ. Sensitivity towards friction is highest at ξ(Ti) = 20% (19 J) and maximum friction sensitivity is found between ξ(Ti) = 35–50% (120 N) according to BAM procedures.

The spectra of several $CsNO_3$ and $RbNO_3$ / magnesium compositions in both the visible and NIR have been investigated by Douda.[40] Douda[58] also tested the effect of minor amounts of both $RbNO_3$ and $CsNO_3$ on the spectral performance of lithium nitrate ($LiNO_3$)/Mg flare compositions.

Thermochemical Properties of Rb and Cs Compounds

To conclude this review, the following reliable data on the nitrate and perchlorate of Rb and Cs are summarized in Table 6. For comparison, values for the potassium salts are also included. In general, reaction mechanisms of the nitrates and perchlorates of Rb and Cs are identical to those of the corresponding potassium salt.

The thermochemical behavior of both Rb and Cs dinitramide (M-$N(NO_2)_2$) compounds, which in general can be seen as high density oxidizers, has been studied in detail by Cliff.[64,65] He could show, that the decomposition of the dinitramide salts occurs via metal nitrate and dinitrogen oxide formation according to equation 8.

$$M - N(NO_2)_2 \xrightarrow{\Delta} M\,NO_3 + N_2O \qquad (8)$$

which is valid where M is Na, K, Rb, or Cs.

Table 6. Properties of K, Rb and Cs Nitrates and Perchlorates.

Parameter	Unit	KNO_3	$RbNO_3$	$CsNO_3$	$KClO_4$	$RbClO_4$	$CsClO_4$
CAS-Nr.		7757-79-1	13126-12-0	7789-18-6	7778-74-7	13510-42-4	13454-84-7
m_r	$g{\cdot}mol^{-1}$	101.103	147.473	194.91	138.549	184.918	232.356
mp	°C	333[62]	310[62]	414[62]	580[60]	597[60]	577[60]
crystal density	$g{\cdot}cm^{-3}$	2.109	3.11	3.685	2.52	2.8	3.327
phase transition	°C	128[61]	167[63]	160[61]	299[59]	280[59]	222[59]
type		rh→tg(#)	tg→c(*CsCl*)	h→c	rh→c	rh→c	rh→c
phase transition	°C	–	188[63]	–	–	–	–
type		–	*C(CsCl)*→h	–	–	–	–
phase transition	°C	–	278[63]	–	–	–	–
type		–	h→c(*NaCl*)	–	–	–	–
dec.p (*)	°C	533[62]	548[62]	584[62]	580[60]	597[60]	577[60]
ΔH_f^{298}	$kJ{\cdot}mol^{-1}$	494.63	495.05	505.97	432.79	437.19	434.72
Oxygen content	wt-%	39.56	27.12	20.52	46.19	34.61	27.54
Price index	KNO_3=1 ~0.5 $/kg	1	~4000	70	5	~3000	150

(*) dec.p designates the temperature at which $p(O_2)$ over the molten salt equals 0.1 MPa.

(#) crystal lattices designations: rh = rhombic, tg = trigonal, c = cubic, CsCl, NaCl, h = hexagonal.

References

1) B. E. Douda, “Theory of Colored Flame Production”, RDTN No. 71 (1964), U.S. Naval Ammunition Depot Crane, IN, USA, p 28.

2) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing Company Inc., New York (1968) p 97.

3) L. F. Trueb, “Die Chemischen Elemente”, S. Hirzel Verlag Stuttgart, Leipzig, 1996 [a]pp 52–53; [b] p 53.

4) R. C. Weast (Ed.) *Handbook of Chemistry and Physics*, 47th ed. The Chemical Rubber Company, Cleveland (1966–1967) p D-59.

5) *Gmelins Handbuch der Anorganischen Chemie*, “Cæsium”, Lieferung 1, System-Nr. 25, Verlag Chemie, Weinheim (1972) [a] pp 50–53; [b] Lieferung 2, p 216.

6) R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, John Wiley & Sons, Inc., New York, London, Sydney (1965) p 371.

7) D. A. Skoog and J. J. Leary, *Instrumentelle Analytik*, Springer Verlag, Berlin, Heidelberg, New York (1996) pp 220–221.

8) *Gmelins Handbuch der Anorganischen Chemie*, “Rubidium”, Lieferung 1, System-Nr. 24, Verlag Chemie, Weinheim (1972) [a] pp 55–65; [b] p 216.

9) G. W. Weingart, *Pyrotechnics*, 2nd ed. (1947) p 187.

10) C. Jennings-White, “Some Esoteric Firework Materials”, *Pyrotechnica, No. XIII* (1990) pp 26–32.

11) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 4th ed., Chapman and Hall, London (1976) [a] p 290; [b] p 146.

12) M. Hiskey, “Comment on “High-Nitrogen Pyrotechnic Compositions”, *Journal of Pyrotechnics*, No. 8 (1998) pp 29–30.

13) C. Jennings-White, “Glitter Chemistry”, *Journal of Pyrotechnics*, No. 8 (1998) pp 53–70.

14) L. S. Oglesby, *Glitter; Chemistry and Techniques*, 2nd ed. American Fireworks News (1989).

15) W. Dornberger, *Peenemünde*, Moewig Taschenbuchverlag Rastatt (1984) p 140.

16) J. Lawton and F. J. Weinberg, *Electrical Aspects of Combustion*, Clarendon Press Oxford (1969) p 283 Lit 71.

17) D. E. Sukhia, "Interaction of Pyrotechnics and Radio Frequency systems", *Proc. 2nd International Pyrotechnics Seminar*, Aspen, CO, USA, (1970) pp 255–267.

18) A. A. Shidlovsky, *Fundamentals of Pyrotechnics* (1964) p 360.

19) L. W. Fagg, "Spectrographic Study of Chemically Generated Cæsium Plasmas", *J. Quant. Spectrosc. Radiat. Transfer.*, Vol. 5 (1965) pp 321–327.

20) P. W. J. M. Boumans, *Theory of Spectrochemical Excitation*, Plenum Press, New York (1966) pp 160–173.

21) C. T. Williams, "Cæsium and Cæsium Compounds" in Volume 5 of *Kirk-Othmer Encyclopedia on Chemical Technology*, 3rd ed. (1979) pp 327–338.

22) J. E. Flanagan, US Patent 4,269,637, Rockwell International Corporation, USA (1981).

23) R. Friedman and A. Maček, "A Novel Chemical System for Generation of Electron-Rich Gases", *Proc. of 10th Int. Symp. Combust.*, The Combustion Institute (1965) pp 731–741.

24) J. S. Malcolm Jr., "Fundamental Research in Explosive Magnetohydrodynamics", *AFOSR TR-76-0435*, Jones (Malcolm) Associates, Inc., CA, USA (1976).

25) K. Baldwin and W.W. Balwanz, "Plasma Diagnostics in Supersonic Flow Containing Cæsium and Potassium", *Trans. Nucl. Sci.*, Vol. 11 (1964) pp 51–63.

26) W. W. Balwanz, "Ionization in Rocket Exhausts", *Proc. of 10th Int. Symp. Combust.*, The Combustion Institute. (1965) pp 685–697.

27) W. Boettcher, E. Goldman, and A. Gallaghan, US Patent 4,406,228, The United States as represented by the Secretary of the Navy, USA (1983).

28) EA-0786; Environmental Assessment and (FONSI) Kauai Test Facility CDX Rocket Operation Sandia National Laboratories Albuquerque, NM, USA, http://nepa.eh.doe.gov/ea/ea0786/

29) S. Altschuler, F. T. Traylor, R. W. Ziemer, and C. A. Knight, US Patent 3,976,008, The United States as represented by the Secretary of the Navy, USA (1976).

30) R. P. Cornia and R. Reed Jr., US Patent 3,983,816, Thiokol Corporation, USA (1976).

31) E.-C. Koch, "Review on Pyrotechnic Aerial Infrared Decoys", *Propellants, Explosives, Pyrotechnics*, Vol. 26 (2001) pp 3–11.

32) D. L. Cohen, "Using Electrical Probes to Measure Ion Velocities in Pyrotechnic Plasmas", *J. Spacecraft*, Vol. 25 (1988) pp 315–317.

33) A. Matuszkiewicz, "Kinetics of Ion Induced Nucleation", in P. E. Wagner and G. Vali (Eds.) "Atmospheric Aerosols and Nucleation" Volume 309 of *Lecture Notes in Physics*, Springer Verlag, Berlin, Heidelberg, New York (1988) pp 422–425.

34) K. G. Vohra, "Gas-to-Particle Conversion in the Atmospheric Environment by Radiation-induced and Photochemical Reactions", in *Proc. of 5th Int. Congress on Radiation Research*, Seattle, June 1974, New York (1975).

35) M. Weber, DE 32 38 444, Pyrotechnische Fabrik F. Feistel GmbH&Co KG, Göllheim, Germany (1982).

36) H. Schroers, W. Rouse, and D. Anderson, "Evaluation of Piepenbrock IR Pyrotechnic Smoke", *ERDEC-TN-019*, April 1997, Aberdeen Proving Ground, MD, USA (1997).

37) E.-C. Koch and J. Schneider, "Reactions in Phosphorus Based IR-Screening Smoke—An Investigation of the Underlying

Phenomena", *Proceedings of the Smoke and Obscurants Symposium XX*, 29–30 April 1998, Aberdeen Proving Ground, MD, USA (1999).

38) C. W. Lohkamp, "Black Nite Flare", *Proc. 5th International Pyrotechnics Seminar*, Vail, CO, USA (1976) pp 307–315.

39) C. W. Lohkamp, US Patent 3,733,223, The United States as represented by the Secretary of the Navy, USA (1973).

40) B. E. Douda, R. M. Blunt, and E. J. Bair, "Visible Radiation from Illuminating-Flare Flames: Strong Emission Features", *J. Opt. Soc. Am.*, Vol. 60 (1970) pp 1116–1119.

41) D. B. Nielson and L. L. Jones, EP 0 430 464 A2, Thiokol Corporation, Ogden, UT, USA (1989).

42) D. R. Dillehay and D. W. Turner, EP 0 652 277 A2, Thiokol Corporation, Ogden, UT, USA (1993).

43) D. B. Nielson, WO 94/02435, Thiokol Corporation, Ogden, UT, USA (1994)

44) D. B. Nielson, WO 94/02436, Thiokol Corporation, Ogden, UT, USA (1994)

45) G. H. Henry III, M. A. Owens, J. L. Terry, M. A. Tucker, and F. M. Bone, US Patent 5,811,724, Primex Technologies, Inc. Marion, IN USA (1998).

46) D. B. Nielson, US Patent 5,639,984, Thiokol Corporation, Ogden, UT, USA (1997).

47) *Encyclopedia of Explosives and Related Items*, B. T. Fedoroff and O. E. Sheffield (Eds.), Picatinny Arsenal, Dover NJ, USA (1962) [a] Vol. 2, p C 145; [b] Vol. 8, p P 155.

48) M. Vanpee, R. H. Thomas, and D. Burgess, "Inhibition of Afterburning by Metal Compounds", in "Heterogeneous Combustion", H. G. Wolfhard, I. Glassman, and L. Green, Jr. (Eds.), Volume 15 of *Progress in Astronautics and Aeronautics*, Academic Press, New York, London (1964) pp 419–448.

49) Y. Spector, E. Jacobson, V. Naishtut, M. Vittenberg, and Z. Beinert, US Patent 5,610,359, Israel (1994).

50) L. A. Burkardt, W. G. Finnegan, F. K. Odengrantz, P. St.Amand, and C. D. Stanifer, US Patent 3,802,971, The United States of America as represented by the Secretary of the Navy, USA (1974).

51) K. Menke, J. Bohnlein-Mauss, H. Schmidt, K. M. Bucerius, and W. Engel, US Patent 5,596,168, Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V. München, Germany (1995).

52) Callery Chemical Company, *MSDS of Cæsium dodecahydrododecaborate methanolate* ($Cs_2B_{12}H_{12}{\cdot}MeOH$), August 4, 2000.

53) D. W. Doll, I. A. Wallace, G. K. Lund, J. C. Hinshaw, and R. J. Blau, WO 95/18779, Thiokol Corporation, Washington, USA (1995).

54) B. Berger, P. Folly, G. Wilfing, and R. Kresse, "Neuer Oxidator für spezielle pyrotechnische Anwendungen", *Proc. of 32nd International Annual Conference of ICT*, July 3–6, 2001, Karlsruhe, Germany (2001).

55) Part 1 of this series appeared as: E.-C. Koch, "Evaluation of Lithium Compounds as Color Agents for Pyrotechnic Flames", *Journal of Pyrotechnics*, No. 13 (2001) pp 1–8.

56) B. J. McBride and S. Gordon, *"Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications"*, *NASA 1311*, June 2000.

57) E. Roth, Y. Plitzko, V. Weiser, W. Eckl, H. Poth, and M. Klemenz, "Emissionsspektren brennender Metalle", *Proc. of 32nd International Annual Conference of ICT*, July 3–6, 2001, Karlsruhe, Germany (2001).

58) B. E. Douda, "Prediction of Line Shapes in Pyrotechnic Flares Containing Lithium", *Proc. 5th International Pyrotechnics Seminar*, Vail, CO, USA (1976) pp 212–222.

59) K. Rajeshwar, V. R. P. Verneker, and J. Dubow, "A Differential Scanning Calorimetry Study of the $MClO_4$ (M = Na, K, Rb, Cs, and NH_4) System: Heats of Crystal-Structure Transformations and other Thermochemical Data", *Combustion and Flame*, Vol. 37 (1980) pp 251–260.

60) M. M. Markowitz and D. A. Boryta, "The Differential Thermal Analysis of Perchlorates. VII. Catalytic Decompositions of the Alkali Metal Perchlorates by Manganese Dioxide", *J. Phys. Chem.*, Vol. 69 (1965) pp 1114–1123.

61) S. Gordon and C. Campbell, "Differential Thermal Analysis of Inorganic Compounds—Nitrates and Perchlorates of the Alkali and Alkaline Earth Groups and Their Subgroups", *J. Anal. Chem.*, Vol 27 (1955) pp 1102–1109.

62) A. F. Hollemann, E. Wiberg and N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101. Auflage, Walter de Gruyter, Berlin, New York (1995) pp 718–719.

63) C. N. R. Rao and J. Gopalakrishnan, *New Directions in Solid State Chemistry*, 2nd ed., Cambridge University Press, Cambridge (1997) p170.

64) M. D. Cliff and M. W. Smith, "Thermal Characteristics of Alkali Metal Dinitramide Salts", *Journal of Energetic Materials*, Vol. 17 (1999) pp 69–86.

65) M. D. Cliff, W. W. Smith, and D. P. Edwards, "Evidence of Nitrate Formation from the Thermal Decay of Alkali Metal Dinitramides", *Propellants, Explosives, Pyrotechnics*, Vol. 24 (1999) pp 43–45.

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An Introduction to Chemical Thermodynamics
Part 3. Free Energy and Equilibrium

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ABSTRACT

This is the third article in a series presenting an introduction to chemical thermodynamics, emphasizing those aspects of particular relevance to pyrotechnics. It shows how the Gibbs free energy varies with temperature and pressure, and how this affects chemical equilibrium. It also shows how a number of useful facts about chemical systems can be predicted from the thermodynamic properties of the reactants and possible products. This is illustrated with examples from pyrotechnics.

Keywords: thermodynamics, free energy, equilibrium constant, thermodynamic modeling

Introduction

The previous article in this series[1] introduced the Gibbs free energy, G, defined by

$$G = H - TS$$

where H is the enthalpy, T is the temperature and S is the entropy. It was shown that the change in the free energy, ΔG,

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

is a measure of the change in the entropy of the universe. If ΔG is negative, the entropy of the universe will increase and the process will be thermodynamically spontaneous. In this article, the relationships between free energy and equilibrium will be explained, and the application of these concepts to pyrotechnic systems will be illustrated with some examples from the literature.

The Standard Free Energy of Formation

All pure substances have a Standard Free Energy of Formation, ΔG_f^o. This is the free energy change when 1 mole of the compound is formed from its elements at some standard state, often a temperature of 298.15 K and a pressure of 1 bar. The bar is a unit of pressure (10^5 newtons per square metre) that is conveniently close to atmospheric pressure (standard atmospheric pressure is 1.013×10^5 newtons per square metre). The free energy of formation of the chemical elements at standard conditions is by definition zero; values for the free energies of formation of many compounds are available in tables of thermodynamic data. Standard free energy changes can be added and subtracted just like enthalpy changes, as described in the first article in this series.[2]

For a chemical reaction

$$w\,\mathrm{A} + x\,\mathrm{B} \rightarrow y\,\mathrm{C} + z\,\mathrm{D}$$

the standard free energy change $\Delta G°$ associated with the reaction is given by

$$\Delta G° = \left[y\Delta G_{f\,C}^{o} + zG_{f\,D}^{o} \right] - \left[wG_{f\,A}^{o} + xG_{f\,B}^{o} \right]$$

where $G_{f\,A}^{o}$ is the Standard Free Energy of Formation of the species A, etc.

Like the enthalpy and the entropy, the Gibbs free energy is an *extensive* function; that is, it varies depending on the amount of substance in a system. The Gibbs free energy of formation of *1 mole* of a substance is called the *molar free energy* of that substance. If a number of different substances are introduced into a system, with no chemical reactions, the total free energy change can be calculated by multiplying the number of moles of each substance by its molar free energy and adding up the results. To reach chemical and thermodynamic equilibrium, substances undergo chemical reactions until the free energy is at a minimum. The reason for this, as discussed in the previous article in this series,[2] is that minimizing the free energy in a system is the same as maximizing the entropy of the system and its surroundings.

Variation of the Gibbs Free Energy with Pressure, Temperature and Volume

Tabulated values of the molar free energy of various substances at specified conditions of temperature and pressure can be used to calculate the free energy changes involved in chemical reactions. To do this, it is necessary to know how free energy varies with temperature, pressure and volume.

By definition

$$G = H - TS$$

and

$$H = U + PV$$

Therefore

$$G = U + PV - TS$$

where U is the internal energy and V is the volume.

For the purposes of this discussion it can be assumed that the only work done by, or on, the system is the work involved in changing the volume of the system in response to pressure, or vice versa. That is, the only work to be taken into account is "pressure-volume" or "expansion" work. Electrochemical effects, for instance, are not considered. For very small (i.e., differential) changes in internal energy, pressure, volume, temperature and entropy, the corresponding change in Gibbs free energy is

$$dG = dU + PdV + VdP - TdS - SdT$$

But for a closed system, doing only "expansion" work,

$$dU = TdS - PdV$$

and these terms drop out of the equation, so

$$dG = VdP - SdT$$

At constant temperature, $dT = 0$, and consequently $dG = VdP$. At constant pressure, $dP = 0$, so $dG = - SdT$.

Variation of Gibbs Free Energy with Pressure, at Constant Temperature

At constant temperature

$$dG = VdP$$

and by integration

$$\Delta G = G_2 - G_1 = \int_1^2 V dP$$

For a perfect gas,

$$V = \frac{nRT}{P}$$

and for n moles at a constant temperature nRT is constant. For a pressure change from P_1 to P_2,

$$\Delta G = G_2 - G_1 = \int_1^2 \left(\frac{nRT}{P}\right) dP$$

$$= nRT \int_1^2 \frac{dP}{P} = nRT \ln\left(\frac{P_2}{P_1}\right)$$

This gives the change in Gibbs free energy with pressure at constant temperature for a perfect gas.

For 1 mole of gas at standard temperature and pressure, $G_1 = G°$, so the molar free energy G at some other pressure P is given by

$$G = G° + RT \ln\left(\frac{P}{P°}\right)$$

where $G°$ is the free energy of one mole of the gas at standard conditions of temperature and pressure ($P°$).

What about a liquid or solid? As previously,

$$dG = VdP$$

and by integration

$$\Delta G = G_2 - G_1 = \int_1^2 V dP$$

In the pressure ranges of interest to pyrotechnics, the volume of a liquid or solid changes very little with pressure. The volume can usually be treated as constant, and in this case

$$\Delta G = V\Delta P$$

This equation applies only for pressure ranges over which the substance can be considered incompressible.

The change in free energy with pressure for one mole of a solid or liquid is very much smaller than that for one mole of a gas, and it can usually be ignored. For example, suppose the pressure of one mole of a substance is increased from 1 to 10 atmospheres, at room temperature (298 K). If the substance is a gas, the free energy change is given by

$$\begin{aligned}\Delta G &= nRT\ln\left(\frac{P_2}{P_1}\right)\\ &= 1\text{ mole}\times 8.3145\text{ joules/K/mole}\times\\ &\qquad 298\text{ K}\times\ln(10/1)\\ &= 8.3145\times 298\times\ln 10\text{ joules}\\ &= 5705.2\text{ joules}\\ &= 5.71\text{ kJ (3 significant figures)}\end{aligned}$$

On the other hand, taking water as an example of a liquid, the volume of one mole of water (18 grams) is around 18 cubic centimetres or 1.8×10^{-5} cubic metres. For a change in pressure from 1 to 10 atmospheres, the free energy change is

$$\begin{aligned}\Delta G &= V\Delta P\\ &= 1.8\times10^{-5}\text{cubic metres}\times 9\text{ atmospheres}\times\\ &\quad 1.013\times10^{5}\text{newtons/sq. metre/atmosphere}\\ &= 16.4\text{ newton meters}\\ &= 16.4\text{ joules}\\ &= 0.016\text{ kJ (2 significant figures)}\end{aligned}$$

This is a bit less than 0.3% of the free energy change that the same pressure change would bring about in the same quantity of gas.

Variation of Gibbs Free Energy with Temperature, at Constant Pressure

At constant pressure

$$dG = -SdT$$

and so

$$\frac{dG}{dT} = -S$$

This is only true for constant pressure; to emphasize this, it is customary to write it in the form

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

where the symbol ∂ indicates partial differentiation and that the variable indicated by the subscript P (i.e., the pressure) must be held constant.

This simple equation is one version of the Gibbs-Helmholtz equation. There is another version that can be derived with the help of the differential calculus.

By definition,

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial T}\right)_P T - G = -H$$

Divide this equation by T^2

$$\frac{\left(\frac{\partial G}{\partial T}\right)_P}{T} - \frac{G}{T^2} = \frac{H}{T^2}$$

It can be shown that

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{\left(\frac{\partial G}{\partial T}\right)_P}{T} - \frac{G}{T^2}$$

The right hand side of this equation is the same as the left-hand side of the previous equation, therefore

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{H}{T^2}$$

This is the other form of the Gibbs-Helmholtz equation. Notice that it shows how *G/T* (rather than *G*) varies with temperature at constant pressure. Another variation of this equation is

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = \frac{\Delta H}{T^2}$$

Variation of Gibbs Free Energy with Chemical Composition, at Constant Temperature and Pressure

The free energy of a reacting mixture will change with pressure and temperature, and it will also change as the amount of each substance in the mixture changes. For a very small change in the number of moles of a substance in a mixture at constant temperature and pressure there will be a corresponding free energy change. The ratio of these changes, given by the partial derivative,

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \mu_i$$

is called the *chemical potential* of the substance *i*. The chemical potential is usually given the symbol μ (mu, the Greek equivalent of the letter 'm'). It follows that *the chemical potential of a pure substance is numerically equal to the molar free energy of that substance*. The chemical potential of a substance has units of joules per mole. It is an *intensive* quantity – that is, it does not depend on the amount of substance.

In reaching equilibrium, systems move from conditions of high chemical potential to the lowest possible chemical potential. This is a bit like the tendency of objects in a gravitational field to move from a position of high potential energy to one of low potential energy, or of electric currents to flow from a high electrical potential to a low one. The reason for the movement from a state of high chemical potential to one of low chemical potential is simply that such a movement corresponds to an increase in the total entropy of the system and its surroundings. In other words, it is nothing more (or less) than the natural tendency of molecules to get into a mess.

If *n* moles of a substance of chemical potential μ are added to a system, the change in Gibbs free energy is given by

$$\Delta G = n\mu$$

More generally, if substances *a, b, c…* are added to a system, the change in Gibbs free energy is given by

$$\begin{aligned}\Delta G &= n_a\mu_a + n_b\mu_b + n_c\mu_c \ ... \\ &= \Sigma n_i\mu_i\end{aligned}$$

where n_i is the number of moles of substance *i,* and μ_i is the chemical potential of substance *i*

Free Energy Changes and Chemical Reactions: Effect of Temperature

Recall that a process will be spontaneous (will continue to equilibrium once it has been started) if its Gibbs free energy change is negative. The equation for the Gibbs free energy change

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

leads to some useful generalizations about chemical reactions. For example, if the entropy change is positive, there will *always* be a temperature at which $T\Delta S$ becomes greater than ΔH. Processes for which the entropy change is positive are those in which the molecular disorder increases. These include the melting of solids, the evaporation of liquids, and the decomposition of complex molecules into simpler ones and ultimately into atoms. The equation for the Gibbs free energy change indicates that as a solid is heated it will eventually melt, if it does not decompose first, and that a liquid will evaporate. Moreover, at a sufficiently high temperature every substance will be decomposed into its constituent atoms.

The temperature required to do this is around 5000 Kelvin. While such temperatures are routinely achieved in the plasma torches commonly used for spectrochemical analysis, they are well above all pyrotechnic temperatures.

Free Energy Changes and Phase Changes: Freezing and Melting of Solids

If the enthalpy change (ΔH) is large and negative, the Gibbs free energy change is likely to be negative. Thus, exothermic processes are often spontaneous. The exceptions are those for which the change in the entropy is negative. The freezing of a liquid is always exothermic, but it also involves a decrease in entropy. The freezing of a liquid becomes spontaneous only when the temperature is low enough for $T\Delta S$ to be less than ΔH.

When $\Delta H = T\Delta S$, and there is no driving force for the change in either direction, the solid and the liquid are in equilibrium. At constant pressure, this occurs at just one temperature. This temperature is the freezing point (or melting point) of the substance. The Gibbs free energy change accounts for the fact that pure substances at constant pressure have fixed melting points.

Free Energy Changes and Phase Changes: Evaporation of Liquids

At the melting point, the solid and liquid are in equilibrium. The free energy change is zero. In other words, at the melting point the free energy of the liquid is exactly equal to the free energy of the solid. As long as both liquid and solid are present, the temperature remains precisely at the melting point, no matter how much heat is supplied to the system. At any given pressure there is one, and only one, temperature at which the two phases can exist in equilibrium.

Contrast this situation with that of a liquid and its vapor. As shown previously, at constant temperature, the free energy of a gas varies with pressure:

$$G = G^\circ + RT \ln\left(\frac{P}{P^\circ}\right)$$

At any temperature, a certain pressure of gas will have a free energy equal to that of the liquid at that temperature, so the gas and liquid will be in equilibrium. The corresponding gas pressure is called the *vapor pressure* of the substance at that temperature. When the vapor pressure becomes equal to the atmospheric pressure, the liquid and vapor are in equilibrium at atmospheric pressure. The corresponding temperature is the *boiling point* of the substance. The Gibbs free energy change predicts that a pure substance will have a fixed vapor pressure at any given temperature and a fixed boiling point at any given pressure, in accordance with experiment.

Free Energy and Chemical Reactions in Gases

If two gases undergo a *chemical reaction* to form two new gases, the reactants and products will be in equilibrium when the free energy of the products equals the free energy of the reactants. For each gas involved in the reaction, the free energy is given by

$$G_i = n_i \left(G_i^\circ + RT \ln\left(\frac{P_i}{P^\circ}\right)\right)$$

where n_i is the number of moles of that gas, P_i is the *partial pressure* of gas i and P° is the pressure to which the standard free energy G_i° corresponds. The term "partial pressure" simply means the pressure that each gas contributes to the total pressure.

For a constant pressure system, as in the present discussion, the partial pressure P_i of each gas is given by the total pressure multiplied by the *mole fraction* of the gas X_i.

$$P_i = PX_i$$

The mole fraction $X_i = n_i / n$ is the ratio of the number of moles n_i of the gas divided by the total number of moles of gas in the system.

Suppose the reaction is a moles of gas A reacting with b moles of gas B to form c moles of gas C and d moles of gas D:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

The free energy of the reactants will be

$$a\left(G^\circ{}_A + RT\ln\left(\frac{P_A}{P^\circ}\right)\right) +$$

$$b\left(G^\circ{}_B + RT\ln\left(\frac{P_B}{P^\circ}\right)\right)$$

and the free energy of the products will be

$$c\left(G^\circ{}_C + RT\ln\left(\frac{P_C}{P^\circ}\right)\right) +$$

$$d\left(G^\circ{}_D + RT\ln\left(\frac{P_D}{P^\circ}\right)\right)$$

where P_A, P_B, P_C and P_D are the partial pressures of gases A, B, C and D.

The free energy change of the reaction will be the free energy of the products minus the free energy of the reactants.

$$\begin{aligned}\Delta G = {} & c(G^\circ{}_C + RT\ln(P_C/P^\circ)) + \\ & d(G^\circ{}_D + RT\ln(P_D/P^\circ)) - \\ & a(G^\circ{}_A + RT\ln(P_A/P^\circ)) - \\ & b(G^\circ{}_B + RT\ln(P_B/P^\circ)) \\ = {} & (cG^\circ{}_C + dG^\circ{}_D - aG^\circ{}_A - bG^\circ{}_B) + \\ & cRT\ln(P_C/P^\circ) + dRT\ln(P_D/P^\circ) - \\ & aRT\ln(P_A/P^\circ) - bRT\ln(P_B/P^\circ)\end{aligned}$$

$$\begin{aligned}& cG^\circ{}_C + dG^\circ{}_D - aG^\circ{}_A - bG^\circ{}_B = \\ & (cG^\circ{}_C + dG^\circ{}_D) - (aG^\circ{}_A + bG^\circ{}_B) = \Delta G^\circ\end{aligned}$$

Therefore

$$\Delta G = \Delta G^\circ + cRT\ln\left(\frac{P_C}{P^\circ}\right) + dRT\ln\left(\frac{P_D}{P^\circ}\right) - aRT\ln\left(\frac{P_A}{P^\circ}\right) - bRT\ln\left(\frac{P_B}{P^\circ}\right)$$

Now, because $x \ln X = \ln X^x$

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_C}{P^\circ}\right)^c + RT\ln\left(\frac{P_D}{P^\circ}\right)^d - RT\ln\left(\frac{P_A}{P^\circ}\right)^a - RT\ln\left(\frac{P_B}{P^\circ}\right)^b$$

and, because $\ln X + \ln Y = \ln XY$

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_C}{P^\circ}\right)^c \cdot \left(\frac{P_D}{P^\circ}\right)^d - RT\ln\left(\frac{P_A}{P^\circ}\right)^a \cdot \left(\frac{P_B}{P^\circ}\right)^b$$

Finally, because $-\ln X = \ln(1/X)$:

$$\Delta G = \Delta G^\circ + RT\ \ln\left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

This equation shows how the free energy change relates to the pressures of gaseous reactants and products at constant temperature. It is called the van't Hoff isotherm.

At equilibrium, the free energy of the reactants equals the free energy of the products, so $\Delta G = 0$ and

$$0 = \Delta G = \Delta G^\circ + RT\ \ln\left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

or

$$\Delta G^\circ = -RT\ \ln\left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

where P_A, P_B, P_C, and P_D are the pressures of gases A, B, C and D *at equilibrium*.

The right hand side of this equation can be written as $-RT \ln K$, where

$$K = \left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

K is called the *equilibrium constant* for the reaction, and therefore

$$\Delta G^\circ = -RT \ln K$$

Relative Activities

As shown previously, at constant temperature the free energy of a gas varies with pressure according to:

$$G = G^\circ + RT\ln\left(\frac{P}{P^\circ}\right)$$

where P is the partial pressure of the gas and G° is the free energy of one mole of the gas at pressure P°. This can be expressed in terms of chemical potentials:

$$\mu = \mu^\circ + RT\ln\left(\frac{P}{P^\circ}\right)$$

where $\mu^\circ = G^\circ$

This applies only to perfect gases. For other substances, it is useful to *define* a property called the *relative activity* such that the chemical potential is given by

$$\mu = \mu^\circ + RT\ln(a_A)$$

where a_A is the relative activity of the substance A. The equation requires the logarithm of the relative activity, a_A, which means that a_A must be a pure number—it cannot be some quantity requiring units. It has to be a ratio of some property of A, at the conditions of interest, to the value of that property at the standard state corresponding to μ°. The relative activity of a perfect gas is obviously P/P°. For a real gas (that is, a gas that does not conform exactly to the ideal relationship PV = nRT) the relative activity can be defined by assigning an "effective pressure" f to the gas such that

$$\mu = \mu^\circ + RT\ln\left(\frac{f}{P^\circ}\right)$$

This "effective pressure" f varies with temperature and has to be determined for each gas. It is called the *fugacity* of the gas. What is the relative activity for a pure solid or liquid?

For combustion problems, it is necessary only to take into account how the Gibbs free energy of a fixed amount of a substance (i.e., the chemical potential of that substance) varies with pressure. As discussed previously, the free energy per mole of a pure solid or liquid changes very little with pressure, and it is usually sufficiently accurate to treat the chemical potential of a pure solid or liquid as constant. That simplifies matters greatly, because if the chemical potential is constant, then for 1 mole of a pure solid or liquid

$$\mu = \mu^\circ + RT\ln(a) = \mu^\circ$$

from which $RT\ln(a) = 0$ and thus $a = 1$. The relative activity of pure solids and liquids is 1.

For perfect (or ideal) solutions, the chemical potential of a component i is given by

$$\mu_i = \mu_i{}^\circ + RT\ln X_i$$

where X_i is the mole fraction of i and $\mu_i{}^\circ$ is the chemical potential of pure i in the same physical state as the solution.

Relative Activities and Equilibrium Constants

The definition of relative activity was chosen so that for *any* reaction

$$aA + bB + cC + \ldots \rightarrow wW + xX + yY + \ldots$$

there is an equilibrium constant K of the form

$$K = \frac{(a_W)^w(a_X)^x(a_Y)^y\ldots}{(a_A)^a(a_B)^b(a_C)^c\ldots}$$

where a_W is the relative activity of W, etc.

The equilibrium constant is related to the standard free energy change for the reaction by

$$\Delta G^\circ = -RT\ln K$$

This equation can be rearranged to give

$$K = e^{-\Delta G^\circ/RT}$$

Equilibrium Constant, Free Energy and the Stability of Compounds

The relationship $K = e^{-\Delta G^\circ/RT}$ can be used to explain the stability of compounds in terms of their free energy of formation.

For the general reaction for the formation of a compound from its elements,

$$aA + bB \rightarrow A_aB_b$$

the equilibrium constant is given by

$$K = \frac{[A_a B_b]}{[A]^a [B]^b}$$

If the standard free energy of formation $\Delta G°$ is large and negative, then $-\Delta G°/RT$ will be large and positive, so K will be large and the equilibrium concentration of the product will be large. As the temperature T increases, the value of $-\Delta G°/RT$ will become smaller, K will decrease and the equilibrium concentration of the product will decrease. In general, the equilibrium will shift more and more towards the reactants as the temperature increases. Substances for which the standard free energy of formation is larger and more negative will withstand a higher temperature before the equilibrium lies in favor of the products. *The standard free energy of formation is thus a quantitative indicator of the thermal stability of a substance.*

Notice that if the reactants and products of a reaction are all solids, then the relative activity of each is 1, and the equilibrium constant is also 1. This means that $\Delta G° = -RT \ln 1 = 0$. The solid reactants and products can be in equilibrium at one, and only one, temperature: that at which $\Delta G° = 0$ (i.e., $T = \Delta H°/\Delta S°$). At all other temperatures, the system consists either *entirely* of reactants or *entirely* of products. This might seem odd, but it is no different from the familiar example of a pure solid being in equilibrium with its liquid at one and only one temperature.

Variation of Equilibrium Constants with Temperature

Recall

$$\Delta G° = -RT \ln K$$

$$\ln K = -\frac{\left(\frac{\Delta G°}{T}\right)}{R}$$

The partial derivative of this equation with respect to temperature, assuming constant pressure, is

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_P = -\frac{\left(\frac{\partial\left(\frac{\Delta G°}{T}\right)}{\partial T}\right)_P}{R}$$

Then, by the Gibbs-Helmholtz equation:

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_P = -\frac{\left(\frac{\partial\left(\frac{\Delta G°}{T}\right)}{\partial T}\right)_P}{R} = \frac{\Delta H°}{RT^2}$$

It is not necessary to restrict this relationship to constant pressure, because neither $\Delta G°$ nor $\Delta H°$ vary with pressure. They are *defined* at a standard pressure, usually one bar. Therefore,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H°}{RT^2}$$

This gives the relationship between the equilibrium constant and the temperature.

The equation can be rearranged to

$$d(\ln K) = \frac{\Delta H^o}{R}\left(\frac{dT}{T^2}\right)$$

Now, $dT/T^2 = -d(1/T)$, so

$$d(\ln K) = -\frac{\Delta H^o}{R} d\left(\frac{1}{T}\right)$$

This can now be integrated, assuming $\Delta H°$ to be constant with temperature, to give

$$\Delta(\ln K) = \frac{-\Delta H^o}{R} \Delta\left(\frac{1}{T}\right)$$

If the equilibrium constant is known at one temperature, this equation provides a way to calculate the equilibrium constant at any other temperature, provided that the relationship between $\Delta H°$ and temperature is known, and that the pressure is constant. As discussed previously,[2] the effect of temperature on $\Delta H°$ can be calculated from the heat capacities of the reactants and products over the temperature range of interest. If the equilibrium constant at one temperature T_1 is K_1, what can be said about the equilibrium constant (K_2) at a higher temperature T_2?

Rearrange the previous equation to obtain

$$\ln K_2 - \ln K_1 = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since T_2 is greater than T_1, $(1/T_2 - 1/T_1)$ will be negative. If ΔH° is also negative (that is, if the reaction is exothermic), $\ln K_2 - \ln K_1$ must be negative and K_1 must be greater than K_2. Recall that a larger equilibrium constant corresponds to more products. Since the equilibrium constant is larger at the lower temperature, the equilibrium at the lower temperature favors the products. Thus, for an exothermic reaction, an increase in temperature results in the equilibrium shifting in favor of the reactants.

The same line of reasoning can also show that for an endothermic reaction an increase in temperature will result in the equilibrium shifting in favor of the products. This is the thermodynamic explanation of *Le Châtelier's Principle*, as applied to the effect of temperature on chemical equilibrium. Le Châtelier's Principle can be stated in various ways, for example: *if a system at equilibrium is subjected to a stress, it will respond in such a manner that tends to relieve the stress*. This is a useful guide to the behavior of chemical systems, and is often all that is needed for a qualitative explanation.

Variation of Equilibrium Constants with Pressure

The discussion of equilibrium constants so far has referred to conditions of constant pressure. The next step is to show how the composition of the equilibrium mixture can change with pressure. Recall that the composition can be expressed in mole fractions given by

$$X_i = \frac{P_i}{P}$$

where P is the total pressure and P_i is the partial pressure of the particular gas.

For the reaction of *a* moles of gas A reacting with *b* moles of gas B to form *c* moles of gas C and *d* moles of gas D

$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$K = \frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b}$$

Now,

$$P_i = X_i P$$

If the pressure P is expressed in atmospheres, and $P^\circ = 1$ then

$$K = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

$$K = \frac{(X_C^c X_D^d)}{(X_A^a X_B^b)} \frac{(P^c P^d)}{(P^a P^b)}$$

But

$$\frac{(P^c P^d)}{(P^a P^b)} = \frac{P^{(c+d)}}{P^{(a+b)}} = P^{(c+d)-(a+b)}$$

and $(c + d) - (a + b) = \Delta n$

where Δn is the change in the number of moles. So

$$K = \frac{(X_C^c X_D^d) P^{\Delta n}}{(X_A^a X_B^b)}$$

$$\frac{\left(X_C^c X_D^d\right)}{\left(X_A^a X_B^b\right)} = K P^{-\Delta n}$$

If Δn is positive, that is, if there are more moles of products than of reactants, the right-hand side of the equation becomes smaller as the pressure P increases. This means that the equilibrium must shift in favor of the reactants. Similarly, if Δn is negative, the equilibrium will shift in favor of the products as the pressure P increases. This is the thermodynamic explanation for Le Châtelier's Principle, as it applies to the effect of pressure on the equilibrium composition of a reacting mixture.

Application to Pyrotechnics

Two useful pieces of information about reacting pyrotechnic mixtures are the maximum temperature reached and the chemical species present at that temperature. In principle, both can be calculated from thermodynamics.

The process for calculating the temperature is conceptually very simple:

1) Calculate the enthalpy change $\Delta H°$ for the reaction at standard temperature and pressure.
2) Assume that all the released heat is available to raise the temperature of the products.
3) Calculate the final temperature from the relationship:

$$\Delta T = \frac{-\Delta H°}{\Sigma n_i C_{p,i}}$$

where ΔT is the temperature rise in Kelvin, $\Delta H°$ is the enthalpy change in joules, n_i is the number of moles of product i, $C_{p,i}$ is the molar heat capacity (at constant pressure) of product i and the symbol Σ means "the sum of". Dolata[3] has shown that this method can be used to predict the temperatures of the flames of burning pyrotechnic mixtures that burn at relatively low temperatures.

It has been known for a long time that such calculations work quite well for the flame temperatures of certain gas mixtures that burn at moderate temperatures. Examples of such mixtures include coal gas / air or hydrogen / air with either gas in excess.[4a] In these calculations the "products" are the real end products of the reaction: carbon dioxide, water, nitrogen and argon in the case of an air / coal gas flame. There is no need to consider any intermediate products that might be formed along the way. For gas flames that burn at higher temperatures, however, these calculations yield flame temperatures that are much higher than the real flame temperatures.

This discrepancy can be understood if it is imagined that the energy released by the formation of the reaction's final products heats those products to such a high temperature that they start to break down again. This decomposition absorbs energy that would otherwise raise the temperature of the flame.

To calculate the temperatures of high-temperature flames one must consider not only the ultimate products (those that are stable at room temperature) but also those intermediate products that are stable at high temperatures. For example, ethylene (C_2H_4) burns in oxygen to form carbon dioxide and water. At the temperature of an ethylene-oxygen flame, however, the following species are in equilibrium: H_2O, O_2, O, H_2, H, OH, CO, and CO_2. The enthalpies of formation of these are known, but the amount of each substance present is not. Nevertheless, the amount of each *element* is obviously constant, and the equilibrium constants of the various dissociation reactions can be calculated for any temperature. Consequently, the problem can be solved by trial and error. One makes a reasonable guess at the temperature and of the partial pressures of two of the substances. With the aid of the equilibrium constants, one can then calculate the partial pressures of all the other products. The sum of these partial pressures should be 1; if it is not, the calculation is repeated. After a few trials, the values for the next trial are chosen by carefully examining the results of the first few and choosing values that are likely to lead in the right direction. With care, the method can yield a result after five or six iterations. The method, which is explained in detail by Gaydon and Wolfhard,[4a] can yield remarkably accurate results. For example, Snelleman[5] measured the temperature of a carefully controlled, pre-mixed air-acetylene flame to be 2554 ± 3 K. The calculated temperature was 2600 ± 3 K. Energy losses from the flame were measured, and when these were taken into account, the calculated flame temperature was 2559 ± 4 K, in agreement with the measured value.

The calculation of flame temperatures of a burning pyrotechnic mixture is much more complicated. For a start, the reaction might never reach thermodynamic equilibrium. Certain reactions might take place at relatively low temperatures, and volatile products of those reactions might be lost before the system can come to equilibrium. Even if equilibrium is reached, unless the mixture is an unusually simple one, the exact composition of the products might not be known. Then, the enthalpies of formation of many common ingredients are not known, or if they are known, they may be difficult to find. Examples of such ingredients are the natural products that are used as binders and fuels in fireworks. A compilation of *estimated* values for these has been published by Myerriecks.[6–8]

Furthermore, the molar heat capacity of each product is not constant but varies with temperature. As a result, the products change with temperature: solids melt, liquids vaporize, and compounds decompose. The energy consumed in all these processes has to be taken into account. If all these problems can be overcome, eventually a combination of temperature and chemical composition is reached at which the enthalpy of the products exactly equals the enthalpy of the reactants. If the enthalpy of the products as a function of temperature is available, the maximum possible temperature reached in a reaction can be obtained graphically. One plots the enthalpy of the products versus temperature and then finds the temperature at which the graph intersects the line representing the enthalpy of the reactants.

For example, consider the formation of iron(II) sulfide from powdered iron and sulfur:

$$\mathrm{Fe} + \mathrm{S} \rightarrow \mathrm{FeS} \qquad \Delta H_f^\circ = -102\ \mathrm{kJ}$$

The reactants are pure elements, so their enthalpies of formation are (by definition) zero. Therefore, the enthalpy of the reaction is simply the enthalpy of formation of FeS. What is the maximum possible temperature that can be reached in this reaction?

Figure 1 is a graph of the molar enthalpy of formation of iron(II) sulfide as a function of temperature (data from reference 9). The graph cuts the zero line at 1463 K. This is the temperature at which the molar enthalpy of formation of iron(II) sulfide equals the room-temperature molar enthalpies of formation of formation of iron and sulfur, and it is the maximum possible temperature that could be achieved in this reaction. The sharp rise in the curve at 1463 K corresponds to the melting of the solid. The maximum temperature reached is the temperature at which the solid product melts. This is consistent with experimental results. A stoichiometric mixture of powdered iron and sulfur glows bright red when heated to reaction, and the product is found to be partially melted. It is quite common for the maximum temperature of a pyrotechnic reaction to be determined by a phase change in the products. For example, the maximum temperature reached in the combustion of many metals in air corresponds to the boiling point of the metal oxide.[4b]

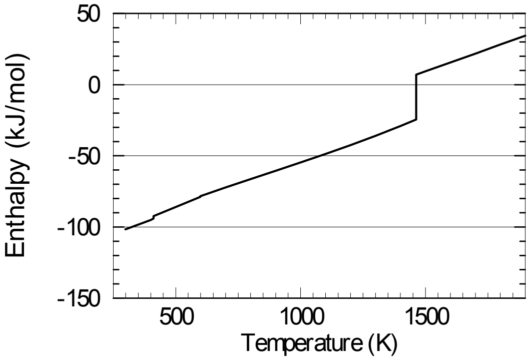

Figure 1. Molar enthalpy of iron(II) sulfide as a function of temperature.[9]

The example just given was very simple because the possibility of some of the product decomposing at the maximum temperature of the reaction was ignored. In most cases, the decomposition of the product must be taken into account. As discussed previously, the increase in entropy associated with the formation of gases favors the decomposition of compounds at high temperatures. The problem is to find the equilibrium composition and the temperature, keeping the elemental composition and total energy constant.

Thermodynamic Modeling

Numerous computer programs have been developed to calculate high-temperature equilibria.[10–12] As noted by Belov,[10] the incentive for developing these programs came from the requirement for better rocket engines. The calculations are done iteratively; that is, an initial estimate is made, the calculation is run, and the results are used as a starting point for the next calculation. This is repeated until the results no longer change within pre-selected limits. Thermodynamic data have to be available, as functions of temperature, for all possible products.

The calculation most useful for pyrotechnics is the determination of the temperature and chemical composition at constant pressure. This is done by minimizing the Gibbs free energy, with the constraint that the total number of moles of each element remain unchanged. The details of these calculations are given by McBride and Gordon.[12] The calculations are least complicated when the equilibrium products are all gases. If solids or liquids (condensed phases) are predicted, the calculations have to be revised to take into account the fact that the relative activity of a condensed phase of a pure substance is essentially constant and equal to 1. The results of thermodynamic modeling can be rather surprising. For example, a simple pyrotechnic mixture of a pure metal fuel with potassium perchlorate might be expected to produce nothing more than potassium chloride and the oxide of the metal. That is certainly what would be produced if the products were at room temperature, but at the high temperatures of the reaction the chemical composition will be very different. Powers and Gonthier[13] analyzed the operation of a pyrotechnically actuated pin-puller device that used a burning mixture of zirconium and potassium perchlorate to move a piston. The mixture was fuel-deficient: $Zr:KClO_4 = 1.4:1$, compared to the 2:1 molar ratio required for the reaction

$$2\ Zr + KClO_4 \rightarrow 2\ ZrO_2 + KCl$$

Presumably, this fuel-deficient composition was chosen to increase the amount of gas generated on combustion. On the basis of the properties of the products at room temperature, one would expect the reaction products to have been solid zirconium dioxide, solid potassium chloride and oxygen gas from the excess oxidizer. The calculations showed, however, that at the high temperature of the reaction even the highly refractory zirconium dioxide was partially vaporized. All the potassium chloride was vaporized, and the following species were calculated also to be present as gases: atomic oxygen (O), atomic chlorine (Cl), atomic potassium (K), atomic zirconium (Zr), diatomic oxygen (O_2), diatomic chlorine (Cl_2), diatomic potassium (K_2), potassium monoxide (KO), zirconium monoxide (ZrO), chlorine monoxide (ClO) and dipotassium dichloride (K_2Cl_2). As the hot products cooled to room temperature this diverse collection of atoms and molecules would react to produce the three products (solid zirconium dioxide, solid potassium chloride and diatomic oxygen gas) that are thermodynamically stable at room temperature. The chemical nature of the products at the high temperatures prevailing during the very rapid operation of the device could not have been determined by conventional chemical analysis.

Farren et al.[14] used thermodynamic modeling to simulate the combustion of pyrotechnic compositions including those used in US Navy colored flares. Their results showed that only about 18% of the strontium in the flame of the red flare was present as strontium monochloride (SrCl), the species that emits the desired red light. Most (~65%) was present as strontium dichloride ($SrCl_2$), while some (~15%) was there as strontium (Sr) vapor. Similarly, in the flame of the green flare less than 5% of the barium was present as the barium monochloride (BaCl) color emitter; most (~93%) was barium dichloride ($BaCl_2$), with a little (~1.5%) barium (Ba) vapor and the rest as barium monohydroxide (BaOH) (~0.7%) and barium dihydroxide ($Ba(OH)_2$) (~0.5%). The authors concluded that thermodynamic modeling "can be recommended as a useful tool to survey prospective pyrotechnic compositions as to their likely product distributions and their likely maximum achievable reaction temperature. However, those compositions showing potential usefulness should certainly be mixed, burned and analyzed in the laboratory before being recommended for use in any new or improved pyrotechnic device".[14] In other words, the predictions of modeling must be verified by practical experiments.

Thermodynamic modeling was used by Koch[15] to support his analysis of the reasons why lithium compounds have so far been ineffective as color-producing agents in pyrotechnics. His calculations showed that very little atomic lithium was expected to be present in the flame of a published composition that gave a pink flame instead of the anticipated scarlet red. Furthermore, Koch showed—by thermodynamic modeling—that appropriately formulated compositions should be capable of generating much higher concentrations of atomic lithium, and ought to be effective emitters of red light. Recognizing that thermodynamic modeling always requires practical validation Koch wrote, "it is hoped that an *experimental* proof will be found soon".[15]

Successful efforts to produce the beautiful deep violet-blue atomic emission of indium in pyrotechnic flames have not yet been reported, although, like lithium, indium imparts an intense color to laboratory flames. Perhaps thermodynamic modeling can point the way to achieving a deep blue flame with indium. The cost of indium compounds would prohibit practical applications, but it would be an interesting exercise.

The basic requirements of an effective colored light composition are straightforward: a high concentration of the color-emitting species, minimum concentration of other light-emitting species and maximum temperature. Since these requirements can be in conflict, to achieve optimum results by formulating, manufacturing and testing can be time-consuming and expensive.

In general, the requirements of a pyrotechnic composition can be stated in terms of

1) the chemical composition of the products (either at room temperature or at the temperature of the reaction) and
2) the maximum temperature of the reaction.

Thermodynamic modeling provides the possibility of developing close-to-optimum compositions on the computer. This should greatly reduce the burden of formulation and testing.

Summary and Conclusion

Chemical systems can be described by a few properties called *state functions*. These include temperature T, pressure P, volume V, internal energy U, enthalpy H, entropy S and Gibbs free energy G.

A system is at *equilibrium* when the state functions have constant values throughout the system.

The change in any state function depends only on the initial and final states of the system, not on the intermediate steps.

Energy can be transferred between a system and its surroundings *mechanically*, as *work*, and *thermally*, as *heat*. The change in the *enthalpy* of a system is the heat absorbed or emitted by the system at constant pressure.

Entropy is related to the degree of molecular disorder in a system. An increase in disorder corresponds to an increase in entropy.

A system plus its surroundings is called the *universe*.

- The energy of the universe is constant (First Law of Thermodynamics).
- The entropy of the universe increases (Second Law of Thermodynamics).

Consequently,

- For a spontaneous process, the Gibbs free energy change is negative. That is, $\Delta G = \Delta H - T\Delta S$ is negative for a spontaneous process.

Consequently:

- If ΔH is negative (heat is released) and ΔS is positive (molecular disorder increases), the process will *always* be spontaneous.
- If ΔH is negative (heat is released) and ΔS is negative (molecular disorder decreases), the process will be spontaneous at a sufficiently low temperature.
- If ΔH is positive (heat is absorbed) and ΔS is positive (molecular disorder increases), the process will be spontaneous at a sufficiently high temperature.
- If ΔH is positive (heat is absorbed) and ΔS is negative (molecular disorder decreases), the process will *never* be spontaneous.

The entropy change ΔS is positive for any process that results in an increase in the molecular disorder. Consequently, if the temperature is increased sufficiently

- Solids will melt.
- Liquids will vaporize.
- Compounds will decompose.
- Gases will ionize.

For a system in equilibrium, the Gibbs free energy change is zero. Consequently, at constant pressure

- Pure substances have fixed freezing (melting) points.

- Pure substances have fixed boiling points.
- There is an *equilibrium constant* K for chemical reactions, given by

  $\Delta G^\circ = -RT \ln K$

The variation of the equilibrium constant with temperature and pressure can be calculated from thermodynamics. This accounts for Le Châtelier's Principle *(if a system at equilibrium is subjected to a stress, it will respond in such a manner that tends to relieve the stress)* as it applies to the effect of pressure and temperature on the equilibrium composition of a reacting mixture.

Thermodynamic modeling allows the maximum temperature and chemical composition of reacting pyrotechnic mixtures to be estimated from the thermodynamic properties of the reactants and possible products.

Table 1 (at the end of this article) shows, for illustrative purposes only, thermodynamic properties of some substances relevant to pyrotechnics. More complete data is available in Reference 9, for example. Table 1 is a continuation of the Table published in the first article in this series.[2] Several typographical errors in the original Table have been corrected in this one.

Acknowledgement

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References

Specific to the Text of this Article

1) B. Sturman "An Introduction to Chemical Thermodynamics. Part 2 – Entropy, Molecular Disorder, and the Second and Third Laws", *Journal of Pyrotechnics*, No. 12 (2000) pp 31–42.
2) B. Sturman "An Introduction to Chemical Thermodynamics. Part1 – Matter, Energy and the First Law", *Journal of Pyrotechnics*, No. 9 (1999) pp 29–49.
3) D. P. Dolata, T. I. Peregrin, "Prediction of Flame Temperatures Part 1: Low Temperature Reactions*", Journal of Pyrotechnics*, No. 1 (1995) pp 37–46.
4) A. G. Gaydon and H. G. Wolfhard, *Flames: Their Structure, Radiation and Temperature*, 2nd ed., Chapman Hall Ltd, London (1960) [a] pp 283–301; [b] pp 344–345.
5) W. Snelleman, "A Flame as a Primary Standard of Temperature", *Metrologia*, Vol. 4, No. 3 (1968) pp 117–122.
6) W. Meyerriecks, "Organic Fuels: Composition and Formation Enthalpy, Part I, Wood Derivatives, Related Carbohydrates, Exudates and Rosin", *Journal of Pyrotechnics*, No. 8 (1998) pp 1–17.
7) W. Meyerriecks, "Organic Fuels: Composition and Formation Enthalpy, Part II, Resins, Charcoal, Pitch, Gilsonite, and Waxes", *Journal of Pyrotechnics*, No. 9 (1999) pp 1–19.
8) W. Meyerriecks, "Six Methods for Estimating the Formation Enthalpy of Organic Compounds", *Journal of Pyrotechnics*, No. 10 (1999) pp 7–16.
9) I. Barin, *Thermochemical Data of Pure Substances*, Parts 1 and 2, 2nd ed., VCH Verlag. MbH, Weinham, Germany (1993).
10) G. Belov, "Thermodynamic Modeling", http://gbelov.tripod.com/
11) E. R. Brown, "An Introduction to PROPEP, a Propellant Evaluation Program for Personal Computers", *Journal of Pyrotechnics*, No. 1 (1995) pp 11–18.
12) B. J. McBride and S. Gordon, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, Part 1: Analysis, Part 2: Users Manual and Program Description*, National Aeronautics and Space Administration Lewis Research Center, Cleveland, OH, USA (1996).
13) J. M. Powers and K. A. Gonthier, "Sensitivity Analysis for a Pyrotechnically Actuated Pin Puller Model", *Proceedings of the 19th International Pyrotechnics Seminar* (1994) pp 240–254.

14) R. E. Farren, R. G. Shortridge and H. A. Webster, III, "Use of Chemical Equilibrium Calculations to Simulate the Combustion of Various Pyrotechnic Compositions", *Proceedings of the 11th International Pyrotechnics Seminar* (1986) pp 13–40.

15) E.-C. Koch, "Evaluation of Lithium Compounds as Color Agents for Pyrotechnic Flames", *Journal of Pyrotechnics*, No. 13 (2001) pp 1–8.

16) R. C. Weast, Ed, M. J. Astle, Assoc. Ed., *CRC Handbook of Chemistry and Physics*, 63rd ed., CRC Press, Inc., Boca Raton (1982–1983).

17) G. Aylward and T. Findlay, *SI Chemical Data*, 4th ed., John Wiley & Sons, Brisbane, New York, Chichester, Weinheim, Singapore, Toronto (1994).

General References and Suggestions for Further Reading

This article includes information from a number of references, including the following, cited in order of publication. More recent editions of some of the books may be available; others may be out of print.

General Chemistry Texts:

B. H. Mahan, *University Chemistry*, Addison-Wesley, Reading, Palo Alto, London, Don Mills (1965).

K. W. Whitten and K. D. Gailey, *General Chemistry*, 2nd ed., Saunders College Publishing, Philadelphia (1984).

R. H. Petrucci, *General Chemistry*, Collier Macmillan, London and New York (1985).

R. Chang, *Chemistry*, 4th ed., McGraw Hill, Inc., New York (1991).

Physical Chemistry Texts:

A. Findlay, *Introduction to Physical Chemistry*, 2nd ed., Longmans, Green & Co, London, New York and Toronto (1933).

J. C. Slater, *Introduction to Chemical Physics*, reprint of 1939 ed., Dover Publications, New York (1970).

S. Glasstone, *Elements of Physical Chemistry*, Macmillan & Co., London (1955).

W. J. Moore, *Physical Chemistry*, 3rd ed., Longmans, Green & Co, London (1957).

C. Heald and A. C. K. Smith, *Applied Physical Chemistry*, MacMillan, London (1974).

S. H. Maron and J. B. Lando, *Fundamentals of Physical Chemistry*, Collier Macmillan, London and New York (1974).

W. J. Moore, *Basic Physical Chemistry*, Prentice-Hall International, Inc, London (1983).

P. W. Atkins, *Physical Chemistry*, 5th ed., Oxford, London (1993).

Thermodynamics Texts:

I. M. Klotz, *Chemical Thermodynamics*, Prentice-Hall, Inc., Englewood Cliffs (1950).

B. H. Mahan, *Elementary Chemical Thermodynamics*, W. A. Benjamin, Inc., New York (1964).

B. J. McClelland, *Statistical Thermodynamics*, Chapman and Hall & Science Paperbacks, London (1973).

E. B. Smith, *Basic Chemical Thermodynamics*, 3rd ed., Clarendon Press, Oxford (1982).

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics.

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]	ΔG_f° [b]	S° [b]	C_p° [b]
Aluminium	Al	26.98	0	0	0.028	0.024
carbide	Al_4C_3	143.96	–209	–196	0.089	0.117
oxide	Al_2O_3	101.96	–1676	–1582	0.051	0.079
sulfide	Al_2S_3	150.16	–724	—	—	—
Ammonium						
chloride	NH_4Cl	53.49	–314	–203	0.095	0.084
nitrate	NH_4NO_3	80.04	–366	–184	0.151	0.139
perchlorate	NH_4ClO_4	117.49	–295	–89	0.186	—
Antimony	Sb	121.75	0	0	0.046	0.025
oxide	Sb_2O_3	291.50	–720	–634	0.110	0.101
sulfide	Sb_2S_3	339.69	–175	–174	0.182	0.120
Arsenic	As	74.92	0	0	0.035	0.025
oxide	As_2O_3	197.84	–657	–576	0.107	0.096
sulfide	As_2S_3	246.04	–169	–169	0.164	0.116
Barium	Ba	137.34	0	0	0.063	0.028
carbonate	$BaCO_3$	197.35	–1216	–1138	0.112	0.085
chlorate	$Ba(ClO_3)_2$	304.24	–772	—	—	—
chloride	$BaCl_2$	208.25	–859	–810	0.124	0.075
nitrate	$Ba(NO_3)_2$	261.35	–992	–797	0.214	0.151
oxide	BaO	153.34	–554	–525	0.070	0.048
peroxide	BaO_2	169.34	–634	—	—	0.067
sulfate	$BaSO_4$	233.40	–1473	–1362	0.132	0.102
sulfide	BaS	169.40	–460	–456	0.078	0.049
Boron	B	10.81	0	–141	0.200	0.122
oxide	B_2O_3	69.62	–1273	–1194	0.054	0.063
Calcium	Ca	40.08	0	0	0.041	0.025
carbonate	$CaCO_3$	100.09	–1207	–1129	0.093	0.082
oxide	CaO	56.08	–635	–604	0.040	0.043
sulfate	$CaSO_4$	136.14	–1434	–1332	0.107	0.092
Carbon	C (graphite)	12.01	0	0	0.006	0.009
monoxide	CO(g)	28.01	–111	–137	0.198	0.029
dioxide	CO_2(g)	44.01	–394	–394	0.214	0.037
Chlorine	Cl_2(g)	70.91	0	0	0.223	0.034
atomic chlorine	Cl(g)	35.45	122	106	0.165	0.022
Copper	Cu	63.54	0	0	0.033	0.024
(I) chloride	CuCl	98.99	–137	–120	0.086	0.049
(II) chloride	$CuCl_2$	134.45	–220	–176	0.108	0.072
(I) oxide	Cu_2O	143.08	–169	–146	0.093	0.064
(II) oxide	CuO	79.54	–157	–130	0.043	0.042
carbonate, basic	$CuCO_3\cdot Cu(OH)_2\cdot H_2O$	221.10	–1051	–894	0.186	—
Hydrogen	H_2(g)	2.02	0	0	0.131	0.029
chloride	HCl(g)	36.46	–92	–95	0.187	0.029
sulfide	H_2S(g)	34.08	–21	–34	0.206	0.034
(water)	H_2O(l)	18.02	–286	–237	0.070	0.075

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics (Continued).

Chemical Name	Chemical Formula [a]	Formula Weight	$\Delta H_\mathrm{f}^\circ$ [b]	$\Delta G_\mathrm{f}^\circ$ [b]	S° [b]	C_p° [b]
Iron	Fe	55.85	0	0	0.027	0.025
(III) oxide	Fe_2O_3	159.69	–824	–742	0.087	0.104
(II,III) oxide	Fe_3O_4	231.54	–1118	–1015	0.146	0.143
Lead	Pb	207.19	0	0	0.065	0.026
(II) oxide	PbO (yellow)	223.189	–215	–188	0.069	0.046
(IV) oxide	PbO_2	239.19	–277	–217	0.069	0.065
(II,IV) oxide	Pb_3O_4	685.57	–718	–601	0.211	0.147
Magnesium	Mg	24.31	0	0	0.033	0.025
carbonate	$MgCO_3$	84.32	–1096	–1012	0.066	0.076
chloride	$MgCl_2$	95.22	–641	–592	0.090	0.071
oxide	MgO	40.31	–602	–569	0.027	0.037
Manganese	Mn	54.94	0	0	0.032	0.026
dioxide	MnO_2	86.94	–520	–465	0.053	0.054
Nitrogen	N_2(g)	28.01	0	0	0.192	0.029
(nitrous oxide)	N_2O(g)	44.01	82	104	0.220	0.038
(ammonia)	NH_3(g)	17.03	–46	–16	0.192	0.035
Oxygen	O_2(g)	32.00	0	0	0.205	0.029
atomic oxygen	O(g)	16.00	249	232	0.161	0.022
Phosphorus	P (red)	30.97	–18	–12	0.023	0.021
(V) oxide	P_4O_{10}	283.89	–2984	–2698	0.227	0.212
Potassium	K	39.10	0	0	0.064	0.030
chlorate	$KClO_3$	122.55	–398	–296	0.143	0.100
chloride	KCl	74.55	–437	–410	0.083	0.051
dichromate	$K_2Cr_2O_7$	294.19	–2061	–1882	0.289	0.219
nitrate	KNO_3	101.10	–495	–395	0.133	0.096
oxide	K_2O	94.20	–361	—	—	—
perchlorate	$KClO_4$	138.55	–433	–303	0.151	0.112
permanganate	$KMnO_4$	158.04	–837	–738	0.172	0.118
sulfide	K_2S	110.26	–381	—	—	—
Silicon	Si	28.09	0	0	0.019	0.020
dioxide	SiO_2 (quartz)	60.08	–911	–857	0.042	0.044
Sodium	Na	22.99	0	0	0.051	0.028
bicarbonate	$NaHCO_3$	84.01	–951	–851	0.102	0.088
carbonate	Na_2CO_3	105.99	–1131	–1044	0.135	0.112
chlorate	$NaClO_3$	106.44	–366	–262	0.123	—
chloride	NaCl	58.44	–411	–384	0.072	0.051
nitrate	$NaNO_3$	84.99	–468	–367	0.117	0.093
oxalate	$Na_2C_2O_4$	134.00	–1318	0	0.000	0.142
oxide	Na_2O	61.98	–418	–375	0.075	0.069
perchlorate	$NaClO_4$	122.40	–383	–255	0.142	—

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics (Continued).

Chemical Name	Chemical Formula [a]	Formula Weight	$\Delta H_f°$ [b]	$\Delta G_f°$ [b]	$S°$ [b]	$C_p°$ [b]
Strontium	Sr	87.62	0	0	0.052	0.026
carbonate	$SrCO_3$	147.63	–1220	–1140	0.097	0.081
chloride	$SrCl_2$	158.53	–829	–781	0.115	0.076
nitrate	$Sr(NO_3)_2$	211.63	–978	–780	0.195	0.150
oxalate	SrC_2O_4	175.64	–1371	—	—	—
oxide	SrO	103.62	–592	–562	0.054	0.045
Sulfur	S (rhombic)	32.06	0	0	0.032	0.023
dioxide	$SO_2(g)$	64.06	–297	–299	0.248	0.040
trioxide	$SO_3(g)$	80.06	–396	–371	0.257	0.051
Titanium	Ti	47.4	0	0	0.031	0.025
dioxide	TiO_2	239.19	–945	–890	0.050	0.055
Zinc	Zn	65.37	0	0	0.042	0.025
oxide	ZnO	81.36	–348	–318	0.044	0.040
sulfide	ZnS	97.43	–206	–201	0.058	0.046

[a] Unless otherwise indicated, these are crystalline solids. Gases are indicated as (g) and liquids as (l).

[b] Values are for 298.15 K, with units of kJ/mol.

Data are from references 9, 16 and 17. If data were inconsistent in the references, the most recent value is quoted. Data were rounded to the number of significant figures presented in the Table.

Studies of Electric Match Sensitiveness

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ABSTRACT

The sensitiveness of a collection of ten electric match types, from four suppliers, was determined under conditions intended to reflect their actual use to ignite fireworks displays. The measurements included determinations of impact, electrostatic discharge (ESD), friction, and thermal sensitiveness. The ESD tests considered discharges both through the bridgewire and from the bridgewire through the composition to ground. When safety shrouds were provided by the manufacturer, additional impact and ESD (through the composition) testing was performed with the safety shrouds left in place on the electric match tips. (Note that users often remove the protective shrouds for convenience during use.) To simulate conditions during use, additional impact and friction testing was performed with Black Powder prime composition in the presence of match tips.

It was found that there was a wide range of electric match sensitiveness, that the presence of the shrouds provided significant decreases in sensitiveness, and that the presence of Black Powder prime did not significantly affect sensitiveness.

Keywords: electric match, e-match, impact sensitiveness, friction sensitiveness, thermal sensitiveness, electrostatic discharge sensitiveness, ESD, sensitiveness testing

Introduction

Although more expensive and time consuming to set up, when compared to traditional reloaded and manually ignited fireworks displays, electrically fired displays have become increasingly common. For the most part, this is because they offer the potential for greater artistry, through the use of intricate display choreography often synchronized to music. However, electrically fired displays also offer the potential for greater display crew safety by requiring a smaller number of firing crew members and by separating them from the mortars and the occasional malfunctioning aerial shell. Unfortunately, too often the full potential for increased crew safety has not been achieved, with the crew sometimes trading accidents caused by aerial shell malfunctions for those caused by the accidental ignition of electric matches during transportation, set-up and disassembly.

A study of electric match (e-match) sensitiveness was completed for ten different match types from four suppliers, and brief summaries of the results have been reported in a series of short articles in *Fireworks Business*.[1] The present article was written to allow full presentation of the data and a number of photographs, as well as to allow a more complete comparison of the results. Table 1 lists the various suppliers and e-match types. Table 1 also presents the abbreviated designations of the e-matches used in many of the data tables throughout this article.

Table 1. List of Suppliers and Types of E-Matches Tested.

Supplier	Product Designation	Abbreviation Used
Aero Pyro[2]	none	AP
Daveyfire[3]	A/N 28 B	DF-B
	A/N 28 BR	DF-BR
	A/N 28 F	DF-F
Luna Tech[4]	BGZD	LT-B
	Flash	LT-F
	OXRAL	LT-O
Martinez Specialties[5]	E-Max	MS-EM
	E-Max Mini	MS-EMM
	Titan	MS-T

More than 1500 individual tests and measurements were performed during this study. However, it is important to acknowledge that, because of the large number of different combinations of e-match types and test configurations used, this sensitiveness testing must only be considered a screening study. For the most part, this is because only a limited number of individual tests were performed during each sensitiveness determination. Also note that the standard sensitiveness tests were often modified in an attempt to better characterize the e-matches in the environment of their use in fireworks displays. Accordingly, the statistical precision achieved is only sufficient to approximately characterize and rank the sensitiveness of the various e-matches, and then only under the specific conditions of this testing. For e-matches producing similar results, had additional numbers of matches been tested or had the conditions been somewhat different, it is possible that slightly different results would have been found. Nonetheless, additional tests or somewhat different test conditions would not be expected to produce substantially different results.

As a consequence of these only being considered screening tests, discussion of the results is often couched in terms indicating a significant lack of certitude. For example, terms such as “it is likely”, “it would seem”, “it is thought”, etc. are frequently used.

The e-matches for these tests were supplied in late 1999. Accordingly, it is possible that current production e-matches from these same suppliers have been modified in some way, which may have caused them to have sensitiveness results different than those reported herein.

Background

Figure 1 is an illustration of a typical electric match. It most commonly consists of an electrically insulating substrate with copper foil cladding, somewhat similar to that used for printed electrical circuits. The size of the e-match tip is often approximately 0.4 inch long by 0.1 inch wide by 0.03 inch thick (10 by 2.5 by 1 mm), exclusive of the pyrotechnic composition. Copper leg wires, used to attach the e-match to the firing control system, are soldered to the copper cladding. Completing the electric circuit within the e-match tip is a thin, high-resistance bridgewire (nichrome) soldered across the end of the substrate. The tip of the e-match is dipped into one or more heat sensitive pyrotechnic compositions, typically depositing about 40 mg of material. Then a protective lacquer coating covers the pyrotechnic composition. For the most commonly used e-matches, when an electric current of approximately 0.5 ampere is passed through the e-match, the relatively high-resistance bridgewire heats sufficiently to cause the ignition of the pyrotechnic composition. This produces a small burst of flame that is used to cause the ignition of a firework. (There are some significant differences in the construction and performance of the ten e-match types studied. However, a proper presentation and discussion of this is well beyond the scope of the present article. Accordingly, information on the construction and performance characteristics of these e-matches must be deferred to a subsequent article.[6])

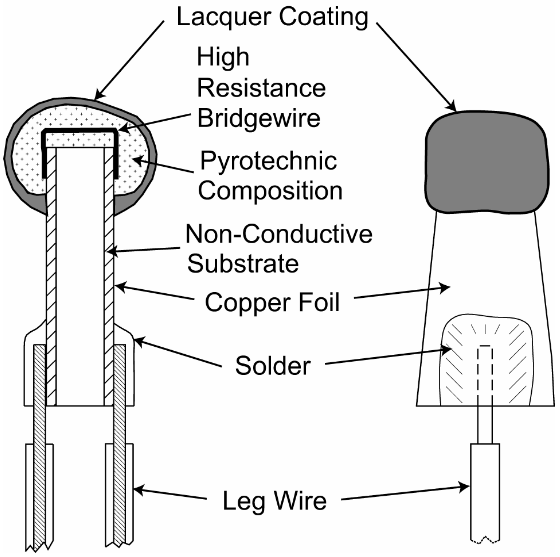

Figure 1. Illustration of a typical electric match in cross-section (left) and viewed externally after rotating 90 ° (right).

Figure 2 is a series of photographs of some of the types of e-matches tested in this study. Two views of each e-match are shown (rotated 90° from each other), as well as one view with a cut-away safety shroud when that was provided by the manufacturer. Some e-match types were not included in Figure 2 because they are similar in appearance to those shown. The Aero Pyro e-matches and Daveyfire A/N 28 B e-matches are similar to the Daveyfire A/N 28 BR e-match shown. However, the Daveyfire A/N 28 B e-match has somewhat less pyrotechnic composition than the A/N 28 BR, and the Aero Pyro e-matches were not supplied with safety shrouds. The Luna Tech BGZD e-match appears identical to their Flash e-match except for a different color coating. The Martinez Specialties E-Max e-match is virtually identical in appearance to their Titan e-match.

Pyrotechnic compositions are said to be metastable, meaning that they are stable under normal conditions, but when supplied with sufficient activation energy, they react to release their store of chemical energy,[7] typically in the form of a flame. For an e-match, the activation energy is intended to be the thermal energy produced by an electric current passing through the high-resistance bridgewire. However, the activation energy can come from other unintended sources, such as mechanical energy from impact or friction, or the electrical energy from an electrostatic spark, etc. When there is an unintended ignition of an e-match, too often this is the initiating cause of a significant accident, sometimes with the most serious of consequences.

In general, hazards are managed by reducing the probability of the accident occurring, reducing the consequences of the accident should it occur, or preferably by reducing both the probability and consequences.[8] In the case of e-matches, the probability of having an accidental ignition is reduced by taking measures to limit the unintentional delivery of energy to the pyrotechnic composition. This can be accomplished using measures as simple as educating workers to take care not to forcefully crush the e-match, or not to allow the forceful rubbing of the e-match against an abrasive surface. In addition, for e-matches used in situations where accidental crushing or rubbing might be expected, some manufacturers provide soft plastic safety shrouds to help protect the e-match tips. Clearly, the firing crew should be instructed to leave the safety shrouds in place and not to remove them during use (as is often done for convenience).

As is generally true for pyrotechnics, the consequences of having an accidental ignition of an e-match can be reduced by limiting the amount of fireworks in the immediate work area. Work should be performed in a manner such that, in the event of an accidental ignition, only one item will ignite and that it is unlikely that anyone will be seriously injured by that single

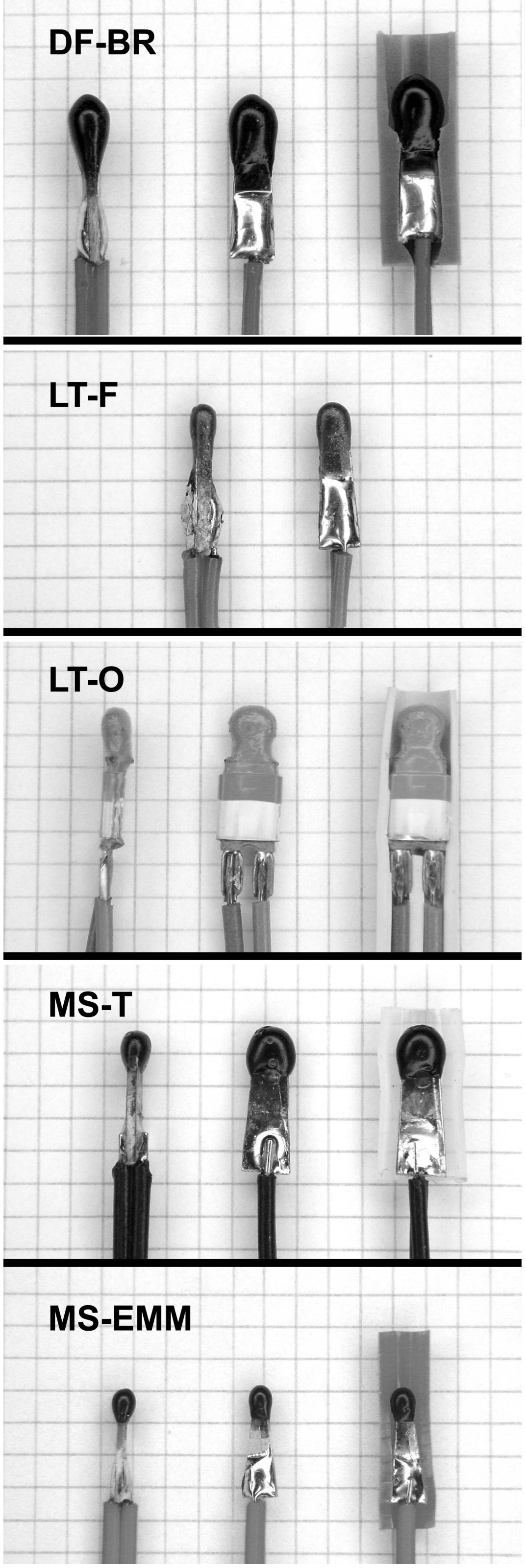

Figure 2. Photographs of some of e-matches studied. (Each background square is 0.10 inch, 2.5 mm.)

ignition. For example, consider the case where an aerial shell has been loaded into its mortar before inserting an e-match into its shell leader and wiring the e-match into the firing circuit. In the event of an accidental ignition of that shell, it is likely that only the one shell would ignite and that it should fire relatively harmlessly into the air. (Of course, that assumes care was taken to not have any body parts over the mortar while working.)

In this study of electric match sensitiveness, it was found that the various e-matches demonstrate a wide range of sensitivity to accidental ignition. However, it is important to note that none were found to be so sensitive as to preclude their safe use, provided appropriate levels of care are taken. Further, it is a general principle of pyrotechnics that materials that are less prone to accidental ignition also tend to be more difficult to ignite intentionally. Thus, it should not automatically be assumed that the least sensitive e-match is the best choice for every application.

Impact Sensitiveness

Normal Configuration

The impact sensitiveness apparatus was of a standard drop-hammer (fall-hammer) design; however, because of the relatively high sensitiveness of e-matches, lighter than normal drop hammers were used. In these tests, a one-half kilogram drop hammer was used with the more sensitive e-matches and a one-kilogram drop hammer was used with the less sensitive e-matches. An additional modification was made in an attempt to better simulate the use environment of the e-matches. Typically, impact sensitiveness testing is performed by placing a sample between two steel anvils that are then forced together by the impact of the drop hammer. However, in this case, the match tips were inserted inside a fold of 0.010-inch (0.25-mm) thick paper card stock (see Figure 3) and the drop hammer was allowed to fall directly on the assembly. Also, because the solder connections on some of the e-match tips were thick enough to have absorbed some of the impact energy, the solder connections of the e-matches were cut off and only the very end of the match tips, with the pyrotechnic composition, were used in the tests. The e-match tips were oriented such that their wide dimension was parallel to the impact surfaces. For these tests, any shrouds supplied with the e-matches had been removed. (Because almost all of the impact energy was absorbed inelastically, no measures were taken to keep the drop hammer from bouncing.)

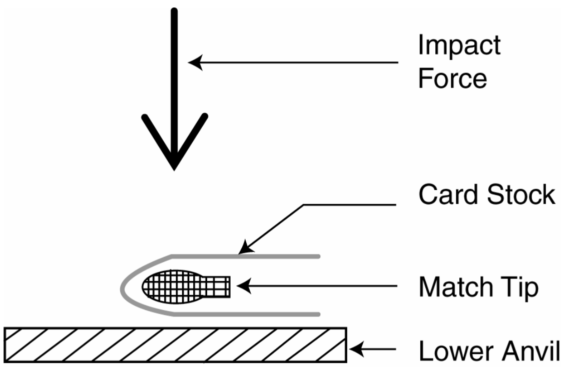

Figure 3. Illustration of the "normal" impact test sample configuration.

For each e-match type, approximately 20 were impact tested using the standard stair-step (Bruceton) method.[9] The results from testing using the *normal* configuration, as shown in Figure 3, are indicated in the "Test" column of Table 2 as "N-1/2" or "N-1", depending on whether the 1/2 or 1 kg drop hammer was used. The individual test results are reported as a pair of numbers, indicating the number of ignitions and non-ignitions, respectively, for each drop height used. The sensitiveness results are the Bruceton calculated heights that caused ignitions 50% of the time and are reported to the nearest inch. When the one-kilogram drop hammer had been used, the reported results were doubled (i.e., normalized to the corresponding half-kilogram drop hammer heights). (There is some concern that such drop-hammer normalization may not be completely correct. However, it was done to allow an easy comparison of results using the two different mass drop hammers.)

Based on these limited results, it would seem that the Aero Pyro, Daveyfire A/N 28 B and A/N 28 BR, Luna Tech BGZD, and Martinez Specialties E-Max Mini e-matches were all approximately equally sensitive, falling in the most sensitive group (50% sensitiveness height of seven to ten inches or 180 to 250 mm). A little less sensitive were the Luna Tech OXRAL and Marti-

Table 2. Results of Impact Sensitiveness Testing.

E-Match Type	Test(a)	Drop Height (inches)(b)											Impact Sens.(c)	BP Sens.(d)
		6	9	12	15	18	21	24	30	36	42	48		
AP	N-1/2	0/4	4/6	7/0									10	4/6
DF-B	N-1/2	0/6	7/3	4/0									8	4/6
	S-1			0/1		1/6		6/3	3/1	1/0			S 44	
DF-BR	N-1/2	0/2	2/6	7/1	2/0								10	2/8
	S-1					0/4		7/4	4/0				S 46	
DF-F	N-1								0/1	1/1	0/2	1/5	>96(e)	7/3
LT-B	N-1/2	0/3	4/4	7/0	1/0								9	8/2
LT-F	N-1											0/6	>96(e)	0/5
LT-O	N-1/2			0/2	1/3	3/3	3/0						18	5/5
	S-1					0/1		0/6	4/5	3/1	1/0		S 62	
MS-EM	N-1/2		0/3	2/4	5/3	3/0							14	3/7
	S-1					0/1		1/5	6/3	4/1	1/0		S 60	
MS-EMM	N-1/2	0/9	9/0										7	4/6
	S-1					0/3		3/6	5/1	1/0			S 60	
MS-T	N-1										0/4	5/5	≈ 96	0/5

a) In column 2, "N" indicates the use of the set-up as shown in Figure 3. "S" indicates testing with the safety shroud in place. "1/2" indicates use of a 1/2-kg drop hammer and "1" indicates use of the 1-kg drop hammer.

b) For conversion of drop height to SI units, 1 inch = 25.4 mm. Reported are the number of ignitions and non-ignitions that occurred at this height. For example, "6/2" would indicate there were 6 ignition and 2 non-ignition events recorded at this particular drop height.

c) This is the height, reported to the nearest inch, that was calculated using the Bruceton method[9] to produce ignitions 50% of the time (i.e., it is the 50% impact sensitiveness). Those entries prefaced by an "S" indicate the result is for an e-match with its safety shroud in place.

d) This is an indication of the effect of the presence of Black Powder prime. It is the number of ignitions and non-ignitions that occurred in the presence of Black Powder, in tests performed at the 50% drop height found previously during testing without Black Powder present.

e) The practical impact height limit for the instrument being used was 48 inches. For a 1 kg hammer mass, this approximately corresponds to an equivalent 96 inches (2.4 m) had a 1/2 kg mass hammer been used. The sensitiveness of these e-matches fell below the limit of the instrument using a 1-kg drop hammer.

nez Specialties E-Max e-matches (50% height of 14 to 18 inches or 360 to 460 mm). The Daveyfire A/N 28 F, Luna Tech Flash, and Martinez Specialty Titan e-matches were all much less sensitive (50% height of ≥96 inches or 2.4 m). (Note that the practical impact height limit for the instrument being used was 48 inches (01.2 m). For a 1-kg hammer mass, this approximately corresponds to an equivalent 96 inches (2.4 m) for a 1/2-kg mass hammer.)

As a point of comparison, rough Black Powder harvested from some Horse Brand black match was recently found to have a 50% impact sensitiveness height (using steel anvils) that was roughly comparable to that of the least sensitive electric matches (Daveyfire A/N 28 F, Luna Tech Flash, and Martinez Specialty Titan). In this configuration, without safety shrouds, all of the other e-match types are five to ten times more sensitive to accidental ignition from impact. Accordingly, such e-matches must be treated with much care and respect.

One additional point should probably be raised regarding these impact sensitiveness results. In performing the testing on completed e-match tips, it appears there may be an effect due to the physical size of the mass of composition. Note that the sensitiveness of the Martinez Specialties E-Max Mini e-match is significantly greater than that for the E-Max e-match. It is possible that this is an effect of a difference in the size of the two e-match tips (see again Figure 2) with the impact force being more concentrated on the smaller e-match tip. It is possible that a similar effect is seen for the Daveyfire A/N 28 B and A/N 28 BR e-matches, where results suggest that the larger A/N 28 BR e-match is a little less sensitive.

Effect of Black Powder

It has been speculated that some e-match compositions may be more sensitive to accidental ignition when in the presence of Black Powder, perhaps because of the sulfur contained therein. Accordingly, the matches in this study were subjected to impact sensitiveness testing in the presence of Black Powder. The normal test configuration was modified slightly, as illustrated in Figure 4. In these tests the inside surface of the piece of card stock around the e-match was heavily painted with a slurry of Black Powder (bound with 5% dextrin) and allowed to dry thoroughly before testing. However, to conserve on the number of individual tests performed, a full set of Bruceton impact tests was not performed. Instead, for each e-match type, a series of just ten individual impacts were used, each time using the 50% impact sensitiveness height found previously in the testing without Black Powder. If the presence of Black Powder had no effect on impact sensitiveness, the number of ignitions should be roughly five out of the ten tests. The results of this testing are presented as a pair of numbers in the final column of Table 2, indicating the number of ignitions and non-ignitions, respectively.

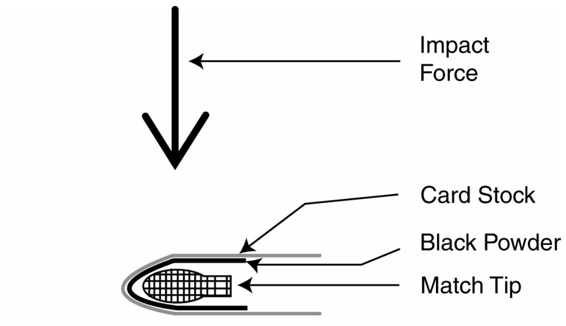

Figure 4. Illustration of the impact test sample configuration, with Black Powder prime present.

Within the precision limits of this testing, for a finding of three to seven ignitions, it must be concluded that any effect due to the presence of Black Powder is probably relatively small. Based on the testing, most of the e-match types are in this category. However, it is fairly likely that a finding of eight or more ignitions indicates added sensitiveness as a result of the presence of the Black Powder. The only e-match falling in this group was the Luna Tech BGZD e-matches. Because these e-matches were already found to be fairly sensitive to impact—even without the presence of Black Powder, it might seem that this is a matter of particular concern. However, it must be recognized that the Luna Tech BGZD matches are intended for use in stage effects where it is significantly less likely to be subjected to impact, than if they were being used in fireworks displays. Further, it is even less likely that they will be subject to a significant impact in the presence of Black Powder.

The Daveyfire A/N 28 F and Luna Tech Flash e-matches had been found to have 50% impact sensitiveness heights *without* the presence of Black Powder that exceeded 96 inches (2.4 m) (as corrected for using a 1/2-kg drop hammer). These e-matches were retested using the same impact (1-kg drop hammer at 48 inches or 01.2 m) with Black Powder present. For the Daveyfire A/N 28 F e-matches in the presence of Black Powder, there were now seven ignitions in ten tests, whereas without Black Powder there had been only one ignition in 6 tests. Accordingly, it would seem that there is an added sensitiveness due to the presence of Black Powder. However, since these e-matches are among the very least impact sensitive e-matches, it is thought not to be of significant concern. For the Luna Tech Flash e-matches, there were zero of six ignitions at 96 inches (1.2 m) without Black powder and zero of five ignitions in the presence of Black Powder. (In both cases the testing was terminated early because more definitive results seemed unlikely.) Accordingly, it is not possible to speculate on the possibility of their being more impact sensitive in the presence of Black Powder; however, they were the least impact sensitive of all the e-matches tested.

In one case, the impact results suggest that there might have been a reduction in the sensitiveness observed. It seems likely that this is an artifact of the test method. It is suspected that the presence of Black Powder provided more material over which the force of the impact was distributed. For that reason it might have been expected that reduced sensitiveness would be found. (This is similar to the size effect discussed above for the E-Max and E-Max Mini matches.)

Effect of Safety Shroud

Some e-match suppliers, in particular those whose customers are likely to use the e-matches to ignite fireworks, supply safety shrouds for their e-matches. (Safety shrouds are a soft plastic covering for an e-match.) These are either pre-installed or available for customer installation. (See Figure 5 for an illustration of a typical e-match and shroud configuration.) Suppliers of e-matches for use in proximate audience pyrotechnics typically do not supply shrouds, or they offer them as an optional feature. In the proximate audience use environment, it is often necessary to install e-matches through small holes in hardware (e.g., into flash pots and concussion mortars) or into small preload devices. Such installation often precludes the use of shrouds and tends to obviate the benefits of safety shrouds because of their use in a more physically protected environment.

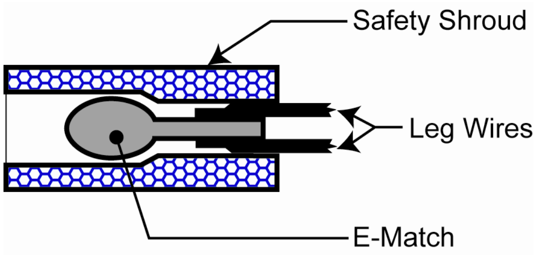

Figure 5. Illustration of a typical e-match with its molded safety shroud in place (not to scale).

While the safety shroud acts to direct the combustion products of the e-match ignition out its open end, it is generally thought that the primary purpose of the shroud is to protect the e-match and thus reduce its sensitiveness to accidental ignition. Accordingly, the e-matches in this study that were supplied with safety shrouds were subjected to impact sensitiveness testing with their shrouds in place.

The safety shrouds found on the Daveyfire e-matches and the Luna Tech OXRAL e-match are specially molded, similar to that shown in Figure 5. The soft plastic appears to be polyethylene, and although removable, the matches were supplied with the shrouds already in place. The shrouds for the Martinez Specialties e-matches were short lengths of soft plastic or rubber tubing (apparently a type of silicone or Tygon tubing) and needed to be installed on the e-matches by the user when desired. Because of the e-match's somewhat arrowhead shape, this was fairly easy to accomplish and the safety shrouds tended to stay in place reasonably well.

The shrouded e-match impact sensitiveness testing was conducted using much the same method as used in the testing without the presence of safety shrouds. However, those e-match types not supplied with shrouds were not retested. One modification to the test configuration was that the e-matches were held in place on a piece of card stock (0.010 inch) using a small piece of cellophane tape. (See Figure 6.) This was to help hold the shrouded e-matches in the same orientation as in the testing without shrouds. In the shrouded e-match tests, there were generally approximately 20 separate test impacts for each e-match type, again using the stair-step (Bruceton) method.[9] The results of the testing are also presented in Table 2, with the data designated as "S-1", where "S" indicated that the e-matches had their shrouds in place, and the "1" indicated that the 1-kg drop hammer was used.

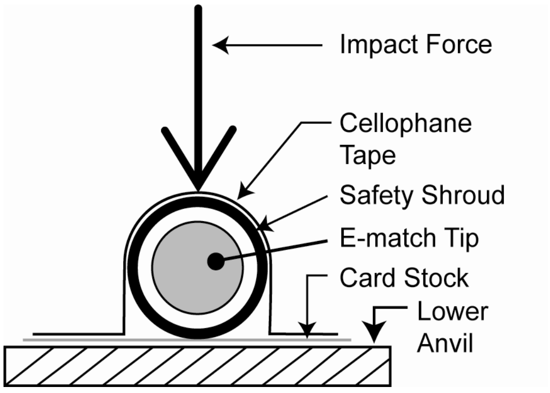

Figure 6. End-on, cross-sectional illustration of the configuration used for shrouded e-match impact testing.

For those e-match types for which previous impact tests without a shroud produced a 50% impact sensitiveness height of at least 96 inches (equivalent for the 0.5 kg drop hammer) no testing was performed with safety shrouds in place. This is because it was thought that the impact sensitiveness of these matches was already so low as not to present a significant potential impact hazard during normal use. (In addition, any e-matches that were not supplied with shrouds were not tested.) As expected, for the five e-match types that were tested, it was found that the presence of the shroud provided a substantial decrease in impact sensitiveness. The decrease ranged from a factor of three to eight and averaged a factor of a little more than five. That is to say, with the shrouds in place approximately five times greater impact energies were required to produce an ignition. Obviously, the presence of the safety shrouds on those e-matches that were fairly sensitive to impact stimulus affords a substantial safety benefit, and display crews should be instructed to leave them in place.

Electrostatic Discharge (ESD) Sensitiveness

In these tests, ESD sensitiveness was determined for two configurations. In the first series of tests, the electric discharge current was passed through the e-match bridgewire in much the same fashion as the intended firing current. This is illustrated in the upper drawing of Figure 7. In the second series of tests, the discharge current passed from the bridgewire through the pyrotechnic composition to ground, as illustrated in the lower drawing of Figure 7.

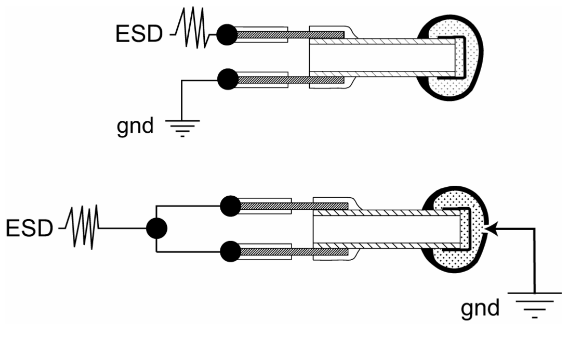

Figure 7. Illustration of the two basic ESD test configurations used in this study.

The high voltage discharge current used in this testing was provided by an instrument whose basic circuit diagram is shown in Figure 8. Each of the three main circuit components (R_c, R_s, and C) are removable so that their values can be selected as appropriate for the specific testing being performed. For these e-match tests, the charging resistor (R_c) was always 3.3 megohms, the series resistor (R_s) was always 100 ohms, and the charge storage capacitor (C) was varied between 0.001 and 0.25 microfarads depending on the ESD sensitiveness of the particular type of e-match being tested. In each case, to assure the full charging of the storage capacitor, the instrument was operated such that the charging time was at least 10 RC time constants. The maximum high voltage available from the power supply used in these tests was 6 kilovolts. In the first test configuration (ESD passing through the bridgewire), solid electrical connections were made directly to the individual e-match leg wires. For each e-match type, approximately 20 individual discharge tests were performed, using the standard stair-step (Bruceton) method.[9]

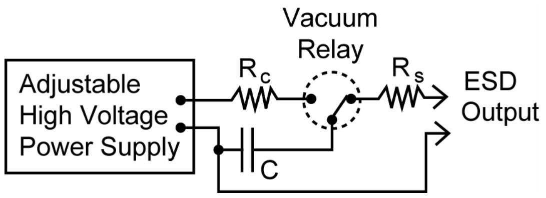

Figure 8. Circuit diagram for the ESD test apparatus used in this study.

While it is more typical to perform ESD sensitiveness testing using a higher voltage (up to 25 kV) than was used in these tests, it is thought that the lower voltages were a somewhat more realistic limit to the charge potential that might be developed on persons working at a fireworks display site in typical summer humidity. Another modification from more typical ESD testing conditions was the use of a series resistance of only 100 ohms as opposed the commonly used value of 500 ohms,[10] (or even 5000 ohms as used in some military ESD testing[11]). For human induced discharges, the series resistor is intended to be a substitute for a contact resistance person delivering an ESD to an e-match. The choice of this lower resistance value was somewhat arbi-

Table 3. Electrostatic Discharge Sensitiveness Test Results.

E-Match Type	Test(a)	Cap. (μF)(b)	Min. (V)(c)	Step (V)(d)	Individual ESD Test Data(e)							Sens. (mJ)(f,g)
					0	1	2	3	4	5	6	
AP	TBW	0.01	4000	250	0/1	0/3	2/6	7/0				120
	TC	0.001	500	250	0/1	1/1	1/3	4/4	5/1	1/1	1/0	0.7
DF-B	TBW	0.01	3500	250	0/7	8/2	3/0					70
	TC	0.001	500	250	0/3	2/4	4/3	3/2	1/1			0.5
DF-BR	TBW	0.01	3500	250	0/5	5/3	3/1	1/1	1/0			70
	TC	0.001	1000	250	0/5	4/4	4/2	2/0				0.8
DF-F	TBW	0.1	2000	250	0/7	7/2	3/0					240
	TC	0.001	1750	250	0/1	1/1	1/3	4/1	3/4	5/1	1/0	3
LT-B	TBW	0.01	4000	250	0/1	0/6	6/4	4/0				100
	TC	0.01	500	500	0/2	2/2	2/6	5/4	4/2	2/1	1/0	20
LT-F(h)	TBW	0.25	3500	250	0/1	0/9	9/9	8/3	4/0			2300
	TC	0.01	500	250	0/2	2/3	5/3	3/1	1/2	2/1	1/0	6
	TBW	0.25	3000	300	0/5	6/5	6/0	1/0				1400
	TC	0.01	400	400	0/7	7/4	5/7	7/4	4/3	4/0		8
LT-O	TBW	0.01	4500	250	0/4	3/4	3/3	3/0				120
	TC	0.001	1500	250	0/4	3/3	3/2	2/1	1/1	1/0		2
MS-EM	TBW	0.01	3500	250	0/3	3/6	7/0					70
	TC	0.001	1250	250	0/2	2/2	3/4	5/0				2
MS-EMM	TBW	0.01	3750	250	0/4	4/4	5/1	2/0				80
	TC	0.001	1750	250	0/2	2/5	4/3	3/0				2
MS-T	TBW	0.1	2000	250	0/2	1/8	9/0					260
	TC	0.25	1000	1000	0/4	4/2	2/2	2/5	4/3	2/0		1000

a) Two test configurations were used. TBW indicates the *through-the-bridgewire* configuration, and TC indicated *through-the-composition* configuration, the upper and lower configurations shown in Figure 7, respectively.

b) This is the value of the storage capacitor (in micro Farads–μF) labeled "C" in Figure 8.

c) This is the minimum voltage used during the testing of this type of e-match using the configuration listed.

d) This is the step size used (i.e., the voltage difference between adjacent stimulus levels).

e) These are the number of ignitions and non-ignitions that occurred at this ESD test voltage. For example, "6/2" would indicate there were 6 ignitions and 2 non-ignitions at this particular voltage. The voltage is equal to the minimum voltage (c) plus the product of the step size (d) and the number of steps.

f) This is the ESD energy that produced an ignition approximately 50% of the time. Because of the limited precision of these results, the energy values for through-the-bridgewire test configuration (TBW) are reported to the nearest 10 mJ, or two significant figures, whichever is less precise.

g) Because of the additional uncertainty associated with the removal of the protective coating, the energy values for through-the-composition test configuration (TC) are reported to only one significant figure.

h) Because of some concern regarding the accuracy of the initially collected data, some additional trials were conducted using a second production lot of the Luna Tech Flash matches.

trary; however, measurements involving a heavily sweating person confirmed that body resistances of no more than approximately 100 ohms are common.

The choice of series resistance for these tests is an important parameter, in that it determines the partitioning of energy between that delivered to the series resistance and that delivered to the item under ESD test. Ignoring impedances other than resistance, the ESD energy being provided divides proportionally between the two resistances (in this case, between the series resistor and the e-match). Accordingly, with a 2-ohm test item and a 100-ohm series resistor, approximately 2% of the ESD energy is delivered to the test item. However, had a 500-ohm series resistor been chosen, only 0.4% (or 1/250) of the ESD energy would have been delivered to the test item. In addition to the 100-ohm body resistance being more likely, it was felt that using a 500-ohm series resistor in these tests might have given the reader a false sense of security regarding the ESD sensitiveness of e-matches under conditions typical of their use at fireworks displays.

Through-the-Bridgewire Test Configuration

The ESD sensitiveness test conditions and results for the *through-the-bridgewire* test configuration are presented in Table 3 with the designation of "TBW" in the column labeled "Test". The value of the charging capacitor for this test configuration ranged from 0.01 to 0.25 micro Farad (μF) depending on the approximate sensitiveness of the e-matches and is given in the column labeled "Cap." The lowest ESD voltage used for each type e-match and the voltage increment between the steps used for that e-match are given in the next two columns of Table 3, labeled "Min." and "Step", respectively. The next series of columns present the data from the individual test firings, where each pair of numbers is the number of ignitions and non-ignitions, respectively. The first of this series of columns, labeled "0", has the data obtained using the minimum test voltage. The succeeding columns, labeled "1" through "6", have the data obtained using stepwise increasing voltages. The final column of Table 3, labeled "Sens.", presents the sensitiveness results given as the discharge energies that produced ignitions in approximately 50% of the tests. (Note that some degree of caution is necessary in interpreting these results, because the test conditions used in these tests were significantly different from those often reported in the literature. Accordingly, the values reported in Table 3 must not be compared with values reported elsewhere, unless an adjustment is made to account for those significant differences in test conditions.)

Regarding ignitions produced by an ESD through the bridgewire, the e-matches can be roughly divided into four groups. Based on these limited results, it would seem that the Daveyfire A/N 28 B and BR, and the Martinez Specialties E-Max and E-Max Mini fall in the most sensitive group (70 to 80 mJ). A little less sensitive are the Aero Pyro, Luna Tech BGZD and OXRAL e-matches (100 to 120 mJ). Significantly less sensitive are the Daveyfire A/N 28 F and Martinez Specialties Titan e-matches (240 to 260 mJ). Substantially less sensitive still are the Luna Tech Flash e-matches (1900 mJ).

As a point of comparison, consider that the approximate maximum ESD energy that can be developed on a typical person (200 pF and 25 kV)[12] is on the order of 60 mJ. However, note that there are conditions under which a person can act as a conduit passing much greater ESD energy, from other objects that may be capable of storing considerably larger charges than a human body stores.

E-Match Tip Protective Coating Evaluation

The e-matches examined in this study all have a protective coating over their pyrotechnic composition. This coating provides a level of protection from physical damage during handling and use, as well as possible damage from exposure to moisture. The coatings also provide a significant degree of electrical insulation, which generally limits the ability to cause an ESD from the bridgewire through the composition (and its coating). However, imperfections are occasionally observed in the e-match coatings, such that discharges through the composition can potentially occur. These imperfections can occur as a normal consequence of manufacturing methods or as a result of the e-match tip being physically damaged (from crushing or abrasion) during handling and use. A close examination of e-match tips from each of the suppliers, revealed occasional visible imperfections (apparent voids or holes) in their coatings. Figure 9 is a collection of electron micrographs of such imperfections observed for each of the various suppliers' e-matches. (It should be mentioned that only one example of a coating imperfection was found for the Aero Pyro matches, shown in Figure 9. Further, because those matches are apparently coated twice, and the imperfection was only in one of the coating layers, thus even in that one case there was ample ESD protection.)

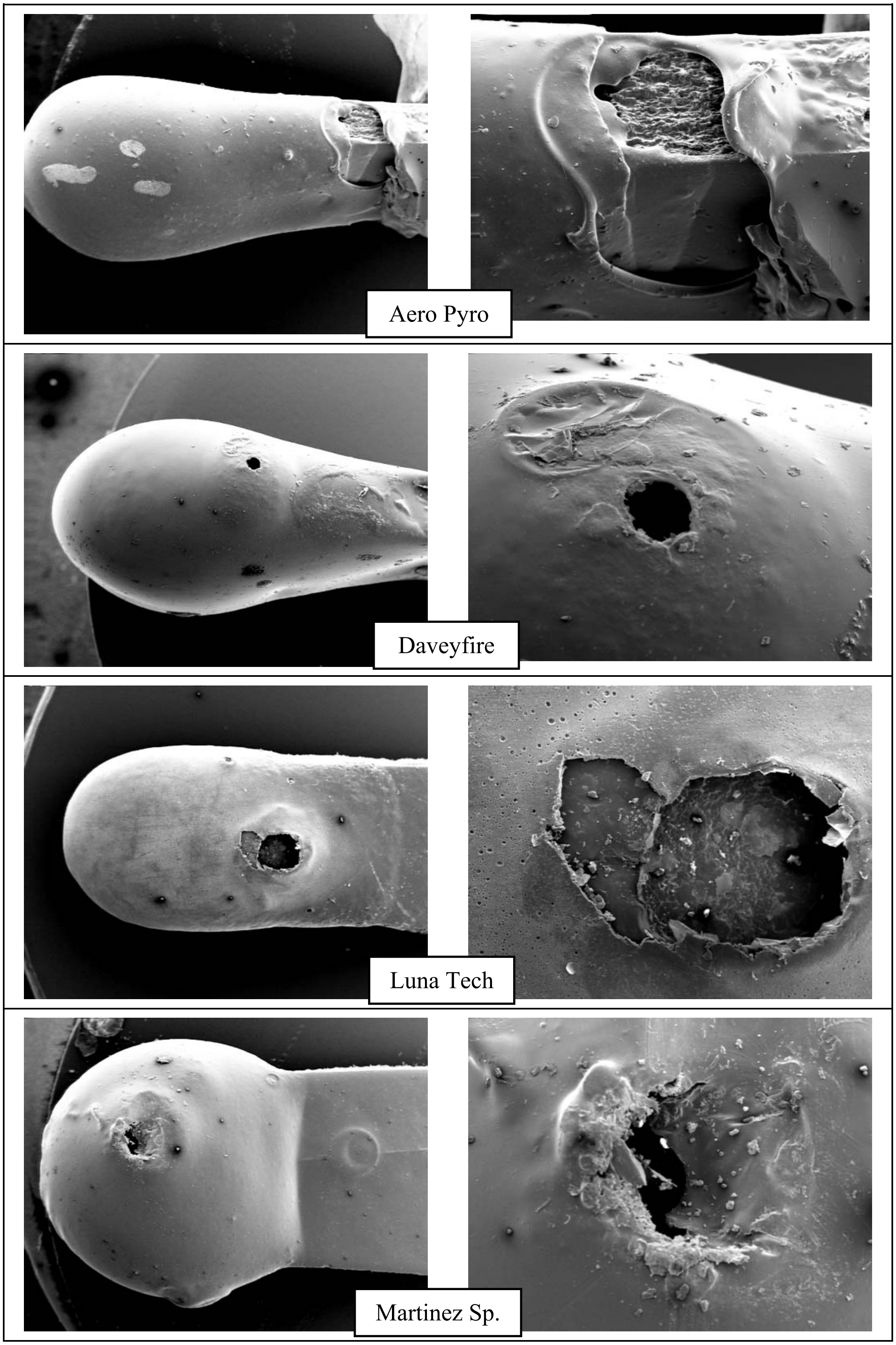

Figure 9. A collection of electron micrographs of imperfections found in some of the e-match tips from the various suppliers, with the image on the right being a close-up view of the imperfection.

Table 4. Minimum E-Match Tip Coating Resistance Measurements.(a)

E-Match Type	Lowest Resistance of Each E-Match Tip (MΩ)(b)										Lowest Resistance (MΩ)	
	1	2	3	4	5	6	7	8	9	10	Of Any(c)	Average(d)
AP	500	500	500	500	500	500	500	500	500	500	>500	>500
DF-B	70	50	500	500	500	500	10	20	500	500	10	300
DF-BR	40	500	500	50	500	500	500	500	500	500	40	400
DF-F	500	500	1	20	500	500	500	500	500	500	1	400
LT-B	<1	3	4	2	3	<1	1	4	2	2	<1	2
LT-F	<1	<1	<1	2	<1	1	<1	3	2	<1	<1	<1
LT-O	20	40	30	60	20	30	60	40	40	<1	<1	30
MS-EM	500	500	500	500	500	500	500	500	500	500	>500	>500
MS-EMM	500	50	300	300	500	500	100	100	500	500	50	300
MS-T	60	<1	2	20	1	3	500	3	<1	<1	<1	60

a) Because of a fairly large uncertainty in the resistance measurements, all values are reported to only one significant figure.

b) This is the lowest single point resistance, in megohms (MΩ), found on each of ten individual e-matches of this type. The reporting of a value of 500 means that at no point on the surface of the e-match tip was the resistance found to be less than 500 MΩ.

c) This is the lowest single point resistance value found on any of the ten individual e-match tips.

d) This is the average of the lowest single point resistances for the collection of ten e-matches. When the lowest resistance value for an individual e-match was >500 MΩ, a value of 500 MΩ was used. When the lowest resistance value was <1 MΩ, a value of 0 was used.

To evaluate the nature of the e-match coating imperfections, a megohm meter, specifically designed to make high resistance measurements, was used to measure coating-to-bridgewire resistances. In stark contrast to typical resistance measuring instruments, this instrument applies a test voltage up to 200 volts (but with very limited current). The intention is that these higher voltages would induce dielectric breakdowns in imperfect e-match tip coatings similar to those produced during an ESD event. One terminal of the instrument was connected to the e-match leg wires, and a test probe—with a small rounded tip—was connected to the other terminal of the instrument. The probe was moved over the e-match tip looking for points with relatively low resistance. (Only those areas of the match tip where pyrotechnic composition was present were investigated.) In most instances, the coatings on the e-matches were found to provide a resistance of more than the maximum instrument reading, 500 megohms (MΩ); however, a fair number of e-match tips had one or more points on their coating where relatively low resistance values were found. The point on the e-match tip found to have the lowest resistance value was noted for each of a collection of ten e-matches of each type. Table 4 has those individual resistance values, plus both the minimum point resistance observed for any e-match tip in each group of ten tips of the same type and the average of the minimum resistance values for each set of ten e-matches. (For comparison, note that the resistance of unglazed Black Powder grains (20 mesh) was found to be in excess of 500 MΩ, and the resistance of glazed Black Powder grains was found to be less than 1 MΩ.) Because of a fairly large uncertainty in the resistance measurements, all values in Table 4 are reported to only one significant figure. (Further, given the nature of dielectric breakdown, the resistance values are expected to depend on the measurement voltage.)

Table 5. Additional Through-the-Composition ESD Test Results.

E-Match Type	Number of Ignitions in 10 trials(a)				
	Without Shroud(b)		With Shroud – 18 mJ(c)		
	18 mJ	180 mJ	g/BP(d)	u/BP(e)	Air(f)
AP	0	2	—	—	—
DF-B	4	(g)	4	1	1
DF-BR	2	(g)	3	0	0
DF-F	6	(g)	3	0	0
LT-B	1	4	—	—	—
LT-F	0	5	—	—	—
LT-O	10	(g)	10	9	10
MS-EM	2	(g)	2	0	1
MS-EMM	7	(g)	7	0	0
MS-T	0	2	0	0	0

a) These tests were performed at 6 kV. To store an ESD energy of 18 mJ, a 0.001 µF charging capacitor was used. To store an ESD energy of 180 mJ, a 0.01 µF capacitor was used.

b) For those e-matches supplied with safety shrouds, they were removed for these tests.

c) These tests were only performed for the e-matches with safety shrouds, and they used the lower stored ESD energies of 18 mJ. The "—" symbol is meant to indicate those e-matches not supplied with safety shrouds, which were not tested.

d) The "g/BP" column is the number of ignitions that occurred when the end of the safety shroud was filled with *glazed Black Powder*.

e) The "u/BP" column is the number of ignitions that occurred when the end of the shroud was filled with *unglazed Black Powder*.

f) The "Air" column is the number of ignitions that occurred when nothing filled the end of the shroud.

g) These e-match types were not tested at the higher ESD energy because there were at least two ignitions at the lower energy.

Through-the-Composition Test Configuration

A limited number of *through-the-composition* ESD sensitiveness tests were conducted. This was accomplished by connecting the positive terminal of the ESD test apparatus to the shunted pair of leg wires of an e-match, connecting the negative terminal of the ESD tester to a steel post, causing the e-match tip to be held in loose contact with the metal post, and applying the ESD energy. As might have been expected, the stair-step (Bruceton) method of testing produced highly variable results. When the e-match tip was well coated, there were no ignitions even with high discharge energy. When there was a significant imperfection(s) in the e-match tip coating, there were ignitions even at low discharge energies. To that extent, the testing served as more of an indicator of when there was a significant coating imperfection as opposed to being purely an indication of the ESD sensitiveness of the e-match composition.

Accordingly, the test was modified from the normal stair-step method. Instead, a collection of ten e-match tips of each type were a tested using a relatively high voltage but storing only a relatively low energy (6 kV with a charging capacitor of 0.001 µF to store energy of 18 mJ). In most cases, when the test produced no ignition of the e-match composition, the ESD spark passed harmlessly over the coated surface of the match. Whenever the first discharge produced no ignition, the same e-match was subjected to two more discharges of the same energy. (On several occasions, an ignition did occur on the second or third discharge. When this happened, it was considered the same as if it had occurred with the first discharge. This was done even though the previous ESD events could have acted to damage the coating to some extent.)

The results of this testing are presented in Table 5 in the column titled "18 mJ", as the number of ignitions in ten trials. Of the ten tests of e-matches of each type, when less than two of them ignited using the 18 mJ stored ESD energy, the test was repeated using a higher discharge energy. In this case, another set of ten e-matches was subjected to ESD energies of 180 mJ (6 kV using an 0.01 μF capacitor). The results of these tests are also reported in Table 5, in the column titled "180 mJ", as the number of ignitions out of ten trials. (Note that in those cases where the manufacturer had provided e-matches with safety shrouds, those shrouds were removed prior to testing.) (It must be expected, under the conditions of these tests, that only a fraction of the energy stored in capacitor C in Figure 8 was successfully delivered to the ESD event.)

Based on the observation of e-match coating imperfections, low coating resistances and the e-match ESD test results reported in Table 5, it seems obvious that coating imperfections afford the ability for ESD events to pass from the bridgewire through the pyrotechnic composition of the match tip. Further, it must be expected that at least on some occasions, damage to e-match tips during use might be sufficient to introduce discharge paths through the composition of e-matches initially with perfect coatings. (Shrouded e-match tips must be significantly less prone to being damaged during use, but in extreme cases, even they could be damaged.) Accordingly, since the ESD protection offered by the e-match coatings can be, or can become compromised, it was decided to perform additional tests to determine the ESD sensitiveness of the exposed e-match compositions themselves.

For these tests, a small portion of the protective coating on the tip of each test e-match was intentionally removed with emery paper before testing. This was done in an attempt to simulate a significant imperfection in the e-match coating or the damage that might occur during prolonged or rough handling and use. In this test series, one terminal of the ESD apparatus was connected to the shunted pair of e-match leg wires, the other terminal of the ESD tester was connected to a metal post, the match tip was held in loose contact with the metal post, and the ESD energy applied. For each e-match type, approximately 20 individual discharge tests were performed, using the standard stair-step method.[9] The data and results of these *through-the-composition* e-match sensitiveness tests are also presented in Table 3, where the test configuration is indicated as "TC". The sensitiveness is reported as the discharge energy that produced an ignition in approximately 50% of the tests. (Note that in those cases where the manufacturer had provided e-matches with safety shrouds, those shrouds were removed prior to testing.)

Regarding ignitions produced by an ESD from the bridgewire through the pyrotechnic composition when the coating is imperfect or damaged (and without safety shrouds), the e-matches can be roughly divided into four groups. Based on these limited results, it would seem that the Aero Pyro and Daveyfire A/N 28 B and BR e-match compositions fall in the most sensitive group (0.5 to 0.8 mJ 50% ignition energy). Somewhat less sensitive (2 to 6 mJ 50% ignition energy) are the Daveyfire A/N 28 F, Luna Tech Flash and OXRAL, and Martinez Specialties E-Max and E-Max Mini e-match compositions. Still less sensitive (20 mJ 50% ignition energy) are the Luna Tech BGZD e-matches. Surprisingly, less sensitive yet (1000 mJ 50% ignition energy) are the Martinez Specialties Titan e-matches.

As a point of comparison, consider that these through-the-composition (TC) ESD ignitions were produced using roughly 100 times less energy than those occurring through the bridgewire. Accordingly, through the composition discharges represent a much greater risk of accidental ESD ignition. Further, shunting the e-matches has no effect in reducing this hazard. Finally, note that most of these 50% ESD ignition energies are a small fraction of the approximate maximum ESD energy (approximately 60 mJ) that can be developed on a typical person (200 pF and 25 kV).[12]

Effect of Safety Shroud and Black Powder

The appearance and design of the safety shrouds, for those e-matches supplied with them, were illustrated above in Figures 2 and 5. The ESD sensitiveness testing with shrouds in place was conducted using much the same method as the through-the-composition testing without shrouds. However, only those e-match types supplied with safety shrouds were tested. The e-matches were used as supplied (i.e., without altering the protective coating over the pyrotechnic composition). One point of electric contact was the shunted leg wires of the e-match, and the other point of electric contact was a flat piece of metal placed across the end of the shroud. In each test, a stored energy of only 18 mJ was used (6 kV stored in 0.001-μF capacitor and discharged through a 100-ohm series resistance).

To test for a variety of possible use conditions, three test configurations were used. In one series of tests, the safety shroud was filled with fine-grained glazed Black Powder (20 mesh). In a second series of tests, the shroud was filled with fine-grained unglazed Black Powder. (Recall that the resistance of unglazed Black Powder grains was found to be in excess of 500 MΩ, and the resistance of glazed Black Powder grains was less than 1 MΩ.) In the third series of tests, the shroud was left empty. In each configuration, a total of ten e-matches were tested. The results of the testing are presented in the last three columns of Table 5.

When filling the safety shroud with glazed Black Powder, note that the presence of the safety shroud apparently provided no decrease in ESD sensitiveness; compare column 4 ("g/BP") with column 2 ("18 mJ" "without shrouds") of Table 5. It would seem the reason is that glazed Black Powder is fairly conductive because of its graphite coating, thus allowing the discharges to gain access to the e-match tips and any imperfections in their coating. In contrast, note in column 5 ("u/BP") that when unglazed Black Powder was used to fill the shroud, there was nearly a total elimination of ignitions (for all but Luna Tech's OXRAL e-matches). Given that the typical grain resistance of unglazed Black Powder exceeds 500 MΩ, such a reduction in the number of ignitions was expected. Finally, in column 6 ("Air") the test with empty (air-filled) shrouds produced virtually the same results found for the tests using unglazed Black Powder.

In the test results for safety shrouds filled with unglazed Black Powder and for empty shrouds, the Luna Tech OXRAL e-matches standout as a notable exception to the reduction in the number of ESD ignitions produced. The apparent reason for this is the limited distance between the end of the e-match tip and the end of the shroud. Typically, this distance is only approximately 0.03 inch (0.75 mm) for the OXRAL e-matches and, under the conditions of these tests, was short enough to allow a discharge to take place even without partially conductive material filling the shroud. (See again Figure 2.) In contrast, the typical distance for the Daveyfire e-match types was approximately five times greater (approximately 0.15 inch or 3.8 mm) and sufficiently great to usually prevent a 6 kV ESD from taking place. In the case of the Martinez Specialty matches, which use short lengths of tubing as safety shrouds to be installed by the user, it is possible to install the shroud with a range of distances between the end of the e-match tip and end of the shroud. For these tests, the e-match tips were installed so that the widest end of the e-match tip (its leg wire end) was pushed just slightly inside the length of tubing supplied.

Additional ESD Discussion

It is perhaps worth reiterating that an ample and well-applied protective coating can offer a high degree of ESD protection. Note that the Aero Pyro e-matches apparently have a double protective coating. Accordingly, while their composition is among the most ESD sensitive, these e-matches tied for producing the least number of intact e-match tip ignitions (zero in ten tests). They equaled the performance of the Martinez Specialty Titan e-matches, which use a composition with approximately a thousand times less ESD sensitiveness. (See again Tables 3 and 5.)

At the time of this writing, it was unclear why two of the Titan e-matches ignited with only 180 mJ of energy in the intact e-match tip ESD tests when the 50% ignition energy was found to be more than five times higher. Laib[13] has suggested that this might be caused by a particularly high percentage of conductive metal particles in the composition. If so, when the coating is intact, the spreading of the discharge energy across numerous potential conductive paths is inhibited by the presence of surface dielectric, whereas the discharge is thus relatively confined to fewer discharge paths in the vicinity where dielectric breakdown through the coating occurs. When the coating is damaged,

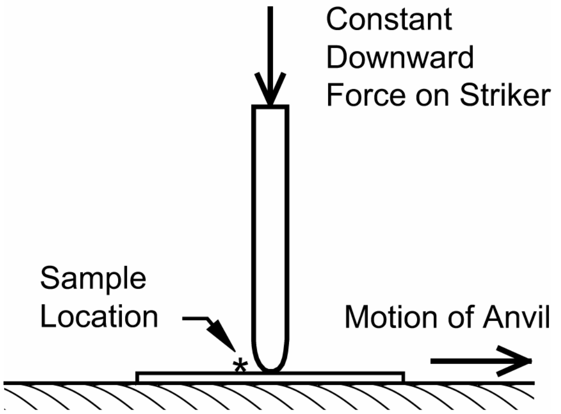

Figure 10. Simplified illustration of a typical friction test apparatus.

more surface conductors are available along with more numerous paths through the material, thus reducing the average ohmic heating available per path, leading to higher required energies.

In interpreting the ESD sensitiveness data presented here, some degree of caution is necessary. The reason is that the conditions for these tests were substantially modified from those commonly used. (This was done in an attempt more nearly to duplicate the typical conditions during use.) Accordingly, the results reported in this article should not be directly compared with other data reported in the general pyrotechnic literature, unless adjusting for the different test conditions being used.

Probably the most important conclusion to be drawn from this study is that, while there is a very wide range of sensitiveness to ESD ignition, under some conditions all of the e-match types could be ignited by an accidental discharge. (If not as a result of an ESD from a person through an e-match with a perfect coating, consider the possibilities of damaged e-match tips or something like a nearby stroke of lightning.) Further, in almost all cases the ESD energy capable of initiating an e-match by a discharge through the composition is very much less than that required for a discharge through the bridgewire. (Note that shunting the e-match leg wires provides no protection against such through the composition discharges.) Finally, some of these 50% ignition energies are so small that they are less than a typical person can feel.[12]

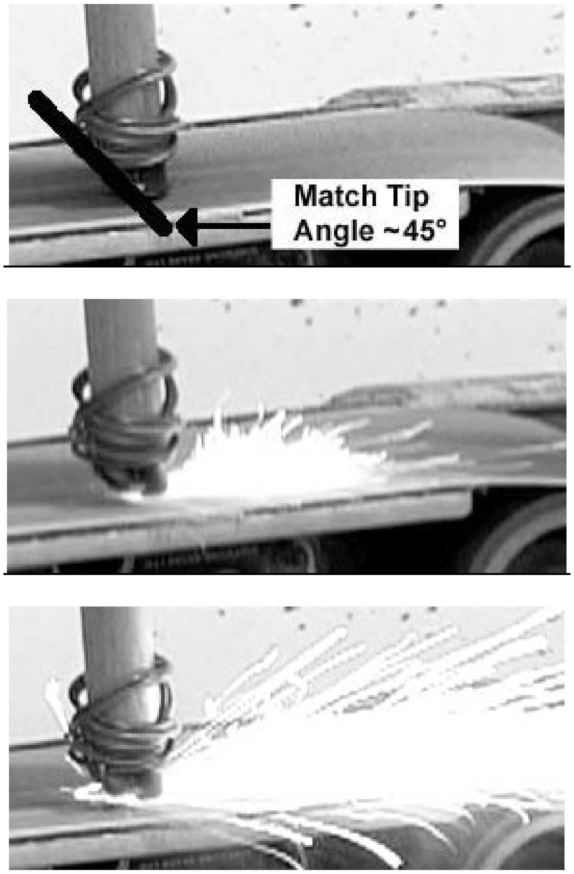

Figure 11. Photographs of the friction test setup as modified for e-matches. There is a time lapse of 1/60th second between images.

Friction Sensitiveness

Normal Configuration

The standard method of friction sensitiveness testing is illustrated in Figure 10. This method works well for loose powders; however, in this case, friction sensitiveness for the intact e-match tips was being sought. Unfortunately, during testing it was found that the standard method was mostly unsatisfactory for intact e-match tips. Often the e-match tips just slid loosely along the surface in front of the striker without ever being caught forcefully between the striker and the abrasive surface. Accordingly, the test setup was modified to use the e-match tip itself as the striker. The tip was supported from behind and held at an approximate 45° angle to a moving abrasive surface, #100 grit sand paper

Table 6. Results of Friction Sensitiveness Testing.

E-Match Type	Force (N)(a)	Time to Ignition w/o BP (s)				Time to Ignition w/ BP (s)			
		1	2	3	Average(b)	1	2	3	Average(c)
AP	1.5	0.37	0.25	0.23	0.28	0.23	0.38	0.25	0.29
DF-B	1.5	0.17	0.20	0.22	0.20	0.25	0.20	0.15	0.20
DF-BR	1.5	0.13	0.25	0.12	0.17	0.15	0.10	0.17	0.14
DF-F	6.0	n/i	n/i	n/i	n/i	n/i	n/i	n/i	n/I
LT-B	3.0	0.20	0.33	0.12	0.22	0.07	0.37	0.56	0.33
LT-F	6.0	n/i	n/i	n/i	n/i	n/i	n/i	n/i	n/i
LT-O	3.0	0.80	0.58	0.32	0.57	n/i	0.38	n/i	0.6(d)
MS-EM	1.5	0.12	0.12	0.10	0.11	0.13	0.28	0.13	0.18
MS-EMM	1.5	0.20	0.22	n/i	0.3(d)	n/i	0.12	n/i	0.2(d)
MS-T	6.0	n/i	n/i	n/i	n/i	n/i	n/i	n/i	n/i

a) This is the minimum applied force that produced an ignition during testing.

b) This is the average time-to-ignition for a set of three e-matches without the presence of Black Powder. “n/i” means no ignition(s) occurred.

c) This is the average time-to-ignition for a set of three e-matches in the presence of Black Powder. “n/i” means no ignition(s) occurred.

d) There were one or two non-ignition(s) observed. The average time to ignition was calculated using twice the longest time to ignition as the time for each e-match failing to ignite during the test. This value is reported to only one significant figure.

(see Figure 11). To configure the test to be somewhat consistent with anecdotal accounts of accidents, it was thought that the force holding the e-match tips against the abrasive surface should be fairly low and the rate of movement along the surface should be fairly high. The combination of a force of 0.33, 0.67 or 1.35 pounds (1.5, 3.0 or 6.0 N) at a rate of movement of 10 feet per second (3 m/s) was found to be reasonably effective for the range of e-match friction sensitiveness of the various e-match types. It must be acknowledged that the test conditions were quite severe (with the e-matches being quickly sanded into non-existence) and that some ignitions could have been produced as a result of frictional heating of non-pyrotechnic elements in the e-matches as they abraded away.

Each test consisted of a set of three trials of the same e-match type and same downward force. For those e-match types failing to ignite during the three trials with the applied force, the next greater force was used for another set of three e-matches. For different e-match types found to ignite with the same applied force, their times-to-ignition were used to discriminate between them in terms of sensitiveness. Ignition times were determined by video taping each test, then playing back the tape and counting the number of individual video fields elapsing before ignition occurred. The raw data from this friction sensitiveness testing and the results are presented in Table 6, with the ignition times in the set of columns labeled “w/o BP”, indicating the testing was performed *without Black Powder* being present. (Note that the testing was performed on bare e-matches without the safety shroud present.)

Friction sensitiveness of the e-matches was found to fall into three groups. In the most sensitive group were the Aero Pyro, Daveyfire A/N 28 B and A/N 28 BR, and the Martinez Specialty E-Max and E-Max Mini; all these e-matches ignited with an applied force of 1.5 N (0.33 lbf). Less sensitive were the Luna Tech BGZD and OXRAL e-matches, which required an applied force of 3.0 N (0.67 lbf) for ignition. Substantially less sensitive still (failing to ignite even with an applied force of 6.0 N (1.35 lbf) were the Daveyfire A/N 28 F, Luna Tech Flash, and Martinez Specialty Titan e-matches.

Configuration with Black Powder and Safety Shrouds

There are a number of anecdotal reports of accidental ignitions occurring when e-matches were being forcefully removed from aerial shell leaders where the e-match was in contact with the Black Powder coating on the black match fuse. Accordingly, it was thought to be appropriate to attempt to determine whether added friction sensitiveness resulted from the presence of Black Powder. In this case, each test e-match was coated with a slurry of Black Powder (fine meal powder bound with 5% dextrin) and allowed to dry thoroughly. (Note that the testing was preformed on bare e-matches without the safety shroud present.) In this series of tests, the same downward force was used as was found to be the minimum capable of producing ignitions without the presence of Back Powder. Using this force, the average time to ignition for a series of three Black Powder coated e-matches was determined. If the presence of Black Powder had little or no effect on friction sensitiveness, it would be expected that the average time to ignition would be roughly the same as found when testing without Black Powder. The raw data and results of this testing are presented in Table 6, with the ignition times in the set of columns labeled "w/ BP", indicating the testing was performed with Black Powder being present. Note that the average times to ignition are all essentially unchanged (i.e., for these test conditions, apparently no increased friction sensitiveness resulted for any e-match in the presence of Black Powder).

Additional friction sensitiveness testing was not performed with safety shrouds present on the e-matches. This is because, during normal use or even abuse, so long as the shrouds survived and stayed in place, it could not be imagined that an ignition would be produced due to friction.

Thermal Sensitiveness

The initial attempt at determining thermal sensitiveness of the complete e-match tips was to insert the various matches into a series of six small wells, 0.25-inch (6-mm) diameter and 0.5-inch (12-mm) deep, drilled into a block of aluminum that was heated electrically. See Figure 12 for an illustration of the thermal test apparatus. The temperature of the block was monitored using a thermocouple inserted into one of the six wells. The power to the electric heating element was adjusted to provide approximately a 5 °C per minute rate of temperature rise in the wells. In preparation for the test, five e-matches of the same type were loaded into the available wells (after cutting off their leg wires). Then, starting at room temperature, the block was heated, and the test continued until all of the test e-matches ignited or until a temperature of 300 °C was reached. Although the temperature of each ignition was noted, the lowest temperature at which any of five test e-matches ignited was considered an indication of their thermal ignition sensitiveness and is reported as "Ramp" ignition temperature in Table 7.

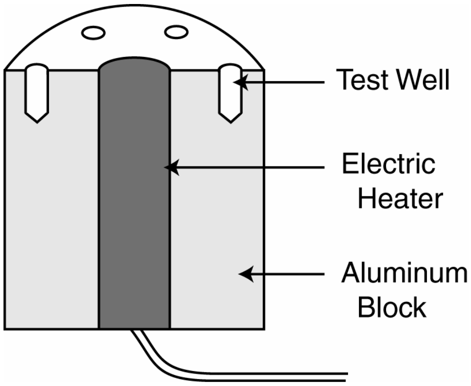

Figure 12. Illustration of the thermal sensitiveness test apparatus.

Even though the rate of temperature rise in the initial testing was fairly rapid (approximately 5 °C per minute), it was found that most of the e-matches being tested decomposed during the heating period without actually igniting. Accordingly, a second series of tests was performed. In these tests, the thermal block was pre-heated to a specific temperature. Then a single e-match tip (with leg wires removed) was placed into a well. The time taken for that e-match to ignite was noted; if the time exceeded 60 seconds, the test was terminated for that temperature. If the e-match did not ignite within 5 seconds, the temperature of the block was increased 20 °C, and the test was repeated using a new e-match tip. The data from this second series of thermal tests are reported in Table 7 as "Time to Ignition" at

Table 7. Results of Thermal Sensitiveness Testing.

E-Match Type	Ramp Ignition Temperature (°C)(a)					Time to Ignition (s) at the Indicated Temperature (°C)							5-Sec Temp. (°C)(b)
	1	2	3	4	5	180	200	220	240	260	280	300	
AP	170	178	192	208	232	19	12	6	2				225
DF-B	165	>	>	>	>	22	12	5					220
DF-BR	245	>	>	>	>	16	10	4					215
DF-F	>	>	>	>	>	>60		>60		>60		>60	>300
LT-B	217	>	>	>	>	>60		>60		9	6	5	300
LT-F	>	>	>	>	>	>60		>60		>60		>60	>300
LT-O	204	205	206	207	209	32		14		5			260
MS-EM	164	>	>	>	>	18		19		10	7	6	≈300
MS-EMM	159	161	162	162	>	29		11		7	5		280
MS-T	>	>	>	>	>	>60		>60		>60		43	>300

a) These are the ramp ignition temperatures for each of five e-match tips tested. Values are listed in order of increasing temperature. The ">" indicates that no ignition occurred below 300 °C.

b) The 5-second ignition temperatures were determined graphically and are reported to the nearest 5 °C.

the temperatures specified. These ignition times were plotted graphically to estimate the 5-second ignition temperature, which was reported in the final column of Table 7 to the nearest 5 °C.

The temperatures found to produce e-match ignitions in these tests are all sufficiently high as to seriously discount the possibility that accidental ignitions caused by thermal sources are likely to be encountered during use on a fireworks display site. Accordingly, it was not thought to be appropriate to rank the different e-match types based on their thermal sensitiveness.

It may be of interest to note that the American Pyrotechnic Association is party to an exemption (DOT-E 11685) allowing the shipment of previously approved fireworks combined with previously approved e-matches. However, one requirement of that exemption is that the e-matches "be certified by the manufacturer to be thermally stable at 150 °C for 24 hours". While a test for this was not conducted, it may be worth noting that, in the ramp temperature tests, several of the e-match types ignited at only slightly higher temperatures.

Additional thermal sensitiveness testing in the presence of Black Powder was not performed. This is because the exterior of the e-matches has a protective coating, and there is no opportunity for the e-match composition to have direct contact with the Black Powder. Accordingly, it is believed that the possibility of the presence of Black Powder having a significant effect on the thermal sensitiveness of e-matches is rather remote. For much the same reason, there was no thermal sensitiveness testing of e-matches with their safety shrouds in place.

Conclusion

Although a large number of individual tests were performed, it is important to recall that this sensitiveness testing was limited in scope and that it must only be considered a screening study. Further, many of the standard tests were modified somewhat in an attempt to better characterize the e-matches in an environment similar to their use for fireworks displays. Accordingly, the statistical precision achieved is only sufficient to approximately characterize and rank the sensitiveness of the various e-matches, and then only under the specific conditions of this testing. For e-matches producing similar results, had additional e-matches been tested or had the conditions been somewhat different, it is possible that slightly different results would have been found. Nonetheless, it is not expected that additional tests or somewhat different conditions would have produced substantially different sensitiveness rankings of the various e-match types.

One further caution is that the e-matches tested were supplied in late 1999. Accordingly, there is no guarantee that current production e-matches have the same sensitiveness characteristics as observed in the tests reported herein.

While there was a large range in sensitiveness observed for the different e-matches under various conditions, none was found to be so extremely sensitive as to preclude their safe use providing appropriate care and safety measures are taken during their use. One obviously appropriate safety measure is to leave the safety shrouds in place on e-matches to be used in any situation where they could be subject to physical abuse. However, probably the single most appropriate safety measure is to educate fireworks display crews of the potential for accidental ignition of electric matches, and the measures to take to minimize both the probability and the consequences of an accidental ignition.[8]

In selecting a supplier of e-matches, it is generally thought to be appropriate to use the least potentially dangerous materials that will successfully and reliably (and economically) perform the needed task. Unfortunately, this study has only reported on the sensitiveness and not on the performance of those e-matches studied. In an attempt to provide some of the additional information needed for users to make the best choice in their selection of e-matches, a second study is under way to characterize the performance of the same ten types of e-matches. As the individual testing is being completed, those results are being reported.[14] Eventually, following completion of the individual tests, a full report will be produced in a companion article to this one.[6]

Acknowledgments

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The authors gratefully acknowledge that the four e-match suppliers provided samples of their products, at no cost, for testing. Further, the American Pyrotechnic Association provided a grant to help cover some of the costs of this study. Note that while many of the company and product names are apparently registered trademarks, they have not been specifically identified as such in this article.

References

1) K. L. and B. J. Kosanke, A series of articles on “Electric Matches:” “General Safety Considerations and Impact Sensitiveness”, *Fireworks Business*, No. 198 (2000); “Sensitiveness to Electrostatic Discharges Through the Bridgewire”, *Fireworks Business*, No. 199 (2000); “Sensitiveness to Electrostatic Discharges Through the Composition”, *Fireworks Business*, No. 200 (2000); “Sensitiveness to Friction and Temperature”, *Fireworks Business*, No. 201 (2000); “Black Powder’s Effect on Sensitiveness”, *Fireworks Business*, No. 202 (2000); “Effect of Shrouds on Sensitiveness”, *Fireworks Business*, No. 203 (2000).

2) Aero Pyro, Inc., PO Box 12853, Reno, NV, 89510, USA. (Has since ceased business.)

3) Daveyfire, Inc., 2121 N. California Blvd, Suite 290, Walnut Creak, CA, 94596, USA.

4) Luna Tech, Inc., 148 Moon Dr., Owens Cross Roads, AL, 35763, USA.

5) Martinez Specialties, Inc., 205 Bossard Rd., Groton, NY, 13073, USA.

6) K. L. and B. J. Kosanke, “A Study of the Construction and Performance Parameters of Electric Matches”, in preparation for the *Journal of Pyrotechnics*.

7) K. L. and B. J. Kosanke, “Introduction to the Physics and Chemistry of Low Explosives, Parts 1 to 3”, *Pyrotechnics Guild International Bulletin*, Nos. 68 to 70 (1990). Reprinted in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 2* (1990 to 1992), Journal of Pyrotechnics (1995).

8) K. L. and B. J. Kosanke, and C. Jennings-White, “Basics of Hazard Management”,

Fireworks Business, No. 129 (1994). Reprinted in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 3* (1993 to 1994), Journal of Pyrotechnics (1996).

9) W. J. Dixon and F. J. Massey, *Introduction to Statistical Analysis*, Chapter 19 "Sensitivity Experiments", McGraw-Hill (1957).

10) S. L. Hingorani, "Electrostatic Discharge Testing of Electroexplosive Devices", *Proceedings of the Pyrotechnics and Explosives Section Meeting*, American Defense Preparedness Association (1990).

11) US Military Standard, MIL-STD 331C.

12) K. Bell and A. S. Pinkerton, "The Fatal Spark", *IEE Review*, Feb. (1992) pp 51–53.

13) G. Laib, private communication (2002).

14) K. L. and B. J. Kosanke, The start of a series of articles on "Electric Matches:" "Physical Parameters", *Fireworks Business*, No. 206 (2001); "Ramp Firing Current", *Fireworks Business*, No. 207 (2001); and "Effective Thermal Output", *Fireworks Business*, No. 217 (2002).

Events Calendar

Pyrotechnics and Fireworks

The Application of Pyrotechnic Principles

June 9–14 2002, Chestertown, MD, USA

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

2002 Mondial SAQ Montreal Fireworks Competition

From June 15 to July 28, for participants and exact dates visit the web site:

web: www.montreal-fireworks.com

Pyrotechnic Chemistry

June 19–21 2002, Sevenoaks, Kent, UK

Contact: Bonnie Kosanke
1775 Blair Rd
Whitewater, CO 81527, USA
Phone: +1-970-245-0692
FAX: +1-970-245-0692
email: bonnie@jpyro.com
web: www.jpyro.com

2002 Les Grands Feux Loto Québec Fireworks Competition

From July 20 to Aug. 7, Montreal Falls Park. For participants and exact dates visit web site.

Contact: Les Grands Feus Loto-Québec
156 Saint-Paul, Suite 100
Quebec City, Quebec, G1K 3W1, Canada
Phone: +1-418-692-3736
FAX: +1-418-692-5650
email: info@lesgrandsfeux.com
web: www.lesgrandsfeux.com

29th Int'l Pyrotechnics Seminar
held in conjunction with
6th Conf. on Life Cycles of Energetic Mat'l.

July 14–19 2002, Westminster, CO, USA

Contact: Alita Roach, Coordinator
Los Alamos National Laboratory
MS P915
Los Alamos, NM 87545 USA
Phone: +1-505-665-6277
FAX: +1-505-665-3407
e-mail: alita@lanl.gov
web: www.intlpyro.org/IPS29.htm

Chemistry of Pyrotechnics & Explosives

July 28–Aug. 2 2002, Chestertown, MD, USA

Contact: John Conkling
PO Box 213
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Phone: +1-410-778-6825
FAX: +1-410-778-5013
email: John.Conkling@washcoll.edu
web: www.John.Conkling.washcoll.edu

2002 HCBS Power Smart Celebration of Light

From July 31 to August 10, for participants and exact dates, visit the web site:

web: www.celebration-of-light.com

British Fireworks Championships

Aug. 3 and 14 2002, Plymouth, UK

Contact: Jim Winship
Phone: +44 (0)1291-628103
FAX: +44 (0)1291-630402

Pyrotechnics Guild Int'l Convention

Aug. 3–9 2002, Fargo, ND, USA

Contact:, Ed Vanasek, Sec. Treas.
18021 Baseline Avenue
Jordan, MN 55352, USA
Phone: +1-952-492-2061
e-mail: edvanasek@aol.com
web: www.pgi.org
Must be member to attend.

British Musical Fireworks Championships

Contact: Carolyn Lowry
Phone: +44 (0)1519-342322
FAX: +44 (0)1519-342326

Energetic Materials

Computational Mech. Assoc. Courses–2002

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

1st Int'l Symp. on Energetic Materials and their Application (ISEM 2002)

May 15–17 2002, Tokyo, Japan

Contact: Prof. Atsumi Miyake
Yokohama National Univ., Dept. Safety Engr.
Tokiwadai, Hodogaya-ku
Yokohama 240-8501, Japan
Phone: +81-45-339-3933
FAX: +81-45-339-4011
email: atsumi@ynu.ac.jp
web: www.icube-t.co.jp/ISEM2002

33rd Int'l Annual Conf. ICT "Energetic Materials – Synthesis, Production & Application"

June 25–28 2002, Karlsruhe, Germany

Contact: Manuella Wolff
Fraunhofer-Inst. für Chem. Technologie (ICT)
P. O. Box 1240
D-76318 Pfinztal (Berghausen), Germany
Phone: +49-(0)721-4640-121
FAX: +49-(0)721-4640-120
email: mw@ict.fhg.de
web: www.ict.fhg.de

12th Int'l Detonation Symposium

Aug 11–16 2002 San Diego, CA, USA

Contact: Sharon Crowder
Phone: +1-925-423-7455
Fax: +1-925-424-3281
email: crowder1@llnl.gov

Int'l Sem. on Energetic Mat'ls, FINNEX 2002

Sep. 9–11 2002 Kittila, Levi, Finland

Contact: Finnish Def. Forces Tech. Res. Ctr.
PO Box 5
FIN-34111, Lakiala, Finland
Phone: +358 3 1815 3211
Fax: +358 3 1815 3486
email: sirpa.kaski@pvtt.mil.fi
web: www.mil.fi/joukot/pvtt/index_en.html

20th Int'l Symp. on Ballistics

Sep. 23–27, 2002, Orlando, FL, USA

Contact: Dr. Joseph Carleone
Aerojet Fine Chemicals
PO Box 1718
Rancho Cordova, CA 95741, USA
Phone: +1-703-247-2588
email: pedmonson@ndia.org
web: www.ndia.org

29th ISEE Conf. on Explosions and Blasting Technique

Feb 2–5 2003 Nashville, TN, USA

Contact: Lynn Mangol
Phone: +1-440-349-4400

13th Int'l Symp. on Chemical Problems Connected with the Stability of Explosives

May 2004 (tentative) Sweden

Contact: Stig Johansson
Johan Skyttes väg 18, SE 55448
Jönköping, Sweden
Phone/FAX: +46-3616-3734
email: srj@telia.com

Multi-Wavelength Laser Opacity Study of a Hybrid Rocket Plume

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ABSTRACT

An instrumentation system was developed to measure the opacity of a hybrid rocket plume as a function of optical wavelength. The source consisted of collineated beams from two lasers, providing seven wavelengths in a single probe beam. Detection was accomplished with a spectrograph equipped with a photodiode array.

Previous work with a two-wavelength system demonstrated the ability to follow the changes in opacity level of a hybrid rocket plume during the various stages of a typical firing cycle. The present work was to investigate the feasibility of using a multiple wavelength system to acquire more detailed information about the particulates present in the hybrid rocket plume.

Qualitative analysis of the plume particulates was done by comparison of the relative extinction coefficients of the laser wavelengths with published extinction coefficient curves from Mie scattering theory. While it was found that light level fluctuations in the system prevent definitive conclusions, the data suggests that the particulate matter in the plume may consist of some optically transparent material. This is in contrast to the absorbing, soot-like material that might be expected in a hybrid rocket plume.

Keywords: combustion diagnostics, rocket ground testing, particle analysis, opacity, aerosol, hybrid rocket

Conversion Chart [English to Metric]

1 lbm = 1 pound mass = 454 g
1 psi = 1 pound per square inch = 0.145 kPa

Introduction

It is desirable to know the characteristics of the particulates present in the plume of a hybrid rocket motor. This information could prove useful in the investigation of combustion instabilities in hybrid motors, and it is important in interpreting other optical plume studies being conducted at the University of Arkansas at Little Rock, Hybrid Rocket Facility (UALR HRF). To this end, a system is being developed to measure the plume particulate characteristics via opacity measurements fit to Mie scattering theory.

For many, Mie scattering theory (developed by G. Mie in 1908) may not be familiar. Mie scattering is characteristic of spherical particles, such as aerosol droplets, for which all wavelengths of incident light are scattered equally. This is in contrast to the more-familiar Rayleigh scattering, the selective scattering of shorter wavelengths by particles that are non-spherical, such as carbon char and soot. Mie scattering is described by a series of infinite terms and, given enough computer time, it can provide a rigorous solution for spherical particles. However, rapid approximations can be used for particles larger than about 5 μm and smaller than about 0.1 μm.[1,2]

Also, “absorbing” and “non-absorbing” particles will be discussed. Absorbing particles are those such as carbon char or soot, which scatter and absorb part of the incident light. An aerosol droplet of India ink would also be an absorbing particle. Non-absorbing particles are transparent, such as aerosolized water droplets, which transmit most of the incident light.

Previous work done at UALR[3] led to the development of a dual wavelength, laser based, opacity measurement system. That work investigated the feasibility of using a laser-based system for plume opacity measurements. The dual wavelength system, consisting of the 633 nm

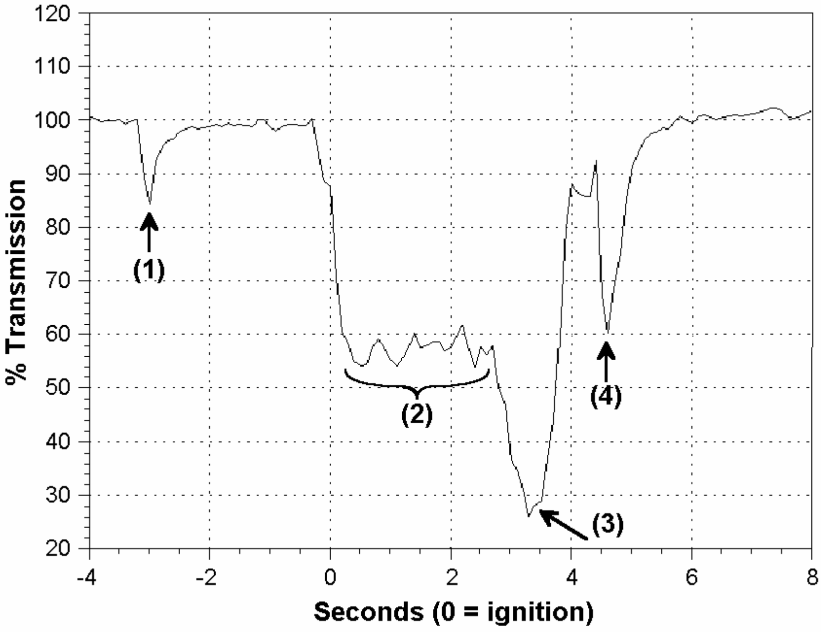

Figure 1. Plot of a single wavelength measurement of percent transmission.

helium-neon (HeNe) laser line and the 488 nm argon ion (Ar^+) laser line, demonstrated the ability of a laser based opacity system to accurately follow the stages of a typical rocket firing at the UALR HRF.

While the dual wavelength system also demonstrated spectral variations in plume opacity, it was not capable of providing concrete information about the nature of the particulate matter. Results from the study did not fit the expected absorbing characteristics of soot particles, but instead indicated the possibility that the particulate matter in the hybrid rocket plume was of a non-absorbing optical nature.

The current work, with a total of seven laser lines for measurement instead of two, sought to extract further information about the optical and physical properties of the plume particulates.

Rocket Plume Opacity

In both the prior and current studies, the stages of a rocket firing sequence are well defined. For reference, a plot of a percent transmission (%T) trace from a single wavelength measurement is shown in Figure 1, and a corresponding description of the stages in a rocket firing follows:

1) At $\tau = -3$ seconds ($\tau = 0$ is the time of motor ignition) oxygen flow to the motor is started. This sudden rush of high pressure oxygen blows out whatever dust or soot is left in the fuel grain from grain manufacture or a previous motor firing. This puff of dust, readily visible to the naked eye, momentarily occludes the probe beam, providing a consistent time marker for the start of the firing cycle.
2) At $\tau = 0$ seconds, the igniter flashes and the fuel grain ignites. The plume opacity increases (%T decreases) as the motor climbs to a steady burn condition, during which time the plume opacity stabilizes at a constant level. Fluctuations in the plume opacity during this phase of the firing are consistent with fluctuations in the rocket chamber pressure and with apparent plume brightness.
3) At approximately $\tau = 2.6$ seconds, the oxygen flow to the motor is shut down, and the motor transitions through a fuel-rich condition as the remaining oxygen in the motor bore is consumed. This sooty, fuel-rich combustion greatly increases the plume opacity. As combustion subsides, pressure in the motor chamber decreases and less smoke is emitted, causing plume opacity to decrease.

4) The last feature of the %T trace occurs at approximately τ = 4.5 seconds, when a nitrogen purge of the motor begins. At this point, smoke accumulated in the motor chamber is expelled, again causing a brief increase in plume opacity. In some cases, the motor continues to smoke for several seconds, preventing the %T trace from returning to 100% before the end of data acquisition. This is of no consequence in this work.

Experimental

Rocket and Firings

All rocket motor plume studies were carried out using the lab-scale system of the UALR HRF, a 2 × 10-inch (51 × 254 mm), gaseous oxygen system with computer control. Fuel for the firings consisted of hydroxyl terminated polybutadiene (HTPB) with 1% by weight graphite additive, a standard fuel grain formulation used at the UALR HRF. Five firings were run at an oxygen mass flow of 0.06 lbm/s to assess the repeatability of the measurements. An additional 14 firings were run with oxygen mass flows between 0.04 and 0.13 lbm/s, giving a variety of conditions. Pressures during these firings were typically held between 200 and 500 psi. Additional details of the rocket and its feed and control systems can be found in previous papers.[4–6]

Apparatus

The experimental apparatus consists of two laser sources, optics for beam collineation and positioning, a spectrograph with photodiode array (PDA) detection, and a portable computer for data acquisition. A diagram of the system is shown in Figure 2.

Probe Beam

The probe beam is constructed by collineating the beams from two lasers. The first laser is a Spectra Physics model 162A-07 Ar$^+$ laser powered by a model 262 Exciter. The model 162A-07 is a single-line laser with a high reflectance Littrow Prism for line selection; however, for this work, the prism was replaced with a Melles Griot Extended MAXBRIte™ mirror. This produced an output beam consisting of the

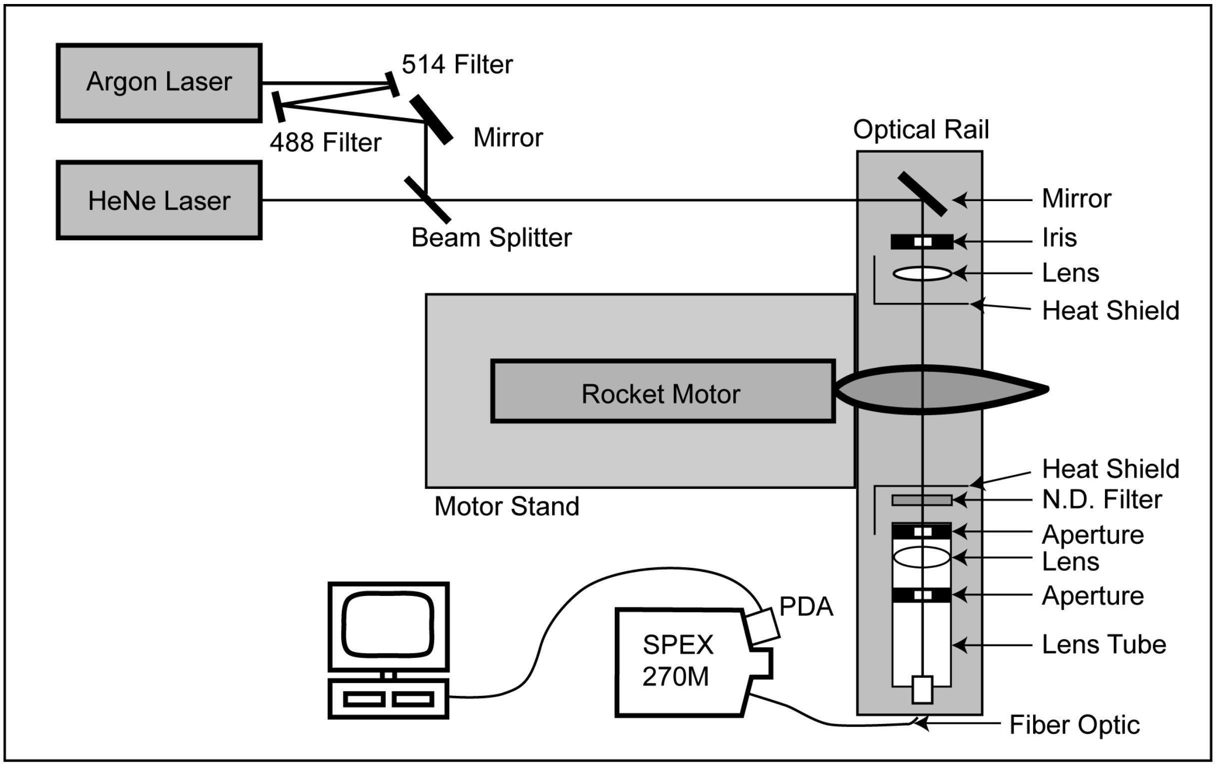

Figure 2. Diagram of opacity measurement system.

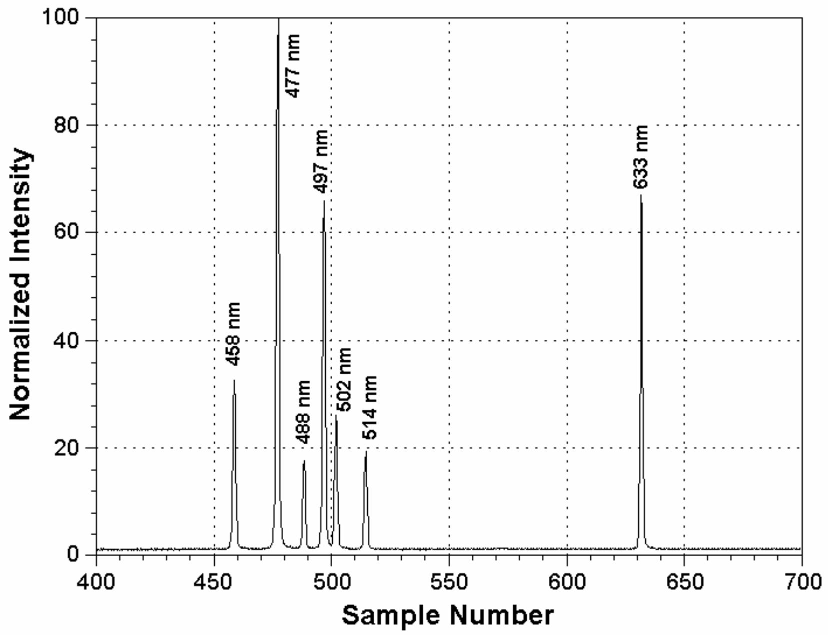

Figure 3. Relative intensities of the laser lines.

following laser lines (rounded to the nearest whole nanometer): 458, 477, 488, 497, 502, and 514 nm. The total power in the Argon laser beam was adjustable to 60 mW.

The 488 and 514 nm lines are more than an order of magnitude stronger than the 502 nm line. This presents a potential problem with the dynamic range of the detector, so line pass interference filters were used as mirrors to reduce the intensity of the 488 and 514 nm lines. While this greatly reduced the total power of the multiline beam, the power was more than sufficient for this work.

The second laser is a Siemens LGK 7626 HeNe laser with an output power of 20 mW. A neutral density filter is used to attenuate the HeNe laser output to match the final level of the Ar^+ laser beam. The HeNe laser beam is combined with the Argon laser beam using a 50/50 beam splitter, as illustrated in Figure 2. A plot of the relative line intensities in the probe beam is shown in Figure 3.

Optics

After the two laser beams are combined, the resultant probe beam is directed to an optical rail mounted at the rear of the rocket motor. A mirror redirects the beam in a direction perpendicular to the motor axis. After passing through an iris used for alignment reference, the probe beam is focused through the plume with a 60 cm focal length lens. After passage through the plume, the probe beam is attenuated by a neutral density filter to cut it to a level suitable for PDA detection. The beam then passes through a 2.5 mm aperture into an enclosed lens tube. Inside the lens tube, the beam is focused by a 25 mm focal length lens through another 2.5 mm aperture. The resulting expanded beam is then incident on the input end of a fiber optic cable. This cable consists of multiple fibers that form a circular aperture at the entrance to the cable and terminate in a slit-shaped aperture at the exit end of the cable. The slit aperture end of the cable is used to couple the probe beam light into the spectrograph.

The purpose of expanding the probe beam before it enters the fiber optic cable is to insure that it completely covers the fiber aperture. If the beam were sharply focused onto the fiber aperture, it would only illuminate some of the fibers in the cable. Slight movements of the probe beam, caused by rocket motor vibrations, would change the beam entrance and exit positions, leading to changes in the detected intensity of the probe beam. Expansion of the probe

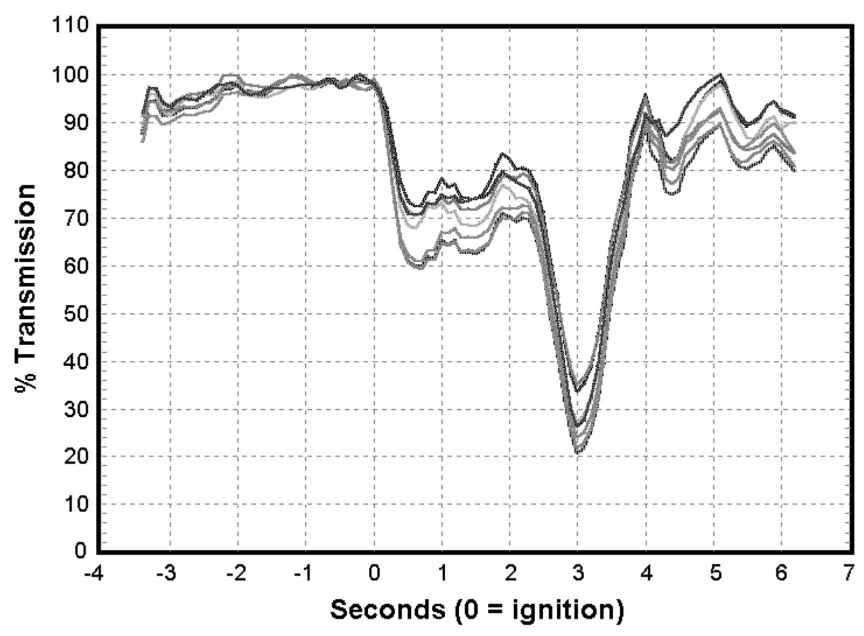

Figure 4. Percent transmission vs. time for the seven laser lines.

beam to a size that covers the fiber aperture provides more uniform illumination of the fibers, significantly reducing the effects of vibrations.

Detector

The spectrograph used in this work was a SPEX 270M with an EG&G Reticon RL1024-SAQ-011 photodiode array and RC1000LNN-011 motherboard.[7] The video output from the PDA system was read with a Computer Boards 1600 A/D converter card (12-bit resolution) in a Best Computer 386-SX portable computer running an in-house generated software package called ESPEC. A 60 µm entrance slit width and 27 ms integration time were used for all motor firings, and scans were taken at 100 ms intervals. For each motor firing, data acquisition was begun at approximately three seconds before ignition and continued for a total of ten seconds.

System Noise

After a suitable warm-up time, the signal from the PDA, with no probe beam, was about 40 A/D counts, or slightly under 1% of full scale. Output values of pixels not corresponding to laser wavelengths remained around the 40-count level during motor firings, indicating essentially no response to optical noise from the plume. There were some fluctuations in the measured intensities of the laser lines, however. The fluctuation levels of all but the 477 nm line were at or below ±4%, while the fluctuations of the 477 nm line were ±9%. A moving average with a bin width of 0.3 seconds was applied to the data during processing, reducing the above figures to ±3% and ±7%, respectively.

Data Analysis

Each data file from a rocket firing consists of A/D counts for 100 scans of 1024 pixels each. The data analysis was performed with software written for the project, and run in Windows95 on a Pentium PC. For each scan, the software finds the pixels corresponding to the seven laser lines and finds the value of these peaks. The software then applies a moving average (0.3 second bin width) to the data and creates seven data plots of A/D count as a function of scan number, one plot for each of the laser lines. Next, the A/D count value that corresponds to 100% T for each laser line is calculated from the portion of the data before motor ignition. A time scale is then calculated from the data scan numbers, and %T as a function of time is plotted for the laser lines. A typical plot is shown in Figure 4.

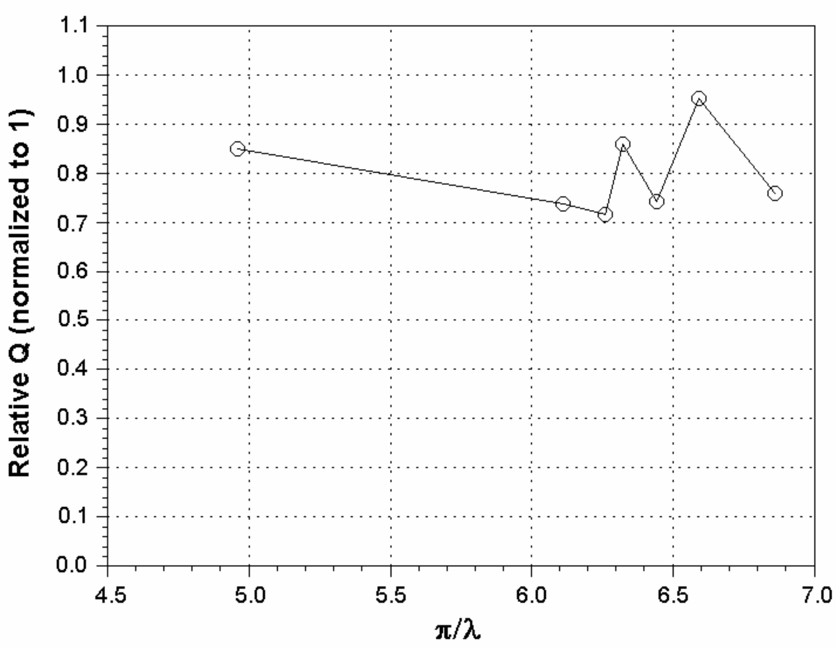

Figure 5. Average of the relative scattering coefficients for five firings at 0.06 lbm/s oxygen flow.

In order to compare the opacity measurement results to Mie scattering curves, the relative scattering coefficients (Q) for the seven laser lines must be calculated. Ratios of Q values can be obtained from %T as follows:

Transmittance (T) is defined[1] as

$$T = \frac{I}{I_0} = \exp\left[-naQt\right] \qquad (1)$$

where,

I = light intensity transmitted through the plume

I_0 = light intensity with no plume

n = number of particles per unit volume

a = cross sectional area of a particle

t = path length through the plume

Taking the natural logarithm of both sides of equation 1 yields

$$\ln T = -naQt \qquad (2)$$

Correspondingly, for two measurement wavelengths,

$$\ln T_1 = -naQ_1t \qquad (3)$$

$$\ln T_2 = -naQ_2t. \qquad (4)$$

Dividing equation 3 by equation 4 and canceling like terms yields

$$\frac{\ln T_1}{\ln T_2} = \frac{Q_1}{Q_2} \qquad (5)$$

The relative scattering coefficients are calculated from the natural logarithm of transmittances and normalized by setting the highest Q equal to one. Plots of scattering coefficients are often plotted as a function of particle size parameter (α) that is given by

$$\alpha = \frac{\pi d}{\lambda} \qquad (6)$$

where,

d = particle diameter

λ = the wavelength of light in the medium

The relative Q values are calculated from the average T exhibited by each laser line during the steady state burn portion of the firings. Since the particle diameter is not known, the relative Q values are plotted against π/λ, as shown in Figure 5. These plots are then compared to published plots of scattering coefficients, as predicted by Mie scattering theory. A sample of such plots is shown in Figure 6.

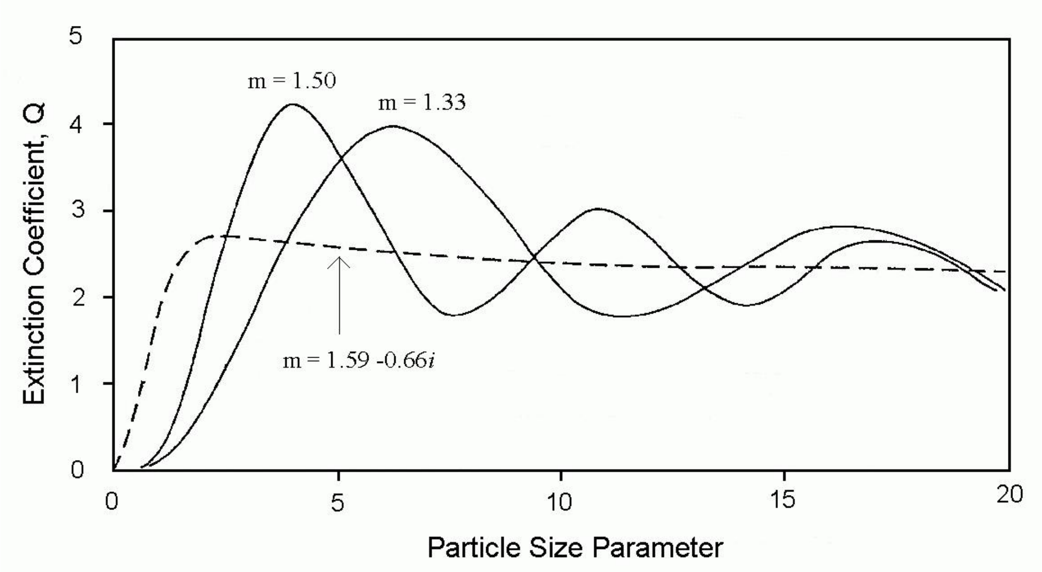

Figure 6. Typical plot of extinction coefficients from Mie calculations. The dashed line is characteristic of absorbing particles, while the solid lines are characteristic of non-absorbing particles.

Results and Discussion

From Figure 6 it is apparent that *Q* decreases monotonically with increasing α for absorbing particles, and that *Q* oscillates with decreasing magnitude as α increases for non-absorbing particles. The plots for non-absorbing particles in Figure 6 indicate the general trend followed by *Q* values for these particles, but they do not reveal the additional fluctuations that are typical of non-absorbing particles.[1] Though it was expected that the particulate matter in the hybrid plume would consist of absorbing soot particles, the relative scattering coefficients do not follow a pattern consistent with that of absorbing particulate matter. Instead, the data suggests that the hybrid plume particulates may be primarily non-absorbing in nature. An investigation of the validity of the data led to the following observations.

Although the laser lines in the probe beam exhibited random fluctuations, the fluctuations in the *Q* values for this work cannot be the result of such random noise. The data in Figure 5 is an average of the relative *Q* values for the five rocket firings that were conducted at 0.06 lbm/s oxygen flow rate. If the fluctuations were due to random noise, they would have, at least partly, averaged out. Furthermore, almost all of the data runs exhibited relative *Q* values that followed the same general oscillatory pattern. For this reason, the oscillations are accepted to be resultant from the optical nature of the plume.

One possible explanation for the *Q* oscillations is a lensing effect from the heat of the plume, causing beam steering. The plume can approximate a cylindrical lens, since it has that shape and the hot gases are of a different refractive index from the surrounding atmosphere. However, this explanation is unlikely for two reasons:

1) A lensing effect would affect the laser lines in a more or less monotonic manner (i.e., the effect would not be so radically variant with wavelength).
2) The probe beam was centered in the plume cross-section to within 0.5 mm, minimizing any lensing effect that might occur if the probe beam were off-center.

It is not expected that the *Q* variations in the data are due to beam steering effects.

At this time, it is impossible to know exactly what the *Q* fluctuations indicate about the plume particulate characteristics, but they may well be part of the fluctuations in curves for normal, non-absorbing particles. A rigorous regression analysis of the data to fit Mie scattering theory would provide more information. Such an approach has been used with some success in measuring aluminum oxide (Al_2O_3) particulates in the plumes of solid rocket motors.[8]

Conclusions

Results from this study and the previous measurements conducted with the dual wavelength system suggest the presence of non-absorbing particulate matter in the hybrid rocket plume. While the exact nature of this matter cannot be determined by these methods, the data seem to show that aerosol droplets of some nature exist in the plume. These droplets can only have come from the fuel-grain polymer material, and strongly indicate that the fuel goes through a melt stage, at least partially, during the burn process. This is not in agreement with the presently accepted model that the fuels pyrolyze through a charring process. If this is true, the actual combustion process likely consists of both charring and melting of the polymer fuel, and it may explain some of the combustion instabilities that exist (pressure pulsing, etc.) for the hybrid class of rocket motors.

Certainly, this multi-wavelength system provides more detailed plume particulate information than the dual wavelength system. Current efforts to improve overall system performance are focused on enhancing laser line stability, including additional spectral lines, and on developing the computational tools for calculating extinction coefficients and fitting data to Mie scattering models.

Acknowledgments

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References

1) W. C. Hinds, Aerosol Technology—Properties, Behavior, and Measurement of Airborne Particles, John Wiley and Sons, New York, 1982.

2) T. T. Mercer, Aerosol Technology in Hazard Evaluation, Academic Press, New York, 1973.

3) M. K. Hudson, A. P. Chouinard, A. J. Adams, C. B. Luchini, and J. D. Willis, “Multi-Wavelength Opacity Study of a Hybrid Rocket Plume”, AIAA Paper No. 96-2833, July 1996.

4) R. B. Shanks and M. K. Hudson, “The Design and Control of a Labscale Hybrid Rocket Facility for Spectroscopy Studies”, AIAA Paper No. 94-3016, June 1994.

5) R. B. Shanks and M. K. Hudson, “A Labscale Hybrid Rocket Motor for Instrumentation Studies,” *Journal of Pyrotechnics*, No. 11 (2000) pp 1–10.

6) R. B. Shanks, “A Labscale Hybrid Rocket Motor and Facility for plume Diagnostic and Combustion Studies,” A Doctoral Dissertation, University of Arkansas at Little Rock, December 1994.

7) D. Snider, M. K. Hudson, R. Shanks, and R. Cole, “Evaluation of Photodiode Arrays for Use in Rocket Plume Monitoring and Diagnostics”, *Proc. Ark. Acad. Sci.*, Vol. 48 (1994) pp 177–180.

8) D. Laredo and D. W. Netzer, “Application of Optical Diagnostics to Particle Measurements in Solid Propellant Rocket Motors and Exhaust Plumes”, Naval Postgraduate School, Monterey, CA, 1994.

A Note on the Design of Experiments

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Introduction

In this note, we will speak about the general design of an experiment and some factors to be considered.

An experiment is used here to mean the deliberate causing of some physical event combined with the taking of data related to the event and the reduction of the data to useful information. This definition does not preclude the repetition of an experiment, although good practice might include iterative modifications to better accommodate the goals of the experiment.

A properly designed experiment will allow a maximum of useful information to be obtained and a low probability of lost data,

Background

The fundamental process of data acquisition, reduction, and analysis is as follows:

- A physical event occurs.
- A transducer changes some physical manifestation of the event into a form that may be recorded.
- A record is made.
- The record is examined, and perhaps transformed in some way, and useful information is obtained.

In an ideal world, we would be able to directly record every physical manifestation of any event with perfect fidelity, assign correct values, and obtain all the information that is desired and available. In the real world, as you might expect, things are a bit different.

Let us examine a few examples that will illustrate some of the problems.

Investigator Desires To Find Out How Loud a Firecracker Report Is

Simplest Method

1) Light one firecracker.
2) Retire to a safe distance.
3) Listen to report of firecracker.
4) Record in notebook—“medium loud”.

Possible Advantages and Problems of Simplest Method

1) Quick, easy, inexpensive.
2) Firecracker used may not be representative. What if it fizzes and spins around on the ground? Does the investigator conclude that firecrackers don’t make a report?
3) How does the distance affect the noise? What if the investigator knows that this firecracker will not hurt his fingers and holds it up to his ear? What if the safe distance is arbitrarily set to be 10,000 meters?
4) Does the transducer (the ear of the investigator) affect the result? What if the investigator is deaf? What if the investigator is only partially deaf?
5) How useful is the result?

More Complex Method

1) Light 25 randomly selected firecrackers from the group of interest at 1-minute intervals.
2) Retire to a distance of 10 meters.
3) Panel of 25 firecracker aficionados, also located at 10 meters from the firecracker, listen to reports.
4) Each member of the panel assigns a numeric value to the perceived loudness of each report.
5) Write the individual reported values in notebook.

Possible Advantages and Problems of the More Complex Method

1) Probably reasonable representation for this type of firecracker.
2) Probably, but not necessarily, a good cross-section of transducers.
3) Was the distance appropriate for the type of firecracker?
4) Was the time interval sufficient to allow the transducers to "re-zero"?
5) How does one calibrate each (set of) transducer(s), such that each value reported may be compared?
6) How does one report the results? What does "7.28" mean?

More Sophisticated Modern Method

Pre-test Section

1) Gather available equipment to acquire, record, and analyze the firecracker report.
2) Investigate the strengths and limitations of the equipment.
3) Perform at least a minimal analysis of the interactions between the physical event and the sequent measurements.
4) Perform a minimal experiment (pre-test) to test the validity of step 3, and adjust as required to stay within the calibration limits of the equipment.

Sample notes from pre-test investigation of the equipment available:

Microphone: linear response 60–140 dB; frequency response 5 to 30 KHz; output from microphone amplifier 0.01 V/dB.

Values for four firecrackers, measured at 2.5 meters, were between 110 and 120 dB.

Bits of debris were found at 4 meters.

Digital oscilloscope (DSO) has input ranges of 0–1 V, 0–5 V and 0–10 V; a maximum of 4000 data points per trace; and time per point rates of 1, 2, 5, 10, 20, 50 × 10^{-6} second.

Computer still has 100 MB of storage space available.

Test Section

1) Set up firecracker test stand and calibrated microphone at 5 meters horizontal distance, and 3 meters from ground. This will help avoid overloading microphone and possible damage from debris, set DSO to trigger from sound with a pretrigger of 2000 points, a sensitivity of 2 V full scale, and a time per point of 10^{-6} seconds.
2) Fire and transfer to separate computer files the results of firing 20 randomly selected firecrackers from the group of interest.
3) Assign time and dB values to each data point recorded.
4) Obtain the statistics, and "interesting information" for each test, and for the test aggregate.
5) Record the statistics and waveforms obtained in notebook.

Why did we do this?

From the capabilities of the equipment and the preliminary test, the following decisions were made:

1) The microphone had an upper frequency response of 35 KHz, so that data would have to be taken at a minimum of 70,000 data points per second to be within the Nyquist limit, or an analog filter would have to be interposed between the microphone and the DSO.
2) The next higher data rate available above 70,000 points/second was 100,000 points/second (10^{-6} seconds/point), which, for a maximum data collection length of 4000 points, would allow a data collection time of 0.040 seconds.
3) The report of a firecracker seemed to take no more than 0.005 second, so that ± 0.020 seconds from the trigger point would be more than enough data.
4) The fuses on firecrackers are not sufficiently accurate in timing to allow triggering from fuse ignition, so data acquisition was triggered from the sound itself.
5) Since we expected some variation in sound, we set the sensitivity of the DSO to the next available range which would allow recording

any expected peaks without clipping and without sacrificing too much sensitivity.

6) Data was transferred to a computer for semi-permanent storage because we don't know ahead of time what we might see, unexpectedly, in the data.

Since the cost of equipment is always a consideration for both the professional and non-professional, the author suggests that whatever money is available be spent as wisely as possible. In general, the author believes that this end is best achieved by obtaining, to the extent possible, equipment that is as flexible and precise as possible to allow for future uses that may be unseen at the present.

At the present time, with judicious selection, it is possible to obtain analog-to-digital data acquisition cards for use with an inexpensive computer. Many of these cards have multiplexed inputs for multiple channels of single ended or differential input at cumulative rates well exceeding 100,000 samples per second with a 16-bit precision and cost less than US$500. Other cards may offer increased precision, higher data acquisition rates, on-board signal conditioning, and other possibly useful features. It will usually be found that a working knowledge of programming will greatly benefit the investigator's equipment budget.

Such a card and a very basic computer will allow many different sorts of potentially accurate measurements to be made. Furthermore, the data collected from such a system may be analyzed, massaged, tweaked, folded, spindled, and mutilated as much as the investigator desires, without ever losing the original data.

An analysis of the entire system to be used in a particular experiment may also yield a way to achieve acceptable accuracy without resorting to other expensive equipment and calibration techniques.

Air Pollutant Emissions from Power Plants

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An examination of the issue of pollution resulting from fireworks displays in contrast to power plant emissions was chosen as a seminar topic during a pyrotechnic chemistry workshop, sponsored by the Partnership for the Advancement of Chemical Technology (PACT) at Miami University, Middletown, Ohio, July 2001.

This brief article presents some of the information found while preparing that seminar. The following are some of the statements found in the literature regarding pyrotechnic pollution: The presence of heavy metals in harbor sediments has been attributed, in part, to frequent fireworks displays over these bodies of water.[1] A study of the accumulation of heavy metals on the bottom of the World Showcase Lagoon at Walt Disney World's EPCOT Center, Florida, included sampling done before the start of nightly pyrotechnic displays as well as continued sampling during the succeeding decade.[2] Special effects during theatrical productions present potential health hazards to the audience.[3] The presence and persistence of pyrotechnically produced aerosols has provided the means to test instrumentation developed for monitoring air quality in real-time, or for on-line analysis of aerosols.[4,5] The abundance of air-born particulates, attributed to fireworks by mass spectrometry or by laser-induced breakdown spectroscopy analysis, increased around July 4, when fireworks are more frequently used.[4,5]

In an attempt to put the above concerns into perspective, US Environmental Protection Agency (EPA) data on emissions from fossil-fueled power plants were examined.[6] This EPA publication listed estimates of hazardous air pollutant (HAP) emissions from fossil fuel electric utility steam generating units. The results of emissions test data from 52 units provided the basis for projecting average annual emissions for each of the 684 power plants. The data was obtained from extensive emission tests performed by Electric Power Research Institute (EPRI), Department of Energy (DOE), the Northern States Power Company, and EPA. Tables 21, 22, and 23 of the EPA publication listed the total inorganic HAP emissions from coal-fired, oil-fired, and gas-fired utility steam generating units, respectively. Tables 24, 25, and 26 of the EPA publication presented the total organic HAP emissions. The quantity of each type of fossil-fuel facility could not be found in the publication, so a listing of the 1990 total emissions for each HAP for the three different fuels burned is reported in Table 1 on the next page. The sum of these three fuels would be the estimated annual total for 1990 from all 684 power plants. Since a typical pyrotechnic fireworks display lasts 20 minutes, the total pounds of each HAP that would be emitted during 20 minutes were calculated and are tabulated in Table 1 beside the annual average tonnage per plant.

It is hoped that the information about US power plant emissions will aid in assessing the relative contribution produced by fireworks.

References

1) Doris Gnauck White , "Pollution Caused by Fireworks" *American Laboratory*, (October 1996) pp 24–26.

2) Thomas A. DeBusk, Jeffrey J. Keaffaber, Benedict R. Schwegler, Jr., and John Repoff, "Environmental Effects on Bodies of Water" *Proceedings of the 1st International Symposium on Fireworks*, Montreal Canada (1992) pp 92–102.

3) Monona Rossol, "Health Effects from Theatrical Pyrotechnics" *Journal of Pyrotechnics*, No. 3, (1996) pp 14–21.

4) J. E. Carranza, B.T. Fischer, G.D. Yoder, D.W. Hahn, "On-line Analysis of Ambient Air Aerosols Using Laser-Induced Breakdown Spectroscopy"; *Spectrochimica Acta Part B—Atomic Spectroscopy*, Vol. 56, No. 6 (2001) pp 851–864.

5) Don-Yuan Liu, Don Rutherford, Matt Kinsey, Kimberly A. Prather, "Real-Time Monitoring of Pyrotechnically Derived Aerosol Particles in the Troposphere", *Journal of Analytical Chemistry*, Vol. 69 (1997) pp 1808–1814.

6) EPA Office of Compliance Sector Notebook Project, *Profile of the Fossil Fuel Electric Power Generation Industry*, September, 1997 EPA/310/R-97-007; www.epa.gov/tio/download/toolkit/fossilsn.pdf

Table 1. Emissions from Fossil-Fueled Electric Generation Plants.[6]

Inorganic HAPs	Coal-Fired tons	Oil-Fired tons	Gas-Fired tons	Total of all 684 Plants tons/yr	lbs/20 min
Antimony	11			11	0.84
Arsenic	54	5	0.16	59.16	4.50
Beryllium	6.6	0.45		7.05	0.54
Cadmium	1.9	1.7	0.054	3.654	0.28
Chromium	70	4.7	1.2	75.9	5.78
Cobalt	21	20.3	0.14	41.44	3.15
Hydrogen chloride (HCl)	137000	2870		139870	10644.60
Hydrogen cyanide (HCN)	240			240	18.26
Hydrogen fluoride (HF)	19500	144		19644	1494.98
Lead	72	10.6	0.44	83.04	6.32
Manganese	180	9.5	0.37	189.87	14.45
Mercury	51	0.25	0.0016	51.2516	3.90
Nickel	48	389	2.3	439.3	33.43
Phosphorous	270	68	1.3	339.3	25.82
Selenium	190	1.7		191.7	14.59
Organic HAPs					
Acrolein	28			28	2.13
Benzene	21	0.88	1.8	23.68	1.80
Carbon disulfide	37			37	2.82
Carbon tetrachloride	28			28	2.13
Chloroform	28			28	2.13
Isophorone	200			200	15.22
Methylene chloride	110			110	8.37

The following article was reprinted from *The Technology of Natural Resins*, by C. L. Mantell, C. W. Kopf, J. L. Curtis, and E. M. Rogers, John Wiley & Sons, Inc. (1942) pp 14–21.

Chapter III — Accroides

Gum accroides is the resinous product obtained from various members of the species *Xanthorrhoea of* the natural order *Juncaceae*, which occurs throughout Australia and Tasmania in red and yellow forms. The resin is also known as red gum, gum acaroid, grass tree gum, “Black Boy” gum, yacca or yacka gum, and Botany Bay resin. The last-named resin is relatively scarce. The yellow variety is the product of *Xanthorrhoea hastilis*. All other *Xanthorrhoea* trees yield the red resin. The bulk, of commercial red gum is obtained from South Australia and Kangaroo Island and is the product of *Xanthorrhoea tateana*.[1]

The *Xanthorrhoea* trees grow slowly and usually attain a height of 7 or 8 feet before branching into a tuft of rushlike leaves about 3 feet in length. The trunks are composed of a fibrous, pithy material surrounded by a jacket approximately 3-inches thick formed by the dying off of old rushlike leaves. The charring of this leafy jacket during forest fires leads to the name of “Black Boy”.

The resin accumulates at the base of the dead leaves along the stem and is collected by stripping the enveloping husk from the core with an axe. Occasionally the husk may be sufficiently soft to permit easy removal, but more frequently, it is a hard coherent mass, which must be mechanically separated from the core. The proportion of resinous husk to the core, which varies with the season, is less in winter than in summer.[2] The cut should not be made directly to the core of the tree, as the leaf bases are then cemented together in large blocks that are subsequently rejected in the sieving operation. On the other hand, when a series of shallow cuts are made, the leafy bases are sufficiently reduced in size to make separation from the resin difficult. The cutting requires considerable skill and should be to such a depth that the leaf bases separate readily. Chopping off the crown of the tree is the customary, though unnecessary, practice. When the crown of the tree is uncut, removal of the husk seems to have little effect upon the tree, provided that sufficient resin is left to protect the core. Even when "lopped", the tree frequently recovers. The husks fall into frameworks placed about the base of the tree. They are then collected and subjected to a sieving operation in a "jigger", which removes most of the leaf bases and any large lumps of caked husk, as well as separates the resin into two grades. The jigger consists of an inclined sieve of wire netting (1/2 to 3/4-in. mesh) above an inclined metal sheet containing smaller perforations. A horizontal shaking motion is imparted to the gratings while the husks are fed in through a hopper at the top. A winnowing operation separates any leaf bases remaining with the coarse gum.[3]

The collection of accroides is subject to licensing according to the district in which the resin is to be collected. The quantity of resin obtainable from an individual tree appears to vary with the species from which collected, and possibly with other factors. Estimates of different collectors vary from 2 to 4 pounds or lower to upwards of 40 or 60 pounds.[4,5,6] A similar situation is met with the amount of resin collected per man per day. Estimates range from 25 to 100 pounds.

The sieving and winnowing method of purifying accroides is subject to high losses of resin. Methods designed to avoid these losses have been studied. A procedure in which the mixed gum and leaf bases are placed on sieves in a steam-heated vat has been in commercial operation. The molten resin runs into trays and is later removed to cooling receptacles. Residue from the screens is utilized as fuel. The product contains but little foreign matter and the yield of resin is increased by one-third over the jigger process, but the tree dies as the result of the lopping and stripping operations employed. The slow growth of the tree, however, makes it desirable that collection methods should not result in its destruction. Solvent extraction methods[7] have also been employed for the purification of accroides. Patents[8] have been granted for a method of purification in which the resin is dissolved in a dilute alkaline solution, filtered, and then precipitated with acid. By proper control of the temperature during precipitation, the resin is obtained in a granular condition, which can be easily handled.

Approximately seventeen varieties of the tree are known, but commercial distinction is made only between the yellow and the more prevalent red gum. The gradings of accroides are according to color, particle size, and material, which is produced as a result of screening, with the commercial grades yellow, red gum coarse, and red gum powdered. The red gum is usually in the form of small dusty pieces of a reddish brown color, which is exported in bags of 140 pounds.

Accroides differs from the other natural varnish resins in that it contains appreciable quantities of free benzoic and cinnamic acids and is thus closely related to the balsams. The resin is of the alcohol-soluble type and is insoluble in aryl and aliphatic hydrocarbons. Like the manilas, both varieties are soluble in alkali. The alcohol solution of red accroides gradually deposits benzoic acid upon standing. The yellow variety also contains benzoic acid obtainable by acidifying the alcohol solution with hydrochloric acid.

The composition of yellow and red accroides has been studied by a number of investigators. The results obtained are listed in Table 3. Both varieties contain a resin-tannol, which yields picric acid upon nitration. The yield, which varies according to the species of *Xanthorrhoea* from which the resin is obtained, is of the order of 50% for the yellow and from 5 to 50% for the red variety.[9] A number of processes have been suggested, and the preparation of picric acid and nitrophenols from accroides has been patented.[10] Small yields and high nitric acid consumption do not permit economic competition with chemical production of picric acid from

Table 3. Chemical Composition of Accroides

Constituent	Formula	Basicity	Percent	Remarks
p-Coumaric acid	$HOC_6H_4CH:CHCOOH$ (*p*-oxycinnamic acid)			These results are for red accroides, the characteristic resinotannol of which is erythroresinotannol, $C_{40}H_{39}O_9OH$
Free[a]		Mono	1	
Combined with benzoic and cinnamic acids and a tannol[a]			2	
p-Oxybenzaldehyde[a]			0.6	
Resinotannol[a]			85	
p-Coumaric acid	$HOC_6H_4CH:CHCOOH$ (*p*-oxycinnamic acid)			These results are for yellow accroides, the characteristic resinotannol of which is xanthoresinotannol, $C_{43}H_{45}O_9OH$
Free[a]			4	
Combined with tannol[a]			7	
Cinnamic acid	$C_6H_5CH:CHCOOH$			
Free[a]			0.5	
Combined with tannol[a]			0.6	
Styracin and probably the phenyl propyl ester of cinnamic acid[a]			1	
p-Oxybenzaidehyde and probably vanillin[a]			0.6	
Resinotannol[b]			80	
p-Coumaric acid	$HOC_6H_4CH:CHCOOH$ (*p*-oxycinnamic acid)			
Free[b]		Mono	0.5	
Combined[b]			1.5	
Cinnamic acid[b]	$C_6H_5CH:CHCOOH$	Mono	0.1	
Styracin[b]			0.1	

[a] A. Tschirch and K. Hildebrand, *Arch. Pharm.*, **234**, 698 (1896).

[b] *Bull. Imp. Inst.*, **18**, 155 (1920).

See also: Nagai, *Ber.* **24**, 2847 (1891); E. H. Rennie. W. T. Cook, and H. H. Finlayson, *Trans Chem. Soc.*, **117**, 338 (1920); H. H. Finlayson, *J. Chem. Soc.*, 2763 (1926).

phenol or chlorobenzene. The belief has been expressed, however, that appreciable quantities of accroides were utilized for the preparation of explosives by Germany during the First World War.

The constituents of accroides are also suitable as the starting point in the synthesis of certain organic dyestuffs. Treatment with sulfuric acid or with sulfur in the presence of an alkali has been patented[11] as a means of producing brown and black dyes.

Attempts to bleach accroides in a manner similar to shellac have been unsuccessful. Simion[12] reported the bleaching of red accroides in acid solution but found that the color returned upon standing. His alcoholic solution of the yellow resin gradually darkened to the color of the red gum solution when exposed to air. Gardner and Parkes[13] applied the usual hypochlorite method for bleaching shellac to accroides but did not obtain satisfactory results.

Penfold[14] studied the removal of coloring matter and insolubles from accroides by solvent extraction methods. He found that use of benzol as the solvent in a modified Scott extraction plant yielded a superior resin containing much less coloring matter and tannins than the crude resin. The product was stated to be directly applicable to the resin industry without need for further bleaching or refining. The purified resin may be bleached directly with chlorine or in solution by the use of peroxides. The bleached resin is stated to be suitable for the manufacture of sealing wax and pale ester gums. It was also reported that the process involved very low costs for fuel, power, and labor and that solvent losses were less than 1 percent of the charge treated.

Accroides differs markedly from the other natural resins in that it is the only material, which, as marketed, is heat-reactive in a manner analogous to that of the heat-reactive phenol-formaldehyde resins. When heated to thermal processing temperatures, the resin is converted into hard, completely insoluble, and unusually resistant films. Manila and Congo copals possess similar properties under specific conditions, but not in the form in which they are marketed. Owing to its heat-reactive properties, accroides is not adapted to the preparation of oil varnishes. Accroides is compatible with cellulose acetate and cellulose nitrate, but not with ethyl cellulose.

The low price and heat-reactive properties of accroides have a definite influence upon its commercial use. One application is as a binder in the preparation of wallboard. It is a substitute for rosin in paper coating and for shellac in spirit varnishes, lacquers, and printing inks. The resin is also used in the preparation of finishes for cellulosic materials, metals, metal foil, and glass as well as in the preparation of molding powders from phenol-formaldehyde resins.[15] Livache and McIntosh[16] mention concentrated solutions of red accroides plasticized with castor oil or balsam as a red coating for windows of photographic laboratories to exclude the active rays of the sun.

References

1) A. R. Penfold, “Grass Tree Resin”, *Technological Museum of Sydney Bull.* No. 16 (July, 1930); M. F. N. Halloway [*J. Proc. Sydney Tech. Coll. Chem. Soc*, Vol. 7 (1935-37) Pub. 1938, pp 41–53.)] has described the chemical and physical properties of resins obtained from various species of *Xanthorrhoea.*
2) J. L. Strevens, “The Technology of Grass Trees”, *Chem. Eng. Mining Rev.* (January to June, 1921).
3) J. C. Earl, “Grass Trees”, Dept. of Chemistry, South Australia, Commonwealth of Australia Bull., No. 6, 1917.
4) H. G. Smith, *Tech. Gazette New South Wales,* No. 9, Part 1 (1919).
5) J. C. Earl, *Loc. cit.*
6) J. L. Strevens, “The Technology of Grass Trees”, *Chem. Eng. Mining Rev.* (January to June, 1921).
7) H. J. Pooley and J. L. Strevens, British Patent 150,638 (1919).
8) H. C. Miller and H. A. Irlam, British Patent 103,006 (1916).
9) H. G. Smith, *Tech. Gazette New South Wales*, No. 9, Part I (1919). According to *Bull. Imp. Inst.*, Vol. 18 (1920) pp 154–162, the yields of picric acid are 30 percent from the yellow resin and 25 percent from the red.
10) H. C. Miller and H. A. Irlam, British Patent 104,352 (1917).
11) H. C. Miller and H. A. Irlam, British Patent 104,353 (1917).
12) F. Simion, *Chem. Ztg.*, Vol. 47 (1923) p 141.
13) H. A. Gardner and H. C. Parkes, *Paint Mfrs. Assoc. Circ. 201* .(March, 1924).
14) A. R. Penfold, “Grass Tree Resin”, *Technological Museum of Sydney Bull.*, No. 16 (July, 1930).
15) German Patent 462,838 (1936).
16) Ach. Livache and J. G. McIntosh, “Manufacture of Varnishes and Kindred Industries”, Vol. 3, Scott, Greenwood & Son, London (1911) p. 237.

Review of *The Chemistry and Characteristics of Explosive Materials*

James R. Cook, PhD

Vantage Press, NY [ISBN 0-533-13533-8], 2001

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This little volume, sensibly priced at $12.95, is a compilation of basic information and general characteristics of a range of explosives, based as the author acknowledges, on previously published data. After a brief general information chapter, it details the physical and explosive properties of nearly 50 explosives in the general categories: Low Explosives, Initiating (Primary) High Explosives, Non-Initiating (Secondary) High Explosives, Binary Explosives and Special Explosives. Consolidated data (Name, Detonation Temperature and Rate of Detonation) follows and the book concludes with an excellent and comprehensive glossary.

If I had two criticisms of this useful book, they would be: It only briefly mentions composite propellants and pyrotechnics, although in some respects these are the most widely used explosives and certainly deserve more space. Secondly, no doubt in order to conserve space, the text flows continuously, rather than, for instance, tabulating the data for each separate explosive in a common page layout. In this way, it is sometimes inelegant in the way that the information is presented.

Nevertheless, this is a useful addition to any explosive specialist's library. I hope that a similar volume detailing the characteristics of a range of propellants and pyrotechnics may be forthcoming.

Review of *Head and Eye Protection: A Guide for Those Who Manufacture, Test, or Use Explosives*

Confederation of British Industry

Explosives Industry Group, 1999
[ISBN – not assigned yet]

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This Guide is the third in a series of four on the subject of personal protection for the explosives industry. Although this study encompasses the needs of other industries, the main focus is very relevant to the fireworks industry. Many of the detailed discussions of hazards considered in the Guide, cite hazards that fireworks manufacturers, as well as, pyrotechnicians are actually exposed to.

The first section discusses the details of British law as it relates to protective clothing and headgear. Although the laws of Britain do not specifically address head and eye protection, the Guide discusses some laws that might remotely apply. The similarity between US and British laws make this section quite valuable. Many states are reviewing their fireworks regulations, and the NFPA continues to develop guidelines that many state legislatures have adopted. Neither the US nor the UK has included specific standards for head and eye protection in their regulations.

After stressing the preference for avoiding the need for the protective gear, several detailed measurements describe protection from a variety of dangers. Many of the dangers described potentially might be encountered by pyrotechnicians—such as high speed particles the size of a large firework star or radiant heat as encountered by a fireworks manufacturer, and these are useful in developing standards for the protective gear needed.

The text emphasizes company training of workers and a company expectation that workers will use safety equipment and conduct themselves in a way to keep them safe. The Guide provides an outline of a training segment that easily could be included with general staff training.

The risk assessment in the appendix is an excellent Guide for fireworks companies to use when reviewing general safety in their warehouses and plants, as well as, outfitting and training their staff. The examples suggest ways to evaluate worker's risk in different activities and some of the responsibilities the worker and the company might have.

The Guide addresses the concerns from the users' perspective and considers the protection as well as the activities the user will have to perform while wearing the gear. They acknowledge that, regardless of any regulations that might be developed, protective clothing that is uncomfortable will distract the user and often will be removed. Several valuable suggestions are made regarding different methods for the protective equipment to protect the user, and how the user can work with the protective clothing to adapt it for the maximum comfort and effectiveness. This well thought out discussion shows that the writers understands the reality of the diverse activities conducted by the pyrotechnician and fireworks manufacturer, as well as the restrictions that can be created for the user with the wrong equipment.

The Guide suggests that there are several ways to address the worker's risk and does not make a specific recommendation as to the type of protection needed. The reader is guided to make their own decisions based on their needs. The Guide states that protective gear, specifically designed for the explosives industry, is not currently being sold. This could be a good opportunity for safety equipment manufacturers to develop something the explosives industry would want or need to buy. This Guide could also serve as a handbook for what needs to be considered in designing protective gear.

The bibliography includes studies done by other industries regarding protective equipment and chemical risk protection.

Review of *Protection against Substances Hazardous to Health*

Confederation of British Industry
Explosives Industry Group, 2001
[ISBN – not assigned yet]

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This Guide was produced by a joint working party of the Explosives Industry Group of the Confederation of British Industry, including the Ministry of Defense and the Health and Safety Executive. Its purpose is to provide advice to those who manufacture, store, transport by road, test, supply, use or undertake the disposal of explosives and explosives articles and substances in Great Britain on the selection of personal protective equipment (PPE) to be used against substances hazardous to health.

Of special interest to me is that their statement of purpose goes on to include protection from both the toxic chemicals used in the manufacture of explosives and pyrotechnics and from the smoke and byproducts created during use. As such, this guide supports my personal quest to have protection against these byproducts included in the National Fire Protection Association's (NFPA 1126) *Standard for the Use of Pyrotechnics before a Proximate Audience*.

Regulatory Structure. The Guide places all its recommendations within the regulatory structure in the UK. It provides a flow diagram showing how 10 different laws harmonize with the 1974 British Health and Safety at Work Act (HSWA) and jointly impact all aspects of explosive work.

I found it fascinating to compare the UK rules with those in the US. Most of the rules are similar, but there were some striking differences. For example, our Occupational Safety and Health Administration (OSHA) only addresses protection for workers while the UK's HSWA places duties on employers and the self employed to protect people other than employees. This may even require employers to provide visitors with personal protective gear, information, instruction and training. US companies are only bound by corporate liability for visitors' injuries.

In another example, the self-employed individual, who in the US has a tendency to slip below some regulatory radar lines, must comply with the UK's Control of Substances Hazardous to Health Regulations as if that person were both an employer and an employee.

However, the crucial and pivotal difference between our laws involves risk assessment.

Risk Assessment. The Guide states that:

> The first duty of the employer under the Management of Health and Safety at Work Regulations 1999 is to undertake a risk assessment to clearly define the source and nature of all potential hazards and people who may be affected by them. This assessment must be performed and significant findings recorded by a person or persons who are adequately trained and competent to perform such duties.

The clear requirement to have a person qualified to make the risk assessment is not included in the US personal protective equipment regulation, which reads:

> 132(d)(1) Hazard assessment and equipment selection.
> (1) The employer shall assess the workplace to determine if hazards are present, or are likely to be present, which necessitate the use of personal protective equipment (PPE).

and

> (2) The employer shall verify that the required workplace hazard assessment has been performed through a written certification that identifies the workplace evaluated, the person certifying that the evaluation has been performed; the date(s) of the hazard assessment; and which identifies the document as a certification of hazard assessment.

I believe that this wording in the US rules explains the common practice of employers choosing the wrong PPE and/or delegating risk assessment and selection of PPE to workers with no formal safety training. In 25 years of workplace inspections, it is rare that I have not seen chemical splash goggles used for impact protection, the wrong gloves used for chemical resistance, and other violations of the PPE rules.

The US Respiratory protection regulations do indicate that training is needed. In 29 CFR 1910.134(c) it states: "The program must be administered by a suitably trained program administrator." However, many schools and theaters, at which I have consulted, interpret this to mean that any trained "administrator" can do the job. I routinely see human resources administrators, technical directors, and teachers doubling as safety directors.

Evidence that OSHA agrees with UK regulators that professionals should be in charge of safety was seen on February 13, 2002 when OSHA announced a settlement agreement with a pyrotechnics and explosives manufacturer. The company, which logged 5 deaths from flash fires since 1991, was fined $832,000. Then OSHA worked out a settlement in which the company would pay only $300,000 in penalties provided the manufacturer:

- hires a third-party certified safety or health professional consultant to audit their workplace every year for the next three years and follows their recommendations;
- hires a full-time safety and health director who has both training and experience in safety and health who will report directly to the company president, and who will have authority to "do whatever is necessary to ensure compliance with applicable OSHA standards including, but not limited to, shutting down operations," and
- meets other compliance program and training rules.[1]

Toxic Substance Exposures. The Guide explains that the UK's Control of Substances Hazardous to Health Regulation (COSHH) defines and sets limits for toxic substance exposure. The COSHH sets two types of limits:

- The Maximum Exposure Limits (MEL), which are set for substances that may cause the most serious health effects such as cancer or occupational asthma and for which "safe" levels of exposure cannot be determined. The workplace air must not exceed this level and it should be reduced as far below this level as reasonably practicable.
- The Occupational Exposure Standards (OES) which are based on current scientific knowledge and which indicate there is no risk to the health of workers exposed to that level of inhalation day after day.

The COSHH defines a toxic substance as:

- a substance listed as dangerous in any of the applicable regulations as very toxic, toxic, harmful, corrosive or irritant,
- substances that have a Maximum Exposure Limit (MEL) or an Occupational Exposure Standard (OES),
- a biological agent,
- dust of any kind when present at a concentration in air equal to or greater than an 8-hour, time weighted average of either 10 mg/m^3 for inhalable dust[2] or 4 mg/m^3 for respirable dust,[2] or
- a substance of any kind that is not mentioned in any of the rules but which creates a hazard to people's health which is comparable with the hazards created by substances mentioned in the acts above. "These will include any substances generated as a by-product of the process."[3]

Selection of Equipment. The UK standards for the use of PPE are covered—respirators, hand protection, eye protection, body and foot protection. And since static electricity can trigger explosions of some pyrotechnic materials, the choice of gear, especially clothing, must also consider this factor.

Training. Users (including visitors) must be trained to wear their PPE whenever and wherever this is required to protect them. Users must also be given appropriate information, instruction and training by a competent person on the requirements and reasons for using PPE, how to obtain and fit PPE, how to store, check, care for, clean and dispose of PPE, and more. Most of these rules are similar to US regulations for PPE and respiratory protective equipment.

Risk Assessment Examples. Annex (Appendix) 3 of the document provides examples of risk assessments. In each case a "Potential Severity Rating" and a "Probability Frequency Rating" are determined and a matrix used to determine the actions that should be taken. The actions often involve personal protective equipment, ventilation, and other engineering controls. There are five case examples:

1) fluon (a fluorocarbon polymer) sieving in an explosives factory
2) manufacture of red phosphorus sheet in an explosives factory
3) firing flash powder effects in a theater
4) cleaning a settlement tank in an explosives factory
5) testing fireworks in an outdoor test facility

Theater Example. While all the risk assessments are useful in understanding the process, Example 3, "firing flash powder in a theater" covers the most diverse problems. The assessment begins by identifying the hazards as:

a) *Hazardous Substances*: The smoke produced on firing a flash powder effect may contain chemicals including carbon monoxide, carbon dioxide, hydrogen chloride, nitrogen [oxides], heavy metals (in the case of coloured flash effects) and aluminum/aluminum oxide dust and fume.

b) *Other Hazards*: On firing, the immediate area around the effect is subject to brief, but intense heating; the flash pot / cartridge may remain smouldering or even catch light after firing; noise on firing, particularly with fine grained flash powder that is used to produce an accompanying report with the flash effect.

It also looks at the people who are affected.

Directly: 10 performers on stage and up to 4 crew members working backstage.

Indirectly: All cast and crew member in addition to the audience.

The frequency and the severity of the exposures are assessed for a sequence that is fired three times during each performance in daily evening performances and in Wednesday and weekend matinees. It is determined that the OES for respirable aluminum and aluminum oxide dusts could be exceeded causing possible respiratory complaints. Other products in the smoke may cause irritation to the eyes and throat. Heat, noise, potential fires, and electrical hazards are also assessed.

A matrix is set up that ranges from 1 to 36 representing conditions from "Low Risk" (1 to 4) to conditions under which the employer should "Stop Work Immediately" (18 to 36). Without controls, the assessment for this indoor pyrotechnic work is found to be 16, which meant the "Risk is high, [and] immediate corrective action is required."

The next section discusses engineering controls. In this hypothetical theater, there is an extraction fan system in the fly that will draw the smoke away from the audience, up into the fly, and exhaust it from the roof. The risk is reduced from a high risk (16) to 8, a "Medium" risk by insuring that:

- the extraction system is used at all times when the pyrotechnics products are used;
- fire fighting measures are in place;
- insuring electrical firing systems meet guidelines;
- pyrotechnic storage is appropriate and limited to small quantities; and
- all scenery on and around the area is treated with fire-resistant materials, and props (which do not come under the fire-retardant rules) are not positioned near the effects.

A drawing of the theater and the direction of air flow is shown. The Guide also states "The effectiveness of the extraction system is to be tested before and during rehearsals, by test firing the effects that are to be used during the performances. More elaborate smoke tests may be carried out if required."

This kind of exhaust fan system does exist in some US theaters and in some cases, there are fire fans which can be activated under certain circumstances. But in most US theaters, I fear, the risk would still be rated in the "high" range under the UK system.

Summary. This Guide is a clearly written outline of the British safety regulations and protective equipment rules as they apply to pyrotechnics and explosives. Although produced primarily for an overseas audience, the publication contains a wide range of useful information relating to the health protection of those working with explosives. In my opinion, some of these rules should be incorporated into US regulations and standards, including 1) placing the onus on the employer to protect non-workers as well as employees, 2) requiring formal risk assessment by trained safety personnel, and 3) considering the byproducts of the pyrotechnic reaction in any risk assessment.

References

1) *Bureau of National Affairs–Occupational Safety and Health Reporter*, Vol. 32, No. 8 [2-21-02], pp, 159–160.

2) "Inhalable dust" is capable of entering the nose and mouth and available for deposition in the respiratory tract. "Respirable dust" is also capable of penetrating the deep gas exchange region of the lung.

3) Predictive modelling of the products of combustion from some high explosives and propellants is under development.
Dr. M. D. Cook, *Predictive Modelling of Products of Combustion of High Explosives and Propellants*. WS3 Chemical Technology Department, Defense Evaluation and Research Agency, Fort Halstead, Sevenoaks, Kent TN14 7BP, UK (in preparation).

Other CBI Guides

Four Guides have been produced by the Confederation of British Industry (CBI). Their titles are:

1) *Fire Protective Clothing: A Guide for Those Who Manufacture or Store Pyrotechnics or Propellants* (November 1995) [ISBN 0 85201 513 5] {Reviewed in *J Pyro.,* Issue 9 (1999)}.
2) *Hearing Protection: A Guide for Those Who Manufacture, Test or Use Explosives* (August 1997) [ISBN 0 85201 548 8] {Reviewed in *J Pyro.,* Issue 10 (1999)}.
3) *Head and Eye Protection: A Guide for Those Who Manufacture, Test or Use Explosives* (May 1999) [ISBN not allocated] {Reviewed in current issue of *J Pyro.*}.
4) *Protection Against Substances Hazardous to Health* (March 2001) [ISBN not allocated] {Reviewed in current issue of *J Pyro.*}.

The guides each cost £11 (approx. US$18). Further details concerning exchange rate, postage, etc. can be obtained by contacting:

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