

Journal of Pyrotechnics

Issue Number 7, Summer 1998

Policy Board Members:

Ettore Contestabile
Canadian Explosive Research Lab
555 Booth Street
Ottawa, Ontario K1A 0G1
Canada

Gerald Laib, Code 9520
Naval Surface Warfare Center
Indian Head Division, White Oak Lab
10901 New Hampshire Avenue
Silver Spring, MD 20903-5000
USA

Wesley Smith
Department of Chemistry
Ricks College
Rexburg, ID 83460-0500
USA

Roland Wharton
Health and Safety Laboratory
Harpur Hill, Buxton
Derbyshire SK17 9JN
United Kingdom

Managing Editor:

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

Technical Editors (in addition to Policy Board Members that edited for this issue):

Per Alenfelt, Hansson Pyrotech AB
Billdal, Sweden

Scot Anderson
Conifer, CO, USA

Ed Brown
Rockvale, CO, USA

Dan Dolata, Clippinger Labs.
Athens, OH, USA

Joe Domanico, US Army, Edgewood
Aberdeen Proving Ground, MD, USA

Frank Feher, Univ. of CA, Irvine
Irvine, CA, USA

Clive Jennings-White
Salt Lake City, UT, USA

Terry McCreary, Murray State Univ.
Murray, KY, USA

Will Meyerriecks
Tampa, FL, USA

Bill Ofca, B&C Products, Inc.
Hyde Park, NY, USA

Barry Sturman
Victoria, Australia

Rutger Webb
Den Haag, The Netherlands

Larry Weinman, Luna Tech
Owens Cross Roads, AL, USA

Tony Wilkinson
Hull, United Kingdom

Robert Winokur, Dept. of Biology
UNLV, Las Vegas, NV, USA

Direct Editorial Concerns and Subscription Requests to:

Journal of Pyrotechnics, Inc.

Bonnie Kosanke, Publisher

1775 Blair Road

Whitewater, CO 81527 USA

(970) 245-0692 (Voice and FAX)

e-mail: bonnie@jpyro.com

web: www.jpyro.com

CAUTION

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

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

Table of Contents

Issue Number 7, Summer 1998

The Production of Music with Pyrotechnic Whistles Fred Ryan	1
High-Nitrogen Pyrotechnic Compositions David E. Chavez and Michael A. Hiskey	11
An Oxygen-Exchange Approach to Pyrotechnic Formulations E. J. Clinger and Wesley D. Smith	15
Artificial Meteor Fireworks D. Caulkins	26
Studies on the Use of Epoxy Resin Binder in Small Rockets R. I. Grose	33
Development of a Video Spectrometer K. L. and B. J. Kosanke	37
Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 2. Stoichiometric Mixtures D. Chapman, R. K. Wharton, J. E. Fletcher, and G. E. Williamson	51
Novel Powder Fuel for Firework Display Rocket Motors Barry Cook	59
Communications:	
Use of the Term Sensitiveness to Describe the Response of Pyrotechnic Compositions to Accidental Stimuli by R. K. Wharton & D. Chapman	65
Some Measurements of Glitter by K. L. & B. J. Kosanke and C. Jennings-White	68
Another Fog Study by M. Rossol	73
Possible Applications for Computer Codes in the Development of Pyrotechnic Compositions by R. Webb	74
Review by John Bergman of Ian von Maltitz's <i>Black Powder Manufacture Methods and Technique</i>	76
Events Calendar	49
Sponsors	77

Publication Frequency

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

Subscriptions

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

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

The Production of Music with Pyrotechnic Whistles

Fred Ryan

PO Box 406, New Alexandria, PA 15670, USA

ABSTRACT

The techniques used by the Western Pennsylvania Skylighters to produce music with pyrotechnic whistles are described. Whistle tubes of various diameters and lengths are used to produce individual notes. The tubes, containing small amounts of compressed whistle composition, are fired electrically. Construction details are given for producing very reproducible notes over five musical octaves. This music was demonstrated at the Pyrotechnics Guild International (PGI) Convention in 1994 ("Stars and Stripes Forever") and at the 1997 PGI Convention (Circus medley music accompanying set pieces) utilizing a computer controlled firing system. Simpler tunes have also been performed using hand-firing techniques such as a "nail board" firing system. Our experience in improving the tonal quality of the music produced, as well as suggested areas for further improvement, is discussed.

Keywords: pyrotechnic, whistle, music, resonators, mode selection, computer

Introduction

Pyrotechnists are quite familiar with whistling fireworks. When a tube, open at one end, is partially filled with whistle composition, a shrill whistling sound is emitted from the tube when the composition is ignited. The pitch of the sound is high at first and descends as the composition burns, with a change in pitch that can vary over many musical octaves. Although many papers have been written concerning the theory of the production of sound by whistle compositions, for our purposes, it is adequate to acknowledge that they are capable of producing a wide audio spectral range of frequencies. If the whistle composition is placed at the bottom

of a tube open at one end, this frequency distribution is modified by the resonant modes of a cylindrical cavity open at one end. This may most easily be understood by considering the effect of the reflected resonant sound waves in the tube. The total set of resonant frequencies in the tube is^[1]

$$\text{Frequency} = \frac{NV}{4(L + 0.3D)}, \quad N = 1, 2, 3 \dots$$

where N is the mode number, V is the velocity of sound, L is the length of the tube from the open top to the closed bottom, and D is the inside diameter of the tube. Only the odd frequencies in this series will be strongly excited by the whistle composition as they correspond to resonant standing waves in the tube that have pressure maxima at the bottom of the tube and therefore have the strongest effect on the burning rate of the whistle composition.

If only a small amount (i.e., a thin layer) of whistle composition is placed in the bottom of the tube, the frequencies produced will vary little for the duration of the note. Since the entire set of odd frequency terms are excited, the note will never be pure but will consist of the sum of the $N = 1$, $N = 3$, $N = 5$, etc. terms. Unfortunately these terms are not simple harmonics of each other so that, if all are excited equally, a screech will result instead of a note that can be used to play music. We will consider only the first three terms in the series, $N = 1$, $N = 3$, and $N = 5$, as the higher terms will in general occur at frequencies beyond the range of human hearing. The trick in achieving a note pure enough to produce music is to construct the whistle-tube/whistle-composition system so that the term $N = 3$ is strongest and to minimize production of the term $N = 5$. The term $N = 1$ will always be produced, but with typical whistle compositions it is much weaker than the term $N = 3$. In this paper we will describe how to obtain

selective production of the $N = 3$ frequency term. Since there will always be some $N = 1$ frequency present (as well as some $N = 5$), the notes sound somewhat like the notes produced by a Calliope, rather than pure notes. In the formula given, the longer the tube is, the lower the frequency of the note. That is only true if one continues to produce the same relative intensity of the $N = 3$ frequency. Unfortunately, as the tube is made longer and longer at constant internal diameter, the back pressure on the whistle composition will at some length cause it to start producing the $N = 5$ frequency stronger than the $N = 3$. Thus making the tube longer and longer at constant inside diameter will lead eventually to the production of a higher, rather than a lower, frequency note. The stability limits are given for tube lengths and inside diameters with a particular whistle composition for the selective enhanced production of the $N = 3$ frequency.

Experimental Details

All of the whistle notes that we use are constructed from either 3/4" or 1-1/4" inside diameter Schedule 40 PVC tubing of the type used in water systems. The maximum length for 3/4" tubing is about 10" and for 1-1/4" tubing about 40" before the stable production of $N = 3$ is lost, and the note jumps to the much higher $N = 5$ frequency. These maximum lengths vary somewhat on the type of whistle composition used and are representative for the composition and ramming pressure that we employ. The result is that the lowest note produced using a 1-1/4" tube is around a middle C note on the piano (261.6 Hz). Lower notes can be produced using larger inside diameter tubing, but we have not established the stability range for such tubing.

The note assemblies consist of an appropriate length of PVC pipe inserted into a modified PVC end cap. A completed note is shown in Figure 1. A 1/2" long section of pipe (the pipe collar) is pressed into the end cap. Epoxy is used to fill the bottom of the end cap and is then machined to produce a flat bottom. A hole is drilled through the side of the end cap for an electric match, which is inserted from the inside of the cap to the outside. The whistle composition is pressed under very high pressure into the end

cap, as described later, and the PVC pipe is inserted into the end cap. Since the PVC pipe collar in the end cap keeps the tube from coming closer than 0.46" from the bottom of the assembly, the lengths of the tubes, as calculated by the previous formula, must be shortened by 0.46" to obtain the desired note. This style of construction allows the whistle composition to be easily pressed into the end cap, independent of the length of the tube.

We used a whistle composition consisting of

Ingredient	Parts by Weight
Potassium perchlorate	64
Sodium salicylate	32
Red iron oxide (Fe_2O_3)	1
Vaseline	6

This composition was described by C. Ville-neuve^[2] and is a modification of compositions first described by S. Öztap.^[3] The method of mixing the composition follows reference 2 with one exception. The red iron oxide is added to the potassium perchlorate, which is then milled in a ceramic ball mill for two hours. This allows intimate mixing of the oxidizer and the oxidation catalyst. Particle sizes are not known, but I estimate that the potassium perchlorate has a final size of around 25 microns. I use the finest pigment-grade red iron oxide that can be obtained. I estimate that the particle size of the red iron oxide was below 10 microns. The sodium salicylate was used as supplied, described as a "fine powder", probably with a particle size between 50 and 100 microns. It is imperative that this composition contain a lubricant (Vaseline), or predictable and reliable note production will not be achieved. We spent countless hours producing notes with dry whistle compositions without being able to achieve the high degree of reliable note production required in playing music. The level of reliability required for producing music is much higher than that required for conventional fireworks. When you play music, everyone knows what note should come next and will notice an error. The whistle composition is pressed into the base assembly by a hydraulic press with a pressure of 3000 psi. The total force being exerted on the 3/4" end plugs is about 1500 lb, and 4000 lb on the 1-1/4" end caps. The amount of composition used depends on the desired dura-

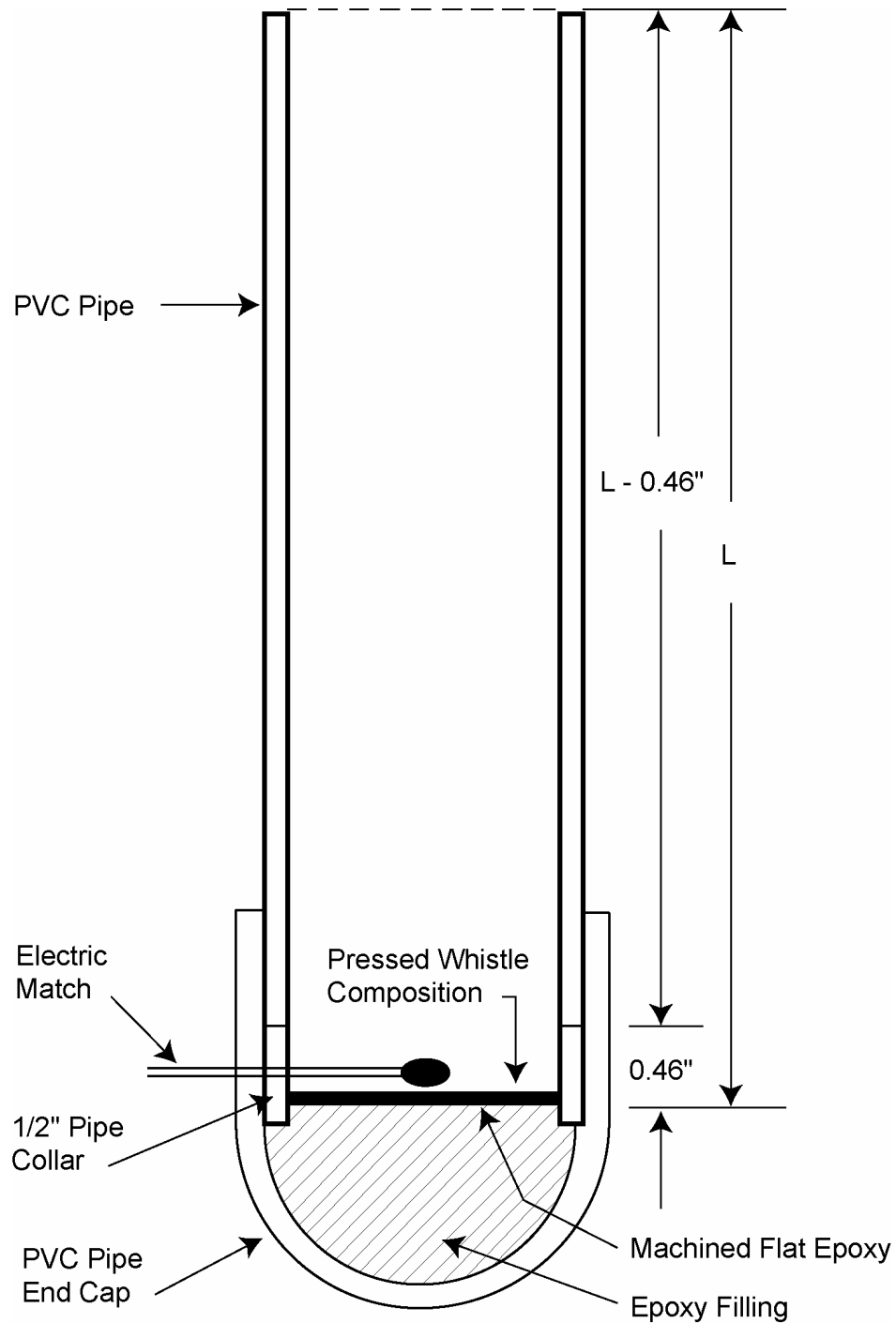


Figure 1. Construction details of a whistle note assembly.

tion of the note. For the 3/4" end caps the quantity used and note duration are listed in Table 1.

The thickness of the compressed whistle composition will of course cause some change in frequency of the note over its duration. The shortest 3/4" tube resonator length that we used

has an effective empty length of 1.5" so that some caution must be used in selecting long note durations for the highest notes. The longest 3/4" resonator length used is 9" so that the percentage change in frequency during burning of

the whistle composition is much less, so longer duration notes can be used.

The whistle composition is not weighed for each tube during charging but rather is added to the end caps using custom made scoops.

Table 1. Note Duration vs. Quantity of Whistle Composition for 3/4" Tube.

Weight of Whistle Comp. (g)	Compressed Thickness (in.)	Approx. Note Duration (s)*
0.35	0.025	<0.1
0.7	0.045	0.2
1.4	0.09	0.4
2.1	0.12	1.0

* Estimated.

So far we have used only one weight of whistle composition for the 1-1/4" tubes, 1.4 grams, which yields a compressed thickness of about 0.03" with a note duration of about 0.2 second. Much longer durations could be used without appreciable change in frequency during the 1-1/4" notes as their tube lengths are longer than the 3/4" tubes.

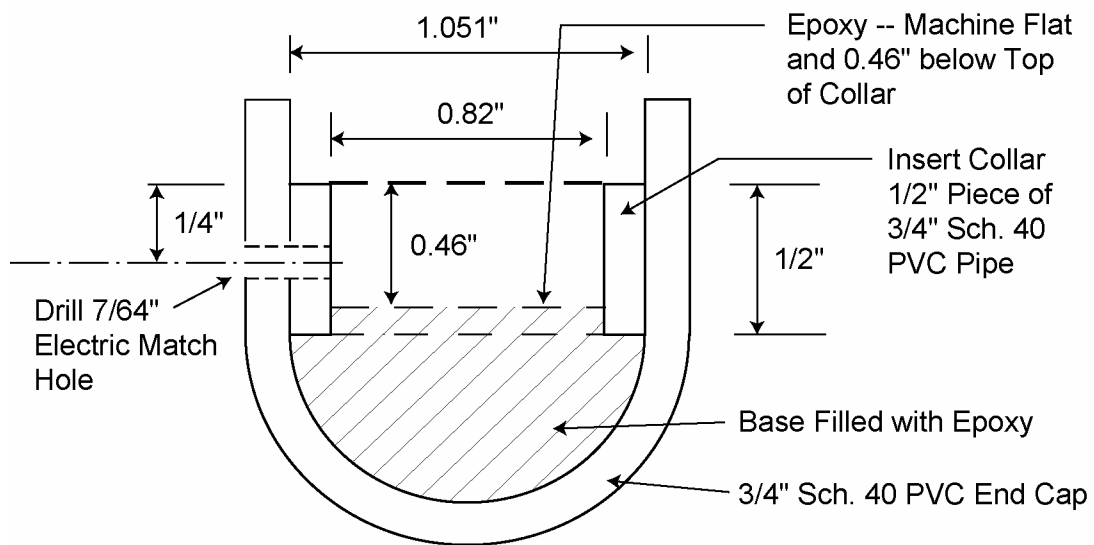
The whistle composition is spread evenly over the bottom of the end cap before pressing and of course a barricade is utilized to prevent injury in the event of ignition during the pressing process. Due to the thinness of the pressed whistle composition layers, the bottom, machined-epoxy surface of the end caps must be flat, so that the note will start and end uniformly. The epoxy used should be a high strength type with low viscosity, aluminum filling, and a long hardening time. We used epoxy manufactured by CIBA-GEIGY, Type RP 3269-1 (two-part, resin and hardener).

Drawings for producing the end caps and the fixturing for the machining operations are shown in Figures 2 and 3.

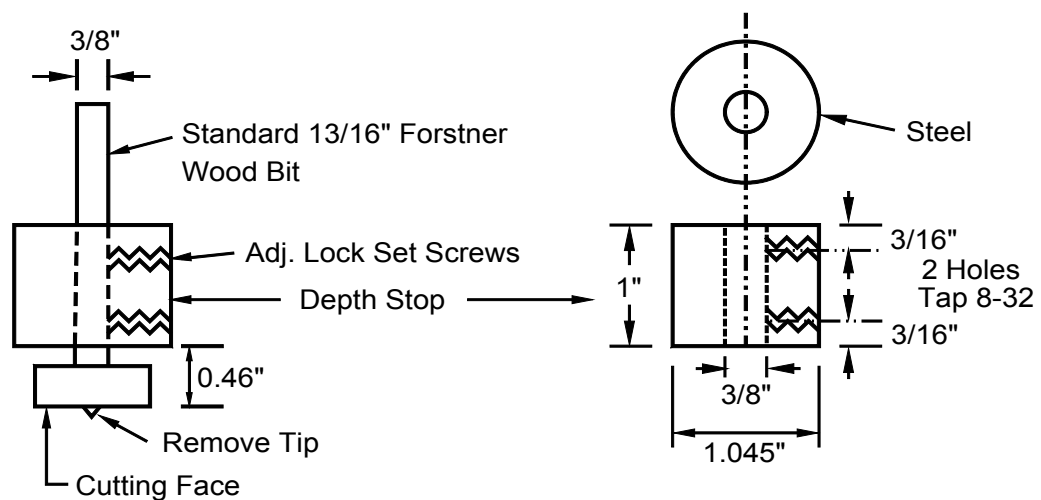
The end caps are machined in a drill press using the end cutters. The 3/4" caps can use a stock, outside-dimension 13/16" Forstner wood bit, available from woodworker supply houses. A slight tip on the front of the bit must be ground away with a hand grinder and a stop must be machined to slip over the shaft of the bit to stop the cut at 0.46" depth. When filling the end cap with epoxy, a slight excess of epoxy should be used to allow for the machining step. The Forstner bit for the 1-1/4" tubing must be modified as shown in Figure 3 by reducing the outside diameter. This was done with a tool-post grinder on a lathe. The end cutters thus produced are self centering on the end caps during the machining procedure.

The electric matches are first dipped into nitrocellulose lacquer and then into fine 7F fireworks-grade Black Powder. This enhances the ability of the match to ignite the entire surface of the whistle composition at the same time. When dry, the wires of the match are inserted from the inside of the end cap to the outside. The match head is placed in the center of the cap about 1/8" above the surface of the whistle composition. A thick "party" toothpick is inserted from the outside and jammed into the match hole, then broken off. While crude, this fastening technique is quick and remarkably strong.

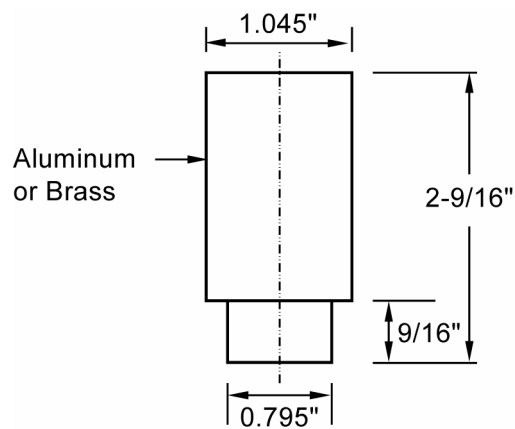
The tubes can be washed after use with a brush and used repeatedly. The end caps can be re-used at least 50 times before erosion becomes too severe.



Construction Details of 3/4" End Cap

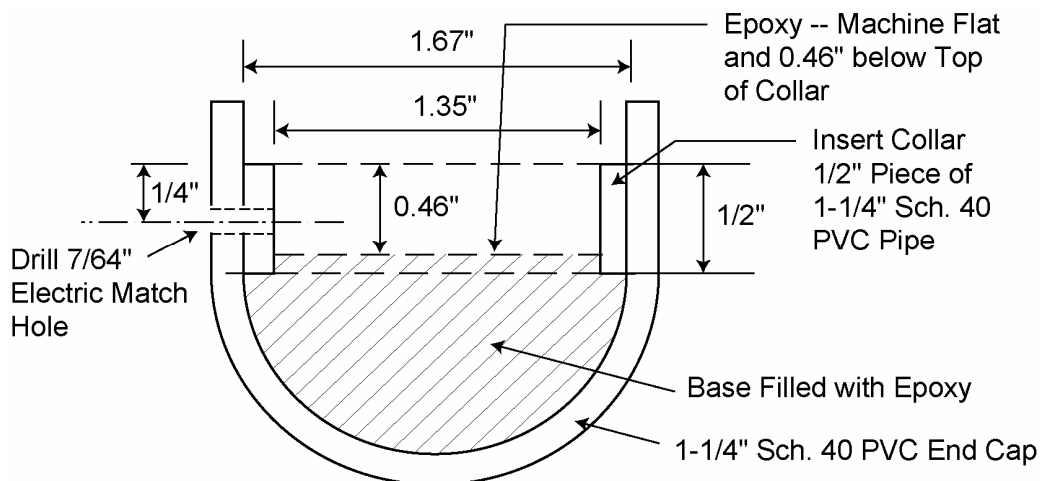


3/4" Cutter Details

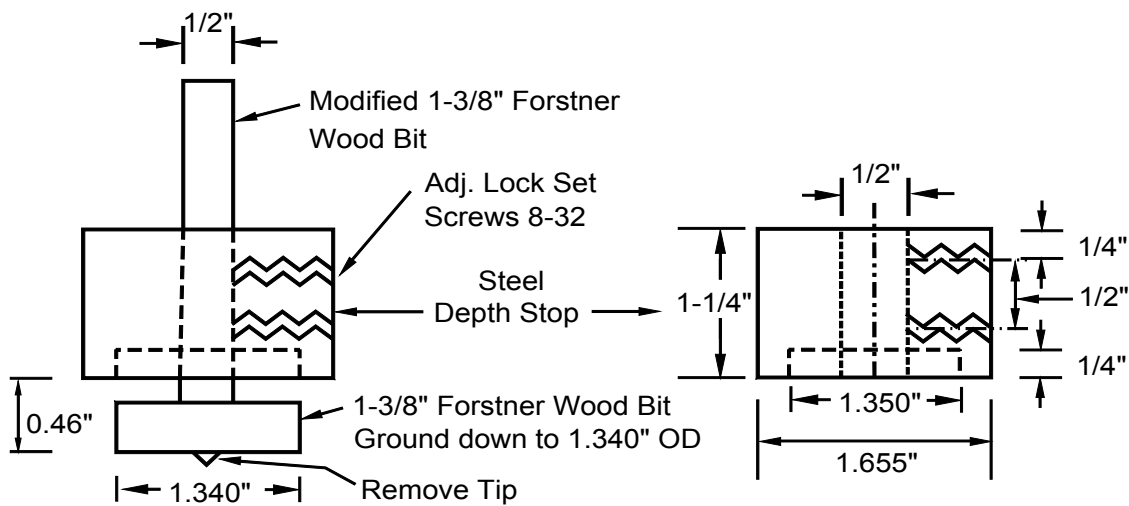


Round 3/4" Tamper Details

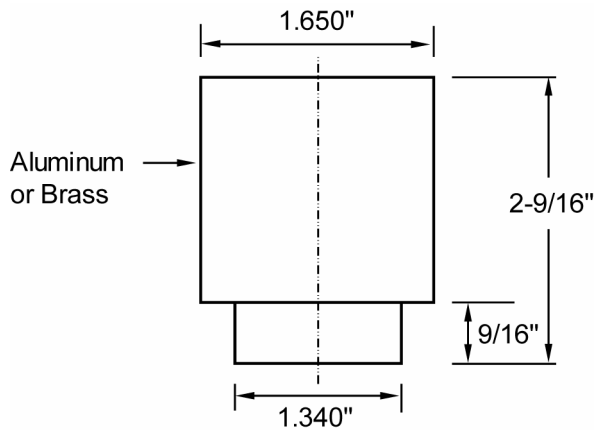
Figure 2. Construction details of 3/4" end cap.



Construction Details of 1-1/4" End Cap



1-1/4" Cutter Details



Round 1-1/4" Tamper Details

Figure 3. Construction details of 1-1/4" end cap.

Table 2 lists the tube lengths for the 1-1/4" tubes corresponding to the frequencies they are capable of producing. Table 3 lists the corresponding lengths and frequencies for the 3/4" tubes.

Table 2. Lengths for 1-1/4" Tubes and Corresponding Frequencies.

N = 3 Note	Frequency (Hz)	Tube Length [L (in.) - 0.46 in.]
C4	261.63	36.3
#C4	277.18	34.21
D4	293.66	32.25
#D4	311.13	30.39
E4	329.63	28.63
F4	349.23	26.98
#F4	369.99	25.42
G4	392.00	23.94
#G4	415.30	22.55
A4	440	21.24
#A4	466.16	20.0
B4	493.88	18.83
C5	523.25	17.72
#C5	554.37	16.68
D5	587.33	15.7
#D5	622.25	14.77
E5	659.29	13.89
F5	698.46	13.06
#F5	739.99	12.28
G5	783.99	11.54
#G5	830.61	10.85
A5	880	10.19
#A5	932.33	9.57
B5	987.77	8.99

Actual ID = 1-5/16".

Formula converted to inches:

$$(N = 3) \text{ Freq.} = \frac{9720}{L + 0.39375}$$

$$\therefore L(\text{in.}) = \frac{9720}{\text{Freq.}} - 0.39375(\text{in.})$$

Note: The desired tube lengths listed are more precise than actually required. A $\pm 1/2\%$ deviation from these numbers does not result in very serious detuning.

Table 3. Lengths for 3/4" Tubes and Corresponding Frequencies.

N = 3 Note	Frequency (Hz)	Tube Length [L (in.) - 0.46 in.]
C6	1046.5	8.58
#C6	1108.7	8.06
D6	1174.7	7.57
#D6	1244.5	7.11
E6	1318.5	6.67
F6	1396.9	6.25
#F6	1480	5.86
G6	1568	5.50
#G6	1661.2	5.15
A6	1760	4.82
#A6	1864.7	4.51
B6	1975.5	4.22
C7	2093	3.94
#C7	2217.5	3.68
D7	2349.3	3.43
#D7	2489	3.20
E7	2637	2.98
F7	2793.8	2.78
#F7	2960	2.58
G7	3136	2.40
#G7	3322	2.22
A7	3520	2.06
#A7	3729.3	1.90
B7	3951.1	1.76
C8	4186	1.62
#C8	4435	1.49
D8	4698.6	1.365
#D8	4978	1.25
E8	5274	1.139
F8	5587.7	1.036

Actual ID = 13/16"

Formula converted to inches:

$$(N = 3) \text{ Freq.} = \frac{9720}{L + 0.24375}$$

$$\therefore L(\text{in.}) = \frac{9720}{\text{Freq.}} - 0.24375(\text{in.})$$

Experimental Results

In our demonstration of "Stars and Stripes Forever" at the 1994 PGI Convention, we used over 900 notes, about half of which were low notes made from 1-1/4" tubing and half high notes were made from 3/4" tubing. The notes were played by ignition of the electric matches with a computer firing system and were choreographed together with appropriate aerial comets and shells. The notes covered five musical octaves, and many chords were played containing up to five notes each. This was a tremendous escalation in scale from the simple melodies we had previously played. As a result, some things were learned after hearing the final result. From this experience the following suggestions were made:

1. Chords with a large number of individual notes do not sound very good. Apparently the tonal impurity of the individual notes, particularly the lower notes, has an additive effect when a chord is constructed and its musical quality is poor. Do not try to construct complex chords; use single notes or simple chords.

2. Do not use the same duration notes for all the notes (as we did at the 1994 Convention). To make the caps interchangeable we used the same amount of whistle composition in all of the 3/4" end caps and in all of the 1-1/4" end caps. That was a mistake. We have since constructed music using four different note durations that correspond more closely to the music as written, and it sounds much better.

3. Where possible, use only the 3/4" tubes to produce higher notes. The 1-1/4" notes do not sound as pure. That is because, as the lower frequency notes are produced, the residual $N = 5$ frequency component, even though suppressed, occurs at frequencies to which the human ear is most sensitive. Those lower notes thereby sound less pure. Even the higher frequency notes produced by the 3/4" tubes improve in perceived purity at the higher frequencies. This is because the $N = 5$ residual component now occurs at frequencies beyond the range of human hearing response.

Our demonstration at the 1997 PGI Convention incorporated all of these suggestions and sounded better musically than the "Stars and

Stripes" presentation. A primary goal for the 1997 Convention was to play the notes faster. Our display consisted of a series of animated set pieces. A clown would march from one set piece to another accompanied by the "Entrance of the Gladiators". To sound right, this composition cannot be played slowly. Notes of the duration used for "Stars and Stripes Forever" were too long and overlapped too much. Accordingly, we developed notes that were less than 1/10 second in duration. Only a few chords were used, and those consisted of only two notes separated by one or two musical octaves. The results sounded significantly better than in 1994.

Generating a Musical Score for Whistles

There are many ways to translate a musical score into a time sequence of commands from the computer to the appropriate firing position for the note to be played. Existing software can create this time sequence and even play back the score to test the accuracy of the music. There are also many computer-controlled firing systems, each with its own firing control software. The approach that we use is somewhat archaic and probably reflects the "old school" approach. Our computer firing system has a software clock with 225 counts per second. The program can accept firing and firing position commands at that rate. The music sequence must therefore be broken into intervals of duration 225 per second or fraction thereof. The musical score on a sheet of music is a flow of notes versus time. It is therefore necessary to convert the time per note and between notes (the time for one measure or fraction thereof) into software clock counts. Since 225 counts per second does not divide evenly, we rounded it to 224 counts per second.

One first obtains a sheet music copy of the composition to be played (or works from memory). Several alterations must then be done. The music must first be simplified, perhaps reducing it to only single notes (the melody). We used a bare sheet of music manuscript paper to write the altered version of the music. In addition to simplifying the score, we shifted the key in which the composition was written to the key used for all of our music. That allows us to use

the same whistle tubes over and over with a minimal need to cut new tube lengths for new music. We then decide how fast the music should be played. For example, the time per measure might turn out to be 1-1/2 seconds. That means that the number of software counts per measure will be $224 \times 1.5 = 336$ counts per measure. One-half of a measure would be 168 counts, 1/4 measure would be 84 counts, and 1/8 measure would be 42 counts. At this time one must decide on the note duration for each note so that the proper amount of whistle composition will be pressed into its end cap. In the example mentioned, let's say that the desired note duration is 1/8 of a measure, or 42 counts. That would be a time duration of $42 \div 224 = 0.1875$ seconds duration. Referring to Table 1, the closest 3/4" end cap to that time is 0.7 grams with a burning time of 0.2 seconds. On the musical score we then indicate the proper end cap to be used with that note. From that modified musical score we then create a time flow of commands to the computer, starting at time zero (zero counts), and adding the count total as the music progresses from note to note. This series of commands also contains instructions to tell the firing system which position to fire at that command. Our whistles are contained in racks that can hold 30, 1-1/4" tubes and 30, 3/4" tubes (a total of 60 tubes per rack) and are wired to handle up to 30 electrical firing events. There are a total of 16 racks so that information must be given to the firing system as to which rack and which position in that rack the firing current should be addressed. A corresponding chart is also created with the note and note duration that should be positioned in a particular rack and rack position for assembly purposes. So far these lists of time sequences of commands and note events at the command have been done on paper by hand and the accuracy checked mentally before entering the list into the computer software. A spreadsheet program would make more sense as errors could be corrected much easier.

A computer firing system is only necessary if a very large number of firing events are required. We have played many simple tunes using only a "nail board" firing system. The person using the "nail board" needs only to know the music and to have a sense of rhythm.

Suggested Future Improvements

The PVC tubing that we have been using contains a white pigment additive making them almost opaque. In spite of this, at night each whistle tube clearly lights up during firing, adding charm to the display. Clear PVC tubing without the pigment is commercially available and would enhance this effect.

Experiments should be conducted to design resonators for the low notes. An obvious choice would be a cylindrical resonator closed at both ends, with an aperture on the side to allow the note to exit. Much purer notes might be possible with such a resonator.

Even shorter notes can be constructed, particularly for the highest notes. For a 3/4" tube a charge of less than 0.2 grams and compressed to about 0.010" should yield a note of shorter duration than 1/20 of a second, where fast notes are required. Such fast notes are, however, impractical for the very low notes due to the transit time of sound from end to end of the resonator and the long wavelengths of the notes.

Acknowledgments

The author is grateful to the members of the Western Pennsylvania Skylighters (a.k.a., West Penn Pyros) for the countless hours of effort they put into the construction of the two PGI demonstrations. While the idea of making music with whistles may have been mine, it would never have become a reality without their efforts. I consider myself fortunate to be associated with them.

References

- 1) *American Institute of Physics Handbook*, McGraw Hill, 1982, p 3-132.
- 2) C. Villeneuve, *Pyrotechnics Guild International Bulletin*, No. 86, 1993, p 15.
- 3) S. Öztap, *Pyrotechnica XIII*, 1990, p 19.



Photo 1. Western Pennsylvania Skylighters assembling whistle note racks.

High-Nitrogen Pyrotechnic Compositions^[1]

David E. Chavez and Michael A. Hiskey*

Los Alamos National Laboratory, Group DX-2 High-Explosives Science and Technology,
Mail Stop C920, Los Alamos, NM 87545, USA
e-mail: hiskey@lanl.gov

* Author to whom correspondence should be addressed.

ABSTRACT

Pyrotechnics produce irritating and obscuring smoke. High-nitrogen materials have been investigated for use in pyrotechnic compositions to reduce smoke production. Compositions containing dihydrazino-tetrazine have been found to produce brilliantly colored flames with little or no smoke or ash production. The preparation of dihydrazino-tetrazine is also discussed.

Keywords: low smoke pyrotechnics, high-nitrogen energetic materials, dihydrazino-tetrazine

Introduction

Almost all pyrotechnic compositions produce smoke. The smoke is derived from two main sources. Partial combustion of fuels accounts for a certain amount of the smoke, as rarely is the mixture's oxygen balance sufficient for complete combustion. Metals account for most smoke. Metal compounds are used in pyrotechnics as both oxidizers [e.g., KClO_4 , KNO_3] and as coloring agents [e.g., $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, Na_3AlF_6 , CuS]. Except in instances where smoke is specifically required, it is generally a nuisance. Spectators typically find smoke to be irritating to the nose and eyes, and smoke also obscures the display.

Metal compounds in pyrotechnics cannot be avoided. Fortunately, lead, mercury and arsenic compounds are typically not used in modern compositions, but metal salts as flame colorants are widely used in concentrations of 20% to 60% by weight. Drastic reduction of metal-salt, flame-coloring agents would result in a much

cleaner burning composition but is usually not possible, as depth of color would suffer. Thus, pyrotechnic formulators are faced with a dilemma, as they are required to strike a delicate balance between color quality and excessive smoke. Indoor displays are further complicated by the simple fact that the smoke is contained in the room. Reduction of metal compounds in pyrotechnics for indoor displays would reduce exposure of cast, crew and audience to such toxic metals as copper, strontium, barium and antimony.^[2]

Results

At Los Alamos National Laboratory, we have been involved with the preparation of high-nitrogen energetic materials for use as explosives^[3] and gas generants^[4] as well as pyrotechnic ingredients. When ignited, high-nitrogen fuels typically exhibit an almost colorless flame and produce no smoke or ash. For use as a pyrotechnic ingredient, a high-nitrogen material must have the proper ratio of carbon, hydrogen and nitrogen as well as an appropriate ambient pressure burn rate.

After examination of a large number of materials, including nitroguanidine, guanidine nitrate, aminoguanidine nitrate, and 3,6-diamino-1,2,4,5-tetrazine, we found that 3,6-dihydrazino-1,2,4,5-tetrazine (Figure 1) (abbreviated Hz_2Tz) gave easily ignited, brilliantly colored flames when mixed in the proper proportions with oxidant and coloring agent. More importantly, these mixtures produced no smoke and little or no ash.

It was found that two equivalents of available oxygen from the oxidant were required for

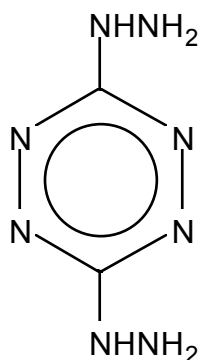


Figure 1. $H_{z_2}T_z$.

sustained burning of $H_{z_2}T_z$. The only oxidants examined were ammonium perchlorate (NH_4ClO_4 , AP) and ammonium nitrate (NH_4NO_3 , AN). These oxidants were examined as they contain no metals.

Flame coloring agents were the commonly used metal salts with the exception of blue (copper) where it was noticed that water soluble copper salts were powerful burn rate accelerants for $H_{z_2}T_z$. Copper(II) sulfide (CuS) was found to give an acceptable blue-colored flame with only a slight increase in burning rate. The levels of colorant were 5 weight percent for AP formulations and 8 weight percent for AN formulations. A small amount of AP is added to the AN formulations as a source of chloride to deepen flame colors.

The mixtures contain no binder. The AP formulations were simply wet with water, pressed to shape in a simple hand press and air-dried. The consolidated material appeared to be strong enough for use as stars in aerial shells. It was not possible to use water in the AN formulations due to the hygroscopic nature of this oxidant. These mixtures were wet with ethanol or isopropanol before being hand pressed to shape, and air dried. AN pieces were much more fragile than AP pieces and more difficult to ignite; thus, they were primed, strengthened, and waterproofed by dipping in nitrocellulose lacquer of the type used to coat Visco® safety fuse. AN formulations which contained strontium exhib-

ited strobing at about 2–3 Hz. Two rarely seen pyrotechnic colors are easily achievable using $H_{z_2}T_z$ as fuel. One is a deep red-purple strobe with AN as oxidant and strontium nitrate and copper(II) sulfide as colorants. A deep turquoise is also made using AP as oxidant and copper(II) sulfide and barium nitrate as colorants.

Synthesis of $H_{z_2}T_z$

$H_{z_2}T_z$ has been known in the literature since 1963.^[5] Its preparation was somewhat tedious in that it involved hydrazinolysis of diamino-tetrazine at elevated temperature.^[6] We have a much simplified procedure utilizing the readily available 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (abbreviated BDDT) which is made from triaminoguanidine hydrochloride and 2,4-pentanedione.^[7]

Stirring the BDDT with 2 equivalents of hydrazine hydrate at room temperature with exposure to atmospheric oxygen results in both aromatization and nucleophilic displacement to yield $H_{z_2}T_z$ in a 92% yield (Figure 2). $H_{z_2}T_z$ is a very insoluble bright red powder that has a fifty percent drop height of 65 cm (Type 12). Black Powder has a drop height of 32 cm. $H_{z_2}T_z$ has a heat of formation of +128 kcal/mol as determined by combustion calorimetry. A flotation density of 1.69 g/cm³ and differential thermal analysis (DTA) exotherm at 160 °C were also measured.

Experimental

The following procedure should only be attempted by those experienced and equipped in energetic materials synthesis with proper laboratory facilities. Materials used are toxic and flammable. Hydrazine and its derivatives should be regarded as possible carcinogens. All reagents were purchased from commercial sources except where noted. Nuclear magnetic resonance (nmr) spectra were obtained on a JEOL GSX-270. Chemical shifts are relative to internal tetramethylsilane for ¹H and ¹³C spectra.

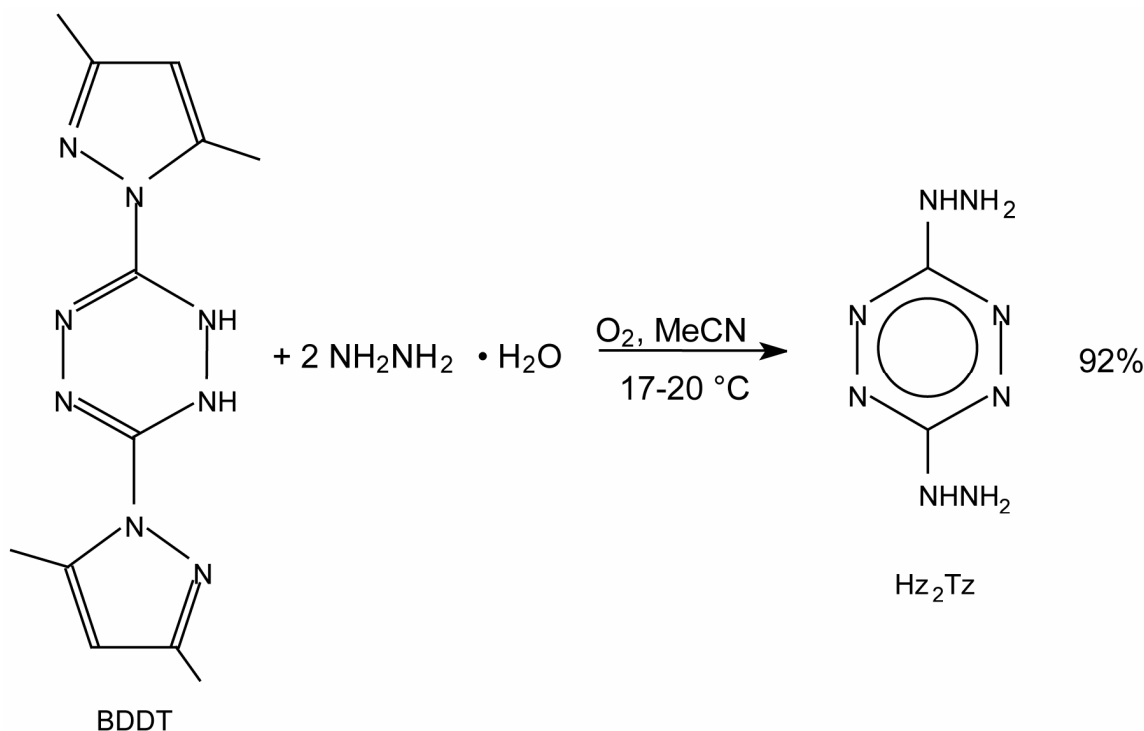


Figure 2. Preparation of Hz₂Tz.

3,6-Dihydrazino-1,2,4,5-tetrazine

The following procedure should be only attempted by those experienced in the synthesis of energetic materials. Proper laboratory facilities are essential. To a 500 ml three-necked jacketed flask equipped with a mechanical stirrer is added 54.5 g of 3,6-bis(3,5-dimethyl-pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (0.2 mol) and 300 ml acetonitrile. The temperature of the bath is reduced to 12 °C and 21 g hydrazine hydrate (0.42 mol) is added dropwise with stirring. After the addition, the funnel is removed and the mixture is stirred 48 h at 17–20 °C with exposure to air in which time a maroon red precipitate forms. This is filtered off on a glass frit, washed with acetonitrile and air dried yielding 26.1 g (92 %). This material is identical in all respects to that previously reported.^[6,7] ¹H nmr (deuteriomethylsulfoxide) δ 4.26 (bs, 4H), 8.39 (s, 2H). ¹³C nmr (deuteriomethylsulfoxide) δ 164.0

Warning: The long term stability of Hz₂Tz and Hz₂Tz mixed with oxidants is excellent. However, the stability of Hz₂Tz with transition metals is suspected to be somewhat less but has not yet

been proven. A blue AN-based star was reported to have spontaneously ignited.^[8]

Ammonium Perchlorate Compositions

The ammonium perchlorate formulations had the following compositions by weight:

AP	47.5 %
Hz ₂ Tz	47.5 %
colorant	5.0 %

Colorants:

Red		Sr(NO ₃) ₂ or CaCl ₂
Yellow		NaNO ₃
Green		Ba(NO ₃) ₂
Blue		CuS
Blue-Green	8:1	Ba(NO ₃) ₂ :CuS
Purple	2:1	CuS:Sr(NO ₃) ₂
Red Purple	1:1:3	CuS:Ba(NO ₃) ₂ :Sr(NO ₃) ₂
White		Sb ₂ S ₃

All ingredients were thoroughly ground together, dampened with water, pressed to shape and air-dried. The only exceptions to the above AP compositions were the white and blue.

White stars doubled the Sb_2S_3 concentration to 10% while blue had the following composition: 50% Hz_2Tz , 41% AP, 9% CuS.

Ammonium Nitrate Compositions

The ammonium nitrate formulations had the following compositions by weight:

Hz_2Tz	45%
AN	38%
AP	8%
colorant	8%

All ingredients were thoroughly ground together, wet with alcohol, pressed to shape, air dried, dipped in nitrocellulose lacquer and re-dried. Blue stars utilized CuO rather than CuS as a somewhat deeper color was obtained.

Conclusion

Pyrotechnic compositions containing Hz_2Tz have been shown to burn with little or no smoke. The formulations have comparable or deeper coloration with a lower concentration of metals. Novel colors are also possible using Hz_2Tz as fuel. The preparation of Hz_2Tz has been simplified and improved over previous methods.

References

- 1) Patent Pending.
- 2) M. Rossol, "Health Effects from Theatrical Pyrotechnics", *J. Pyrotechnics*, No. 3, 1996, pp 14–21.
- 3) M. D. Coburn, M. A. Hiskey, K.-Y. Lee, D. G. Ott, and M. M. Stinecipher, "Oxidations of 3,6-Diamino-1,2,4,5-tetrazine and 3,6-Bis(S,S-dimethylsulfilimino)-1,2,4,5-tetrazine", *J. Heterocyclic Chem.*, Vol. 30, 1993, pp 1593–1595.
- 4) M. A. Hiskey, N. Goldman, and J. R. Stine, "High-Nitrogen Energetic Materials Derived from Azotetrazolate", Accepted for publication in *J. Energetic Materials*, 1997.
- 5) H. J. Marcus and A. Remanick, "The Reaction of Hydrazine with 3,6-Diamino-s-tetrazine", *J. Org. Chem.*, Vol. 28, 1963, pp 2372–2378.
- 6) H. J. Marcus, "Tetrazine Compounds", U. S. Patent 3,244,702, April 5, 1966.
- 7) M. D. Coburn, G. A. Buntain, B. W. Harris, M. A. Hiskey, K.-Y. Lee, and D. G. Ott, "An Improved Synthesis of 3,6-Diamino-1,2,4,5-tetrazine. From Triaminoguanidine and 2,4-Pentanedione", *J. Heterocyclic Chem.*, Vol. 28, 1991, pp 2049–2050.
- 8) Personal Communication, Russ Nickel, Precision Theatrical Effects.

An Oxygen-Exchange Approach to Pyrotechnic Formulation

E. J. Clinger

Sotsyalisticheskaya 65/3, Kharkov 310093, Ukraine

and

Wesley D. Smith

Department of Chemistry, Ricks College, Rexburg, ID 83460-0500, USA

ABSTRACT

An old model of pyrotechnic reactions is presented in such a way that modern pyrotechnists are able to create new formulations using the principles of chemical stoichiometry but without having to know the exact products of the reaction involved. According to the model, pyrotechnic reactions occur in two distinct steps. The oxidizers produce molecular oxygen, then the fuels consume it. How this oxygen (including, in some cases, oxygen from the atmosphere) is distributed among the components of the mixture leads to the coefficients on the reactant side of the corresponding chemical equation. And from them, the composition of the formulation can be calculated. Using the oxygen-exchange approach, one can add or replace ingredients in a given formulation and come up with a stoichiometrically equivalent composition.

Keywords: oxygen exchange, pyrotechnic formulating, oxidizer, fuel, chemistry

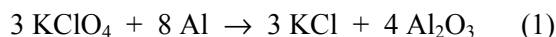
Stoichiometry

The ideal way to formulate a pyrotechnic composition is to mix the ingredients according to the stoichiometry of the chemical reaction involved.^[1] However, that approach requires a detailed knowledge of the reaction including its balanced chemical equation. Specifying the reactants is easy enough; they are merely the components of the proposed formulation. But the task of predicting all the products of a pyro-

technic reaction is far from simple, even for an experienced chemist. In this paper, we present a method of formulating mixtures using the principles of stoichiometry but without having to know the exact identity of the products.

Introductory Examples

By way of introduction, let us examine the combustion of flash powder. The main reaction is probably



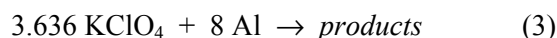
We say “probably” because we have relied only on our chemical intuition here. We have not searched any of the original scientific literature on it. All we know for certain is that we start with potassium perchlorate and aluminum. The products are a matter of assertion. And even if this single equation *does* represent the major chemical change, it would not account for any of the competing side reactions that are always present in a real-world process. Nevertheless, equation 1 tells us to mix our flash powder in the proportion of three moles potassium perchlorate (or $3 \text{ mol} \times 138.55 \text{ g/mol} = 415.65 \text{ g}$) to eight moles aluminum (or $8 \text{ mol} \times 26.98 \text{ g/mol} = 215.84 \text{ g}$) for a total weight of $(415.65 + 215.84 =) 631.49 \text{ g}$. This theoretical formulation, 65.8% KClO_4 ($415.65/631.49 \times 100\%$) and 34.2% Al ($215.84/631.49 \times 100\%$) by weight, is nearly identical to one of Lancaster’s compositions,^[2] which, presumably, has been well-tested.

Unlike ordinary combustibles (e.g., candle flames or campfires), a stoichiometric mixture of potassium perchlorate and aluminum, reacting by equation 1, does not depend on atmospheric oxygen in order to burn. It will deflagrate in the tightly-pasted confinement of a bottom shot or perhaps even in the vacuum of outer space. We say that such a composition has a zero oxygen demand. There is no deficiency of oxidizer in the mix; neither is there an excess.

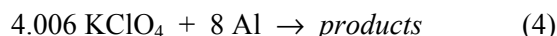
The commonly-quoted flash formulation, however, is 70.0% KClO₄ and 30.0% Al by weight.^[2] This corresponds to a mole ratio of

$$\frac{\left(\frac{70.0 \text{ g KClO}_4}{138.55 \text{ g/mol KClO}_4}\right)}{\left(\frac{30.0 \text{ g Al}}{26.98 \text{ g/mol Al}}\right)} = 0.4544 = \frac{3.635}{8} \quad (2)$$

In other words, instead of following the stoichiometry of equation 1, the 70:30 formulation comes from a reaction that could be written as



In like manner, Shimizu's Thunder No. 4 formulation^[3a] (72.0% KClO₄ and 28.0% Al by weight) might be derived from the reaction



Here, the mole ratio of 4.006 to 8 corresponds to the mass ratio of 72 to 28.

Both of these compositions may have an excess of oxidizer, *if* the products are assumed to be the same as those of equation 1. On the other hand, equations 3 and 4 may actually represent new and different reactions from that of equation 1—various oxides of chlorine or potassium might be included as additional products, for instance. For our present purposes, however, we do not have to know.

We can balance the reactant side of the chemical equation for any pyrotechnic reaction if we know the composition of the mixture. We need not know any information about the products. We can always give the left-hand side of the equation whatever coefficients it needs. Different blends of the same components could, in

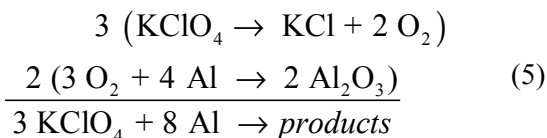
reality, yield different products, or they could simply be non-stoichiometric mixtures that give the same products. But it does not matter as long as we allow ourselves freely to adjust the coefficients of reactants in the balanced chemical equation.

Oxygen-Exchange Reactions

The point of adjusting coefficients, however, is not to write chemical equations for existing compositions but to create new ones. In order to provide this procedure with some practical predictive power, we need a chemical starting point. If somehow we had to know the finished formulation beforehand, we would be running around in circles. Thus, we must first come up with some chemically-plausible products for the pyrotechnic reaction of interest and use them as a point of departure. These reactions, with both reactants and products, can be tabulated.

Since nearly all pyrotechnic reactions involve the element oxygen, we can make reaction tables quite conveniently by following the century-old method of Tsytoovich.^[4] We imagine the reaction as proceeding in two steps. First, the oxidizer decomposes into molecular oxygen. Second, the fuel reacts with that molecular oxygen. These two steps are then combined so that the molecular oxygen balances. That is, the two intermediate reactions are adjusted (including, in some cases, certain amounts of outside, atmospheric oxygen) so that the same amount of oxygen is involved in both. The overall reaction then retains all the stoichiometric information of the direct reaction.

For example, to obtain equation 1, we first decompose the KClO₄ to produce O₂ and then consume that O₂ with the Al



We balance the equation by making sure the same number of oxygen molecules—in this case, 6—are both produced by the oxidizer and consumed by the fuel. No atmospheric oxygen is involved here.

Table 1. The Decomposition of Some Common Pyrotechnic Oxidizers To Produce Molecular Oxygen. The Factor n_o Is the Number of O_2 Molecules Produced Divided by the Number of Oxidizer Molecules Consumed.

Oxidizer	Formula	For. Wt.	Decomposition Reaction	n_o
Ammonium perchlorate	NH_4ClO_4	117.49	$4 NH_4ClO_4 \rightarrow 2 N_2 + 6 H_2O + 4 HCl + 5 O_2$	1.25
Barium nitrate	$Ba(NO_3)_2$	261.34	$2 Ba(NO_3)_2 \rightarrow 2 BaO + 2 N_2 + 5 O_2$	2.50
Strontium nitrate	$Sr(NO_3)_2$	211.63	$2 Sr(NO_3)_2 \rightarrow 2 SrO + 2 N_2 + 5 O_2$	2.50
Potassium chlorate	$KClO_3$	122.55	$2 KClO_3 \rightarrow 2 KCl + 3 O_2$	1.50
Potassium nitrate	KNO_3	101.10	$4 KNO_3 \rightarrow 2 K_2O + 2 N_2 + 5 O_2$	1.25
Potassium perchlorate	$KClO_4$	138.55	$KClO_4 \rightarrow KCl + 2 O_2$	2.00

The advantage of employing oxygen as an intermediate is that it is much easier to write chemical equations for how the combustion of individual fuels consume O_2 , and for how lone oxidizers decompose to produce it, rather than predicting the complicated exchanges of electrons in the fuel/oxidizer mixtures themselves. Further, a plausible equation for the reaction between or among any number of oxidizers and fuels can be created from the information on just two tables. Table 1 gives the oxygen-producing reactions for common pyrotechnic oxi-

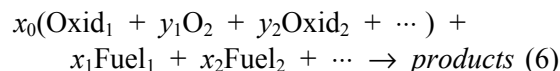
dizers. Table 2 shows how common pyrotechnic fuels consume oxygen.

Table 2. The Oxidation of Some Common Pyrotechnic Fuels in the Presence of Abundant Molecular Oxygen. The Factor n_f Is the Number of O_2 Molecules Consumed by Each of the Fuel "Molecules". Substances Marked with an Asterisk Have Empirical Formulas (Which Only Reflect their Elemental Composition) Rather Than Molecular Formulas (Which Indicate the Structure of Specific Molecules).

Fuel	Formula	For. Wt.	Oxidation Reaction	n_f
Aluminum	Al	26.98	$4 Al + 3 O_2 \rightarrow 2 Al_2O_3$	0.75
Antimony trisulfide	Sb_2S_3	339.68	$2 Sb_2S_3 + 9 O_2 \rightarrow 2 Sb_2O_3 + 6 SO_2$	4.50
Charcoal*	$C_{322}H_{184}NO_{37}$	4659.0	$C_{322}H_{184}NO_{37} + 350 O_2 \rightarrow 322 CO_2 + 92 H_2O + NO$	350
Dextrin*	$C_6H_{10}O_5$	162.14	$2 C_6H_{10}O_5 + 12 O_2 \rightarrow 12 CO_2 + 10 H_2O$	6.00
Hexamine	$C_6H_{12}N_4$	140.19	$C_6H_{12}N_4 + 9 O_2 \rightarrow 6 CO_2 + 6 H_2O + 2 N_2$	9.00
Iron	Fe	55.85	$4 Fe + 3 O_2 \rightarrow 2 Fe_2O_3$	0.75
Lampblack	C	12.01	$C + O_2 \rightarrow CO_2$	1.00
Magnesium	Mg	24.305	$2 Mg + O_2 \rightarrow 2 MgO$	0.50
Magnalium (50/50)*	Al_9Mg_{10}	485.88	$4 Al_9Mg_{10} + 47 O_2 \rightarrow 18 Al_2O_3 + 40 MgO$	11.75
Parlon*	$C_5H_6Cl_4$	207.91	$2 C_5H_6Cl_4 + 13 O_2 \rightarrow 10 CO_2 + 6 H_2O + 4 Cl_2$	6.50
PVC*	C_2H_3Cl	62.50	$4 C_2H_3Cl + 11 O_2 \rightarrow 8 CO_2 + 6 H_2O + 2 Cl_2$	2.75
Red gum*	$C_{31}H_{35}O_{16}$	663.61	$4 C_{31}H_{35}O_{16} + 127 O_2 \rightarrow 124 CO_2 + 70 H_2O$	31.75
Sulfur*	S	32.06	$S + O_2 \rightarrow SO_2$	1.00
Titanium	Ti	47.88	$Ti + O_2 \rightarrow TiO_2$	1.00

Oxygen-Exchange for a Generalized Reaction

Consider the generalized reaction between one or more oxidizers and one or more fuels. We write the chemical equation as



Here the x 's and y 's are the (unknown) coefficients necessary to balance the equation. If there is just one oxidizer, x_0 is its coefficient. As a mathematical convenience, we take the coefficients of the other oxidizers, Oxid_i , to be a multiple, y_i , of x_0 . Note the explicit participation of atmospheric oxygen, O_2 , in the process. Its coefficient is $x_0 y_1$. In flash powders, burst charges, and rocket fuels, for example, y_1 may be zero. But for the open-air burning of stars, comets, gerbs, and the like, significant quantities of outside oxygen (and non-zero y_1 's) may be necessary to describe the actual reactions, even though O_2 is never regarded as part of any formulation's recipe.

Now let n_{oi} be the number of O_2 molecules produced by Oxid_i , and let n_{fi} be the number of O_2 molecules consumed by Fuel_i according to Tables 1 and 2. For oxygen balance, the number of O_2 molecules consumed by the fuel(s) must be the same as those produced by the oxidizer(s) plus those extracted from the atmosphere. Thus, we have

$$x_0(n_{o1} + y_1 \cdot 1 + y_2 n_{o2} + \dots) = x_1 n_{f1} + x_2 n_{f2} + \dots \quad (7)$$

(The number of O_2 molecules involved with each atmospheric oxygen molecule is, of course, 1.) This gives us one mathematical equation with potentially many unknowns. In a balanced *chemical* equation, we can multiply each of the coefficients by the same arbitrary number and still have a balanced equation. So in equation 7 we are free to choose any value we wish for *one* of the coefficients x_i or y_i . (We can let $x_1 = 1$, for example.) Then we solve for x_0 .

$$x_0 = \frac{x_1 n_{f1} + x_2 n_{f2} + \dots}{n_{o1} + y_1 \cdot 1 + y_2 n_{o2} + \dots} \quad (8)$$

When there is only one oxidizer, one fuel, and no atmospheric oxygen involved, as in the flash examples above, we can obtain x_0 uniquely for each chosen x_1 . But if two or more oxidizers, fuels, and/or atmospheric oxygen participate in the mix, an infinite number of sets of x_i and y_i values satisfy equation 8, and they are freely adjustable. Once we have chosen the x_i and y_i values, we can calculate the weight percent w_i of any component in the formulation:

$$w_i = \frac{A}{x_0 M_{o1} + x_0 y_2 M_{o2} + \dots + x_1 M_{f1} + x_2 M_{f2} + \dots} \times 100\% \quad (9)$$

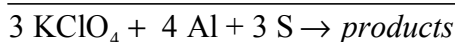
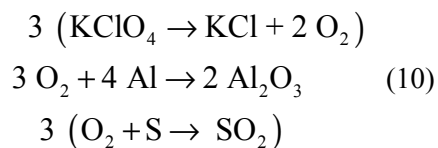
where M_{oi} or M_{fi} is the formula weight of component i , x_0 is given in equation 8, and A equals $x_0 M_{o1}$, $x_0 y_i M_{oi}$ or $x_i M_{fi}$ depending on whether the component is the first oxidizer, another oxidizer, or a fuel, respectively. Notice that the amount of atmospheric oxygen does not appear explicitly in equation 9. It influences the value of x_0 , but it does not contribute a separate term to the denominator of equation 9—the total mass of composition. That is to say, oxygen's part in the eventual chemical reaction is accounted for, but O_2 is not a component of the manufactured formulation.

Stoichiometric Equivalence

One of the most daunting aspects of pyrotechnic formulation by trial-and-error is the sheer number of tests that must be carried out. A Shimizu publication,^[5] for instance, documents 152 experiments on triangle diagrams and 82 more in tables just on blue flame compositions alone. However, with the oxygen-exchange approach, we can create, on paper, many formulations which are stoichiometrically equivalent to any given published composition. Such equivalence in no way insures an identical pyrotechnic effect, but the results, in our experience, are often quite similar. It allows us to build on the painstaking work of others without having to be so indefatigable. In a phrase, our formulations can have higher "convenience quotients". The quality of their performance versus the man-hours necessary for their optimization is much greater.

Adding a Component

As an illustration, suppose we wish to add some sulfur to the equation 1 mixture. Proceeding with full knowledge that sulfur will make the mixture more sensitive to accidental ignition, especially by impact,^[6] we seek an equivalent combination. To do so with a zero oxygen demand, we must either increase the amount of oxidizer to consume the extra fuel, or we must replace some of the aluminum with sulfur. Either way, the two fuels must share the one oxidizer. We recall from equation 5 that 6 oxygens are produced by the potassium perchlorate. In the absence of outside oxygen, those 6 oxygens must be divided between the aluminum and the sulfur. If they are divided evenly, we have



This combination, 67.1% KClO_4 , 17.4% Al , and 15.5% S , is close to another formula^[7] (67:17:16) attributed to Lancaster, but it is not the only possibility. Dividing the oxygen between the two fuels in all possible ways gives the formulations along the straight line in the triangle diagram of Figure 1. All these compositions fall into the region where sound accompanies the reaction, except when the amount of aluminum falls below about 5%. The loudest of them, however, are in the immediate neighborhood of equation 10.

One way to obtain the formulations that fall above or below the straight line is to allow atmospheric oxygen to participate. We can give the compositions either a positive or a negative oxygen demand. Shimizu's Thunder No. 3^[3a] (64:23:13), for example, lies below the line. It can be viewed as coming from a process in which atmospheric oxygen is a necessary reactant, namely

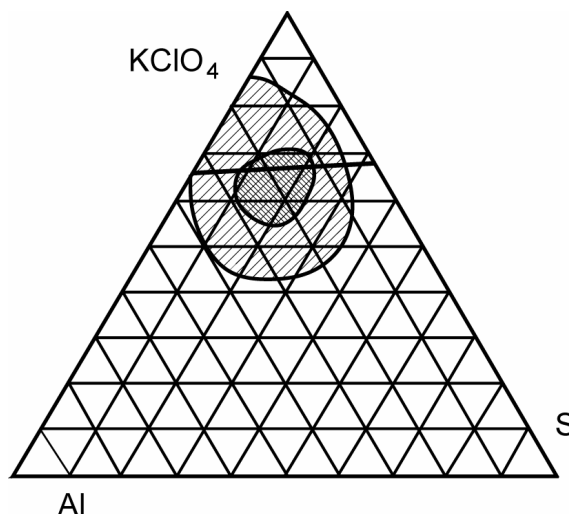
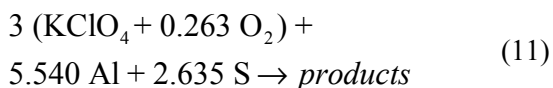


Figure 1. Regions of sound production in flash powder mixtures (reference 2). Those in the darker region produce louder sounds.

Here, oxygen's coefficient, $y_1 = 0.263$, is positive. Thus, this formulation, like all others below the line, has a positive oxygen demand.

We calculated the coefficients of equation 11 as follows: First, we chose one of them at random. We took $x_0 = 3$ so that the equation would have a 3 KClO_4 term just like equation 1, but any other choice would have been just as good. Next, we used that coefficient together with the 64% KClO_4 of the formulation to calculate the denominator of equation 9. (We could also have used the 23% Al amount—or the 13% S —as the means of determining it.) Knowing the value of the denominator and the other percentages of the formulation, we then solved equation 9 repeatedly for the remaining coefficients. Finally, the value of y_1 came from equation 7.

For compositions above the straight line, like equations 3 and 4, oxygen can also take part, but with a *negative* coefficient. A negative coefficient in a chemical equation simply means that the substance belongs on the opposite side of the arrow. In these above-the-line formulations, the potassium perchlorate can be regarded as present in excess of its stoichiometric necessity. As such, it would produce more oxygen than is needed to consume the fuel(s), and that extra oxygen would appear among the products.

Table 3. Percent Compositions of Fish’s “Excellent” Formulations for Green Flame (reference 8) and for Three Magnalium Compositions Derived from the Magnesium Formula by Oxygen Exchange.

Component	Fish’s Formulations		Derived Formulations		
Barium sulfate	40.5	42.5	41.5	40.8	42.3
Magnesium	17.0	—	—	—	—
Magnalium	—	13.0	14.9	15.4	14.3
Parlon	18.5	19.5	19.0	19.6	18.3
Potassium perchlorate	24.0	25.0	24.6	24.2	25.1
Hexamine	+10.0	+10.0	+10.0	+10.0	+10.0
Boric acid	+3.0	+2.0	+3.0	+3.0	+3.0
Red gum	+3.0	+3.0	+3.0	+3.0	+3.0
Oxygen Demand	2.856	—	2.856	3.142	2.570

It would be interesting to test whether molecular oxygen *literally* participates pyrotechnically in these ways. But, as we have said, the oxygen-exchange approach would work regardless of the experiments’ outcome. Balancing the intermediate oxygen—be it real or imaginary—is nothing more than a self-consistent method of tracking reaction stoichiometry.

Substituting Ingredients: Green Flame

Fish,^[8a] after a thorough study of colored-flame compositions containing metal fuels and Parlon, came up with two formulations for green flame which he labeled as “excellent”. These are quoted in Table 3.

Suppose that we knew one of these two formulations but not the other. Could we create an “excellent” magnalium formulation if we knew only the magnesium composition, or vice versa, without resorting to brute-force trial-and-error? The oxygen-exchange technique gives us a good chance.

Following the procedure of the previous section, we obtain the chemical equation corresponding to Fish’s magnesium formulation.

Here, the coefficient of Mg was chosen arbitrarily, and the stoichiometric contributions of hexamine, boric acid, and red gum were ignored, since they would retain their constant percentages in any derived formulations. The data for barium sulfate is from Table 4.

Our next objective is to create a stoichiometrically equivalent equation that contains magnalium instead of magnesium. Consulting Table 2, we determine that the magnesium in equation 12 consumes $10(0.50) = 5$ molecules of O_2 . Since each formula unit of magnalium consumes 11.75 oxygens, Al_9Mg_{10} (the empirical formula for 50/50 magnalium) needs a coefficient of $5/11.75 = 0.4255$ to use the identical amount of molecular oxygen. Substituting magnalium, with this coefficient, into equation 12, we obtain^[9] the formulation in the third column of Table 3. This has the same y_1 oxygen-demand coefficient as the magnesium composition in the first column. If we increase y_1 by 10% or decrease it by 10%, we get the formulations the fourth and fifth columns, respectively.

Now we have three new formulations to evaluate—not the three dozen or three hundred of an exhaustive test. Since none of them matches Fish’s result exactly, we cannot tell *a priori* whether any would also be judged “excellent”, but the chances are good one or more of them will measure up. Each will produce at



Table 4. The Decomposition of Selected Oxidizers Not Listed in Table 1. The Factor n_o Is the Number of O_2 Molecules Produced Divided by the Number of Oxidizer Molecules Consumed.

Oxidizer	Formula	For. Wt.	Decomposition Reaction	n_o
Barium sulfate	BaSO ₄	233.39	2 BaSO ₄ → 2 BaO + 2 SO ₂ + O ₂	0.50
Bismuth(III) oxide	Bi ₂ O ₃	417.96	2 Bi ₂ O ₃ → 4 Bi + 3 O ₂	1.50
Copper(II) oxide	CuO	79.545	2 CuO → 2 Cu + O ₂	0.50
Lead tetroxide	Pb ₃ O ₄	685.0	Pb ₃ O ₄ → 3 Pb + 2 O ₂	2.00

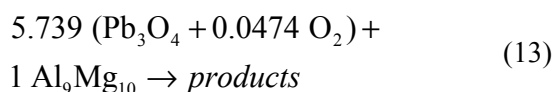
least a “good” green flame because the latitude of effectiveness for such mixtures is rather large.^[8b] And all three are very close to the recommended composition. The third one, in fact, has almost the identical percentages of oxidizers (but it may be weak in its amount of chlorine donor). The second has the same amount of Parlon (but it has lower percentages of barium sulfate and potassium perchlorate). Regardless of the differences or similarities among them, however, their “convenience quotients” will certainly be high.

Substituting Ingredients: Crackle

With crackling microstars, the Chinese have developed a truly exciting effect. Their compositions, however, usually contain lead oxides which are highly toxic. A typical formulation, attributed to Swisher,^[10] is given in Table 5. It is a mixture of lead tetroxide and magnalium. In an effort to defeat the toxicity problem, Jennings-White^[11a] came up with a lead-free crackle composition by replacing the lead oxidizer with a blend of bismuth(III) oxide and copper(II) oxide. He then did many laboratory tests to arrive at an optimal result—which remains as the only sure way to do so, this paper notwithstanding. But formulations like his can be predicted theoretically with the oxygen-

exchange approach.

Choosing the coefficient of magnalium as 1, we obtain the corresponding chemical equation for Swisher’s crackle:



Since the one formula unit of magnalium consumes 11.75 oxygens, the lead tetroxide must produce an equal amount, minus that which is supplied by atmospheric oxygen. Thus, the contribution of the lead oxidizer is $11.75 - 5.739(0.0474) = 11.48$ oxygens. For a stoichiometrically equivalent formulation, any substitute combination of bismuth(III) oxide and copper(II) oxide must also produce 11.48 oxygens. All possible mixtures of Bi₂O₃, CuO, and magnalium that meet these criteria are represented by the line on the triangle diagram in Figure 2. (Mixtures to the right of the line have greater oxygen demands; those to the left have lesser.) However, from Shimizu’s study^[10] on lead microstars, we find that whenever his compositions contained CuO, it was present only in the 5-17% range. If CuO is included in these proportions in our derived lead-free formulations, the results fall on that part of the line inside the region of effectiveness. As one example, if we fix the CuO percentage at 10%, we get the first

Table 5. The Percent Compositions of Various Formulations for Crackling Microstars.

Component	Swisher	Jennings-White	Derived Formulations	
Lead tetroxide	89.0	—	—	—
Bismuth(III) oxide	—	75.0	75.8	75.0
Copper(II) oxide	—	10.0	10.0	10.7
Magnalium	11.0	15.0	14.2	14.3
Oxygen Demand	0.0474	—	0.0474	0.0474

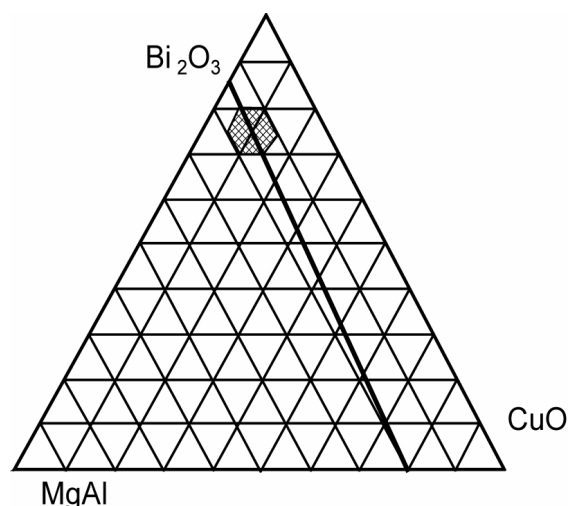
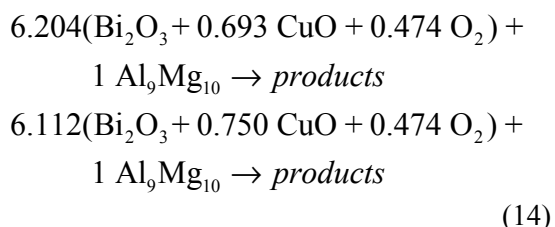


Figure 2. Region of effectiveness of lead-free crackling microstars (reference 11).

derived formulation in Table 5. As another, if we cause four-fifths of the 11.48 oxygens to come from Bi_2O_3 and one-fifth to come from CuO , we get the other tabulated composition. These correspond to the reactions,



respectively. Both of them fit well within those “adjacent formulations in the triangle diagrams at a 5% level of resolution” that Jennings-White^[11b] says should “function fairly well”.

Formulating from Scratch

The quest for new and better fireworks effects is the driving force of pyrotechnic research. Blindly testing multitudinous formulations whose compositions are chosen at random is one way to go about it. But that approach is neither efficient nor artful. If we first peruse as many published formulations^[7] as we can, however, we can make some broad generalizations. These are found in Table 6. These rough figures are meant to be used only as first approximations. Exceptions can be found in many compositions, even among the examples in this paper.

But if we start within these ranges, we are more likely to be in the ballpark. To achieve these initial proportions, and as we proceed toward the final formula, we repeatedly adjust the coefficients in the appropriate chemical equation. We do this and the accompanying calculations, rather than just adjust the parts-by-weight in the mixture directly, because the oxygen-exchange method continually keeps the components in stoichiometric balance.

To illustrate, let us create a gerb mix with ammonium perchlorate as the oxidizer and iron metal as the fuel and the source of sparks. If we choose a zero oxygen demand, we have a two-component system, and we can calculate its stoichiometry without adjusting any coefficients. From the reaction

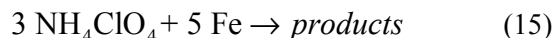


Table 6. Approximate Ranges of Content for Selected Components in Typical Pyrotechnic Mixtures.

Component	Example	Percent
Oxidizers	KClO_4	77–84
	KNO_3	58–75
	KClO_3	35–45
Color Oxidizers	$\text{Sr}(\text{NO}_3)_2$ or $\text{Ba}(\text{NO}_3)_2$	56–66
Metal Fuels	Mg	11–30
	Magnalium	11–30
	Al	5–45
	Ti	0–20
Chlorine Donors	Parlon, PVC, etc.	6–20
Binders	Dextrin, Starch, etc.	1–14

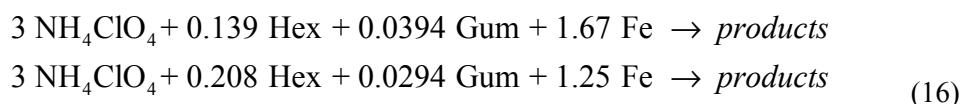
Table 7. Sets of Stoichiometrically Equivalent Formulations Illustrating the Development of a Gerb Mix by the Oxygen-Exchange Technique.

Component	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
NH ₄ ClO ₄	55.8	71.7	74.8	49.4	53.3	39.0	41.8
KNO ₃	—	—	—	—	—	14.5	15.6
Hexamine	—	4.0	6.2	7.1	11.5	6.5	10.5
Red Gum	—	5.3	4.2	9.5	7.7	8.8	7.0
Iron	44.2	19.0	14.8	34.0	27.5	31.2	25.1
Oxygen Demand	0	0	0	2	2	2	2

we obtain the preliminary Mix 1 in Table 7. However, for several reasons, we sense that this formulation needs improvement. First, the percent of metal fuel is on the high side, according to the guidelines in Table 6. We should do something to decrease it. Second, we want the mixture to ignite easily and remain lit. With iron as the only fuel, we know that these aims will be notoriously difficult to achieve; therefore, we should include one or more additional fuels. Finally, we want the particles of carbon, dissolved in the molten iron, to reach their ignition temperature and explode in the atmosphere as sparks.^[3b] Thus, we should give the mixture a positive oxygen demand.

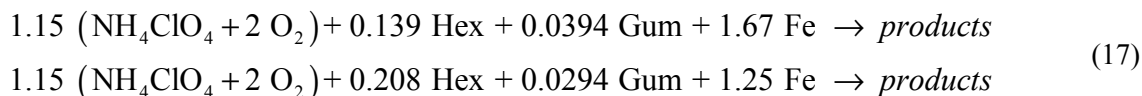
As part of the improvement, we add hexamine as a more energetic fuel and red gum as an auxiliary fuel and binder. But in what proportions should they be mixed? Intuition tells us

Mix 3 comes from our assigning 1.875 oxygens to the hexamine and 0.9375 oxygens each to the red gum and the iron. Because the n_f values for these fuels—the number of oxygens consumed per mole—are quite different from each other, so are their coefficients in the chemical equations



and so are their percentages by weight in the formulation in Table 7. It is not obvious, without the oxygen-exchange approach, to see how those percentages are related.

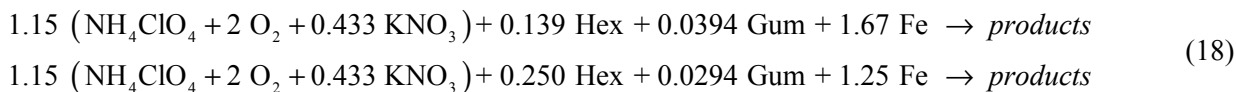
Now we allow atmospheric oxygen to participate in these equations, with $y_1 = 2$. And this changes the percentages in more non-obvious ways. Mix 4 is the modification of Mix 2, and Mix 5 comes from Mix 3. The chemical equations become



that perhaps we should give slight emphasis to the hexamine. But lacking any concrete motivation, we choose first to give the three fuels about equal thirds of the available oxygen and second, for intuition sake, to give them a 50:25:25 oxygen ratio in favor of hexamine. The three moles of ammonium perchlorate in equation 15 each give 1.25 moles of molecular oxygen for a total of 3.75 oxygens. Giving each fuel $3.75/3 = 1.25$ oxygens, we obtain Mix 2.

As a final modification, we replace some of the ammonium perchlorate with potassium nitrate. This milder oxidizer will slow the burn rate of the composition to a pace more appropriate for gerbs. As with the fuel mixture, the relative amounts of oxidizers are arbitrary. But the beauty of this technique is that it provides such a wide range of viable choices. By this point, we have zeroed in on the formulation well enough that large differences in the distribution

of oxygens have small effects on the resulting percentages. We choose here to have the nitrate supply about 30% of the oxygens that the perchlorate produced in the previous formulations. But choosing, say, 20% or 40% would have changed the outcome here and there only by a percent or two. The “final” equations, for Mix 6 and Mix 7, are



Mix 7 is quite similar to a formulation that one of us (EJC) developed and put into commercial production in the Ukraine. (It uses the Russian-manufactured binder *iditol* in place of the red gum.) This product, a gerb called “Cold Fountain”, shoots a plume of brilliant sparks over two meters high. Remarkably, for most of that height, the plume is benign enough that it will not burn bare skin—hence the name.

Conclusions

A pyrotechnic formulation is a combination of oxidizers and fuels. Starting with a reasonable set of decomposition reactions for the oxidizers and a set of plausible combustion reactions for the fuels, we can form a preliminary chemical equation for the formulation’s eventual reaction. We balance it by balancing the oxygens involved—including as much atmospheric oxygen as we please. This equation will then have standardized products that come from the tabulated oxygen reactions. There is nothing mystical about these products. Anyone may alter them into a different self-consistent set. Whatever their identities, they may or may not be present in the actual reaction, and it does not matter. We focus only on the coefficients of the reactants. With proper adjustment, we transform the preliminary coefficients into those for the equation that corresponds to the optimized pyrotechnic formulation.

Of course, for any new composition, we do not know the optimized formula. The only way that can be discovered is by extensive testing. So the “proper adjustment” of the coefficients involves a certain art. We start either with a

published formulation or with a bare-boned mixture of one oxidizer and one fuel. Then we make additions or substitutions as dictated by our experience, education, or intuition. All during this creative process, we rely on the model that molecular oxygen is the currency of exchange in the reaction. The oxidizers jointly produce oxygens, we say, and, together, the fu-

els consume those same oxygens. When we control (on paper) the distribution of these oxygens by means of adjusting coefficients, we are also specifying the composition of the mixture. And all the while, we are keeping the proportions stoichiometrically consistent.

The oxygen-exchange approach does not eliminate the need for experimentation. It has no built-in method of evaluating a formulation. It cannot specify the ideal mesh size of a component or the identity of the solvent most useful in binding. Nor does it account for kinetic or thermodynamic differences in reactions. But it can be a powerful means of narrowing the experimentation to a few theoretically-promising candidates, and thereby it can increase the “convenience quotients” of new formulations.

References

- 1) See, for example, W. D. Smith, “Introductory Chemistry for Pyrotechnists. Part 1: Atoms and Molecules”, *Journal of Pyrotechnics*, Issue 1, 1995.
- 2) R. Lancaster *et al.*, *Fireworks: Principles and Practice*, Chemical Publishing Co., New York, 1972, p 120.
- 3) T. Shimizu, *Fireworks: The Art, Science and Technique*, Pyrotechnica Publications, Austin, TX, 1981; (a) p 230; (b) p 75.
- 4) A. A. Shidlovskiy, *Principles of Pyrotechnics*, Mashinostroyeniye Press, Moscow, 1964, p 52.
- 5) T. Shimizu, “Studies on Blue and Purple Flame Compositions Made with Potassium

- Perchlorate”, *Pyrotechnica* VI, 1980, pp 5–21.
- 6) C. Jennings-White and K. Kosanke, “Hazardous Chemical Combinations: A Discussion”, *Journal of Pyrotechnics*, Issue 2, 1995.
 - 7) An excellent and ever-growing database of pyrotechnic formulations is maintained by Andrew Krywonizka on the Internet: <http://www.pangea.ca/~gryphon>, 1998.
 - 8) Troy Fish, “Green and Other Colored Flame Metal Fuel Compositions Using Parlon”, *Pyrotechnica* VII, 1981; (a) pp 25–37; (b) p 30.
 - 9) Spreadsheet programs that perform these calculations are easily written. Two examples, one for Corel Quattro Pro and one for Microsoft Excel, are available on the Journal of Pyrotechnics Web Site: <http://www.98.net/jop>, 1998.
 - 10) T. Shimizu, “Studies on Mixtures of Lead Oxides with Metals (Magnalium, Aluminum, or Magnesium)”, *Pyrotechnica* XIII, 1990, pp 10–18.
 - 11) C. Jennings-White, “Lead-Free Crackling Microstars”, *Pyrotechnica* XIV, 1992, pp 30–32.
-

Guidance for Authors

Style Guide

The *Journal of Pyrotechnics* has adopted the *ACS Style Guide*. It is not necessary that authors have a copy; however, a copy can be purchased from the American Chemical Society, Distribution Office, Dept. 225, 1155 16th Street NW, Washington, DC 20036, telephone (800) 227-5558.

Manner of Submission

Submissions should be made directly to the publisher at the address on the inside front cover. Upon receipt of an article, the author will be sent an acknowledgment and a tentative publication date. For specific requests regarding editors, etc. please include a note with that information. Preferably the text and graphics will be submitted on a diskette (either 3-1/2" or 5-

1/4") in IBM format with a printout as backup. The Journal is currently using Microsoft Word for Windows 7.0, which allows for the import of several text formats. Graphics can be accepted in several formats. Please inform us if materials need to be returned to the author.

General Writing Style

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

(Continued on page 32)

Artificial Meteor Fireworks

D. Caulkins

Millennium Meteor Fireworks Project, 437 Mundel Way, Los Altos, CA 94022-1118, USA
e-mail: dcaulkins@igc.org

ABSTRACT

The use of ballistic-missile-delivered artificial meteors is discussed as a means of generating large scale pyrotechnic displays. Possible delivery vehicles are suggested, and designs are presented for the artificial meteors, payloads, and deployment missions. Safety and cost issues are discussed.

Keywords: artificial meteor, ballistic missile, ICBM

Introduction

This paper discusses the use of now-obsolete ballistic missiles to generate very large and spectacular displays of Artificial Meteors, at a cost not much more than that that now spent on ordinary fireworks displays. Television pictures of Scud missile re-entries during the Gulf War are an existence proof of the fact that even short-range low-throw-weight ballistic missiles can produce “artificial meteor” effects.

Artificial Meteor displays over a number of the world’s cities could provide a suitably large scale commemoration of humanity’s entry into the next millennium.

Artificial Meteor Fireworks

Artificial Meteor (AM) firework displays can be much brighter, more numerous, and more spectacular than natural meteors (see Appendix A for details on natural meteors). An AM is an object whose mass is in the range of 1 to 100 grams; a group of AMs is launched into space by an obsolete ballistic missile. Ballistic missiles have throw weights ranging from hundreds of pounds for smaller missiles up to many

thousands of pounds for ICBMs like the Russian SS-18 and the American MX. The expensive parts of the missiles—rocket engines, guidance computers, and control systems—are already paid for. All that is needed is to replace the warheads with packages of inexpensive AMs. Each AM would have a mass in the range of 10 to 100 grams, one or two orders of magnitude greater than most natural meteors. Thus each missile could carry tens of thousands of AMs.

Large conventional pyrotechnic shells can produce spherical displays of stars approximately 450 meters in diameter. AM displays can produce spherical arrays of AMs that are 50,000 meters in diameter, more than 100 times bigger.

Design of Individual AMs

Natural meteors are composed of a variety of elements, and typically leave white or yellowish trails lasting for less than a second. AMs can and should produce colored trails, and these trails can last much longer than those of typical natural meteors. The usual pyrotechnic coloring agents could be used to produce colored trails: yellow (sodium), red (strontium), green (barium), blue (copper), etc. It may be desirable to include chlorine donor materials to deepen the colors.^[3] Since there is no fuel required, no allowance need be made for fuel spectra in the design of the coloring agents.

Some AMs could be made with concentric layers of different color-generating materials; they would produce trails which would change color as ablation exposed the various layers. AMs need none of the usual star composition fuels or oxidants to produce a colored trail; atmospheric friction provides all necessary energy. Any mass entering the atmosphere at a velocity of about 11 kilometers per second has potential energy 15 times greater than an equivalent mass of high explosive.

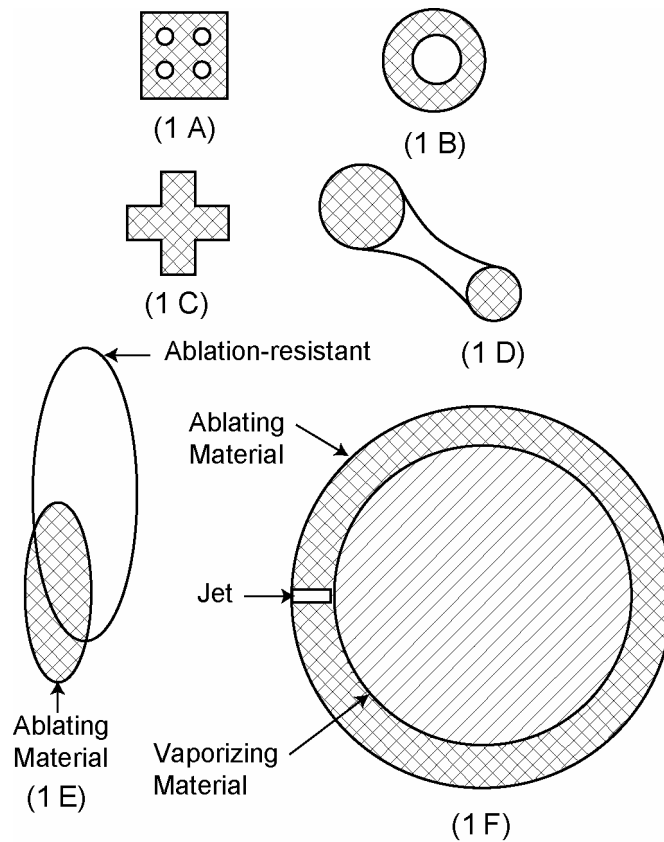


Figure 1. Artificial meteor designs. [1A – A cube with four cylindrical holes; 1B – A hollow cylinder; 1C – A six-armed rectangular cross; 1D – Two unequal spheres connected by a web; 1E – An ellipsoid of pyrotechnic ablating material formed on an ablation-resistant angled vane; and 1F – A sphere of pyrotechnic ablating material containing a material that will vaporize from the heat of ablation.]

The conditions producing incandescence in an AM involve higher temperatures and lower pressures than those encountered by typical stars from a conventional pyrotechnic shell. Some experiments would be desirable to be sure that the planned coloring agents function as intended. Even though the AMs are much further away than conventional pyrotechnic stars, the colors of their trails should still be visible. Astronomical objects subtending comparable angles but at much greater distances appear colored to the naked eye; the planet Mars is a good example.

AMs should have special shapes to insure that they are completely consumed while well above any man-made objects, like airplanes. A good design target would be reduction to zero mass at or before an altitude of 15 kilometers.

The ideal shape would be one that stayed brightly incandescent for as long as possible, but was guaranteed to have been reduced to a mass of a fraction of a gram at an altitude of 15 kilometers. A shape with holes or internal cavities would probably have the right performance.

There are at least two other interesting possibilities:

- Some of the AMs could be made with aerodynamic shapes that would cause them to perform various maneuvers as they fall, producing non-straight trails. For additional variety some AMs could be filled with substances that would produce gas jets when heated by ablation; the reaction force from these jets could cause additional changes in trajectory.

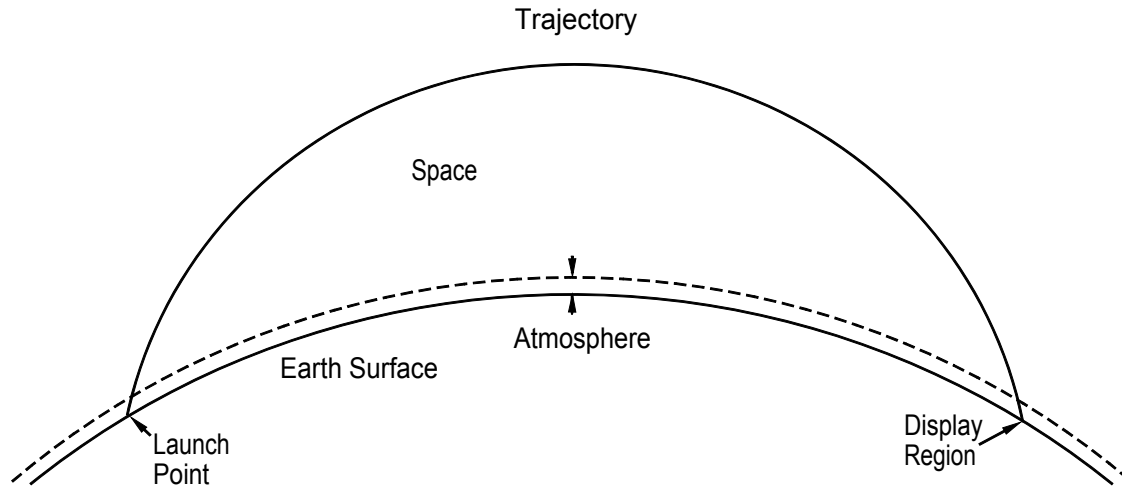


Figure 2. Artificial meteor missile trajectory.

- AMs travel at supersonic velocities; they could be designed to penetrate the atmosphere to a point where sonic booms would be produced.

Cross sections of some possible AM designs are shown in Figure 1. Figure 1-A is a cube with four cylindrical holes; Figure 1-B is a hollow cylinder, and Figure 1-C is a six-armed rectangular cross. The last three have aerodynamic properties; Figure 1-D is two unequal spheres connected by a web—the web will cause tumbling until it burns away, splitting into two AMs. The same design could be used with three or more web-connected AMs. Figure 1-E has an ellipsoid of pyrotechnic ablating material formed on an ablation-resistant angled vane. As the ellipsoid ablates away, the center of gravity will change and the rotation of Figure 1-E will also change. Figure 1-F is a sphere of pyrotechnic ablating material containing a material that will vaporize from the heat of ablation. Reaction force from the resulting vapor jet will cause the sphere to take an erratic path, producing an irregular trail.

The AM trails would be observed by an audience 80 to 100 kilometers away; it is not clear that these irregularities in the AM trails would be visible.

System Design

Vehicles

There are many military vehicles available for deploying AMs. The best would be ICBMs similar to the American MX or the Russian SS-18—these have throw-weights of many thousands of kilograms (tens to hundreds of thousands of AMs) over ranges of 10,000 kilometers with an accuracy on target of less than a kilometer. Smaller ballistic missiles of the IRBM type could also be used.

Payload

Alteration of a ballistic missile for AM generation is not difficult—remove the warhead and replace it with one or more canisters containing the AMs and their bursting charges.

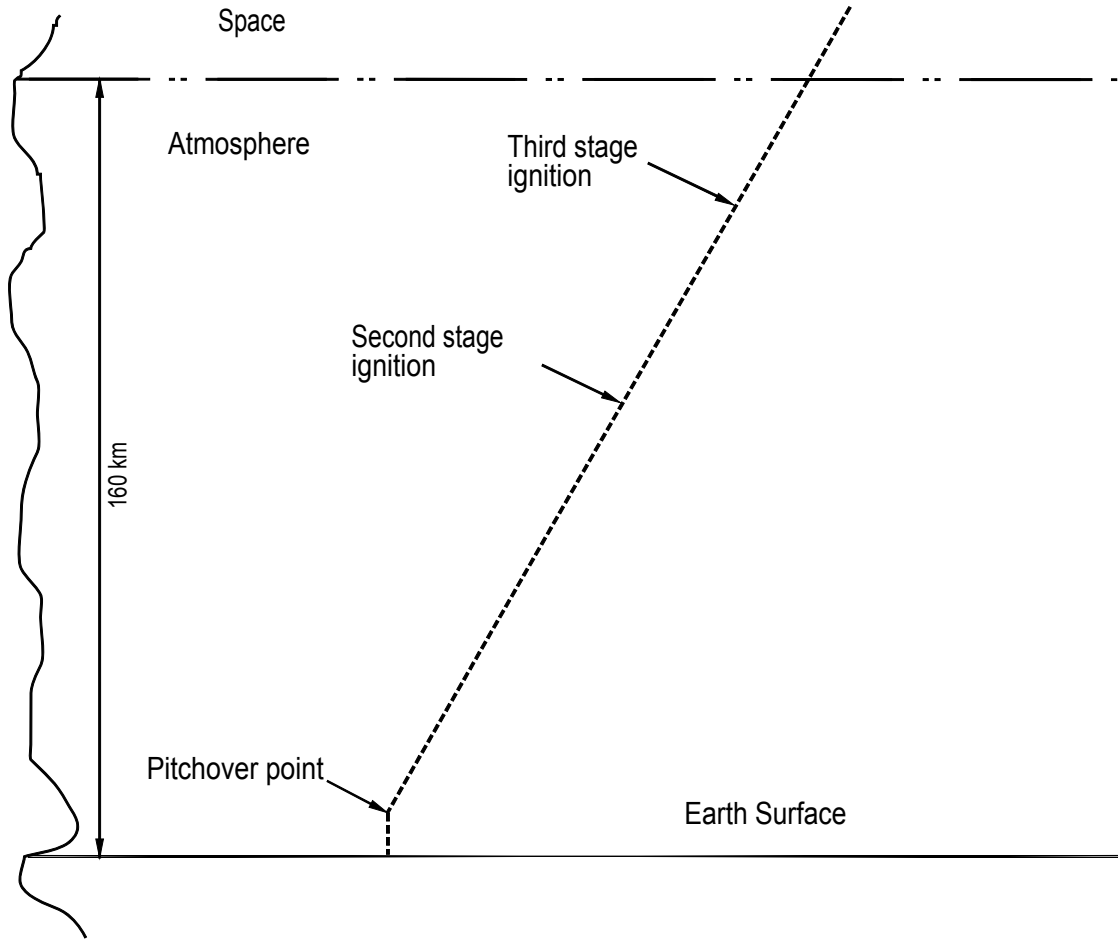


Figure 3. Artificial meteor missile launch.

The payload for an AM deployment mission would consist of spherical or cylindrical canisters containing AMs of the kind described above. Each canister would have redundant bursting charges at its center designed to deploy the AMs into a spherical cloud after the missile boost phase was finished and before reentry. The AM canister(s) would have radio transceivers which would permit the payload to be tracked, and to be destroyed if it failed to perform as designed.

Deployment

The AM carrier missile target coordinates are set to deliver the payload to the desired display point. Safety checks are made, and when the missile is ready for launch a phone call is made to the target area; if the weather there is

suitable (small or no cloud cover) the missile is launched about 30 minutes before the desired display time.

A profile of a typical AM missile flight is shown in Figures 2, 3, and 4. The entire trajectory is shown in Figure 2. Figure 3 shows the launch trajectory; the AM missile behaves just as it was designed to in its military role in lifting the payload into space on the correct trajectory to the target.

Figure 4 shows the final part of the flight; first and second stage missile separations have occurred. When the payload is in the correct position, a bursting charge is fired, deploying the AMs into an expanding spherical cloud. If there is any remaining missile payload or third stage structure, this too will be fragmented with

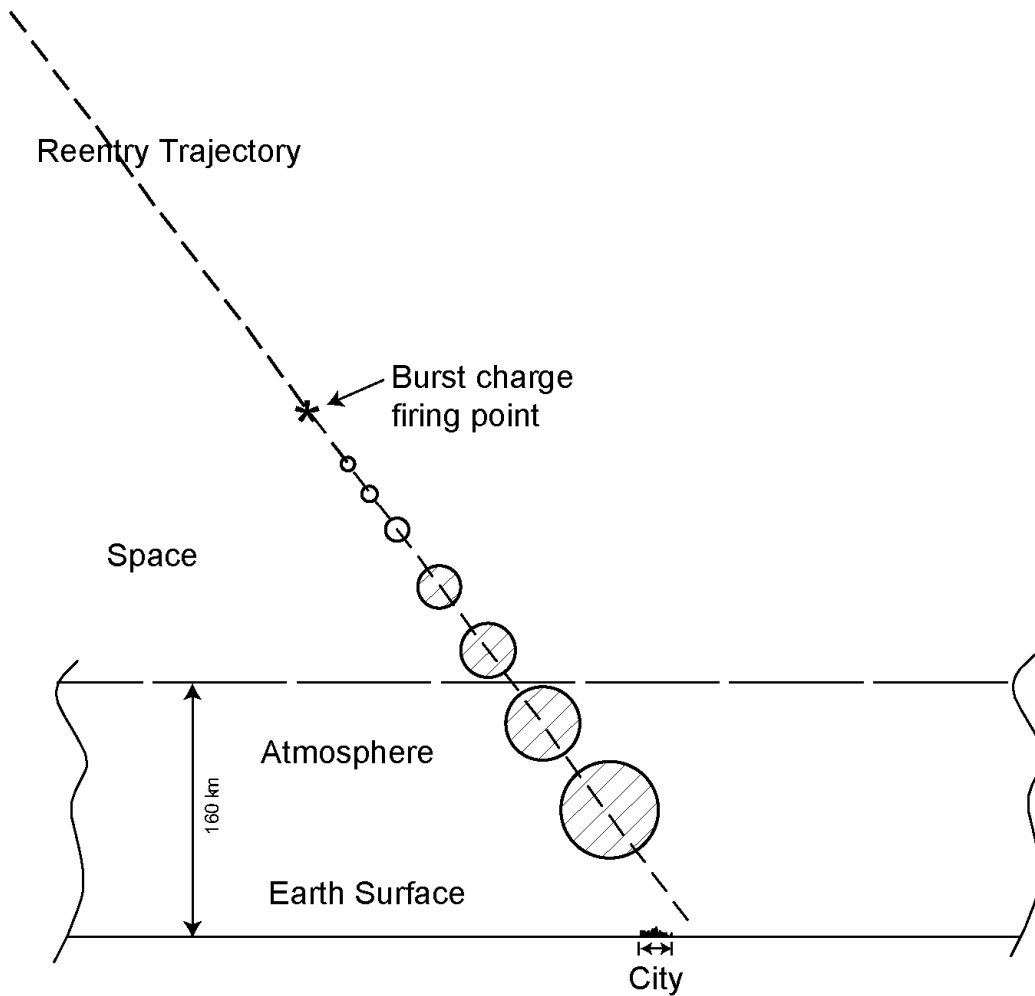


Figure 4. Artificial meteor reentry and display.

explosive charges, adding a few more AMs to the display.

During payload reentry the velocities imparted to the tens of thousands of AMs by the bursting charge cause them to form an expanding sphere from 5 to 20 kilometers in diameter, enough to fill most of the night sky over the target area.

As each AM in the cloud reaches an altitude of about 120 kilometers it will begin to produce a glowing trail.

Each canister could include several AMs designed to produce sonic booms in the leading edge of the cloud; the noise produced by these will alert viewers to look up and see the rest of the display, which will last for several seconds

as determined by the size of the spherical AM cloud.

If a display lasting longer than a few seconds is desired and MIRV'd missiles are available, each RV in the MIRV could be used for a separate AM canister. Retro rockets on each RV could be used to cause the AM canisters to arrive sequentially, separated by as much time as desired.

Practice Launches

It would be desirable to do some practice launches to test the design of the AMs. For this purpose IRBMs or smaller unguided rockets could be used.

Safety

Some people may worry about use of missiles in this way; after all, the AM missiles were originally designed to destroy cities. Several techniques can be used to make creation of AM displays safe.

- The payload radio transceivers will be used to monitor performance and position during the boost and mid-course parts of the flight. If any malfunctions are detected, the missile and/or its payload can be reduced to fragments by explosive charges. Note that in many cases this will still produce AM displays at or near the target area.
- Most of the ballistic missiles suitable for AM have first and second stage motors; the casings of these motors will fall to earth along the track of the missile. To avoid any possible damage from first and second stage motor impacts, the AM missiles should be launched over an ocean. For this reason and because of the economy of using existing launch facilities, places like Vandenberg Air Force Base (near Lompoc in California) and Cape Canaveral (Florida) might be used. Islands would also make good launch sites. Submarine or surface ship launched missiles could also be used to solve this problem.
- For those who may be concerned with pollution from the materials deposited in the upper atmosphere by AM trails, it should be noted that natural meteors deposit much more material every day than would be caused by several AM displays every month for a year.

Cost

The great majority of the cost of an AM missile has already been paid during its service as a weapon. Construction of the payload should be comparable in cost to the construction of a large shell for an ordinary fireworks display. In some ways the payload is easier to make; the AMs (stars) require no dangerous energetic compositions. All necessary energy will be supplied by air friction during reentry.

Glossary

Ablation – Removal of material by melting or vaporization produced by the heat of friction as an object enters the earth's atmosphere from space.

ICBM – Intercontinental Ballistic Missile.

IRBM – Intermediate Range Ballistic Missile.

Meteor – A solid object entering the earth's atmosphere and producing a luminous trail.

Meteorite – A meteor of large enough mass not to be completely consumed during its transit of the atmosphere; it reaches the ground. Artificial meteors are designed never to become meteorites.

MIRV – Multiple Independently-targetable Reentry Vehicle.

Pitchover – The point in the launch trajectory of a ballistic missile where the missile is rotated around the pitch axis to acquire velocity in the direction of the target.

RV – Reentry Vehicle; each MIRV "bus" carries several.

Throw-weight – The weight of the payload that a ballistic missile can deliver to its target.

Appendix A

Natural Meteors

The active life of a natural meteor starts when it first encounters atmospheric density sufficient for friction to heat it to incandescence, leaving a visible trail in the night sky. This typically occurs at about 120 kilometers. Usually a meteor is first seen at about 100 kilometers above the surface of the earth, and disappears at about 50 kilometers. Initial meteor velocities fall between 11 and 72 kilometers per second.^[1]

One of two things can happen to a meteor:

- 1) For the typical small meteor weighing a few grams or less the trail remains visible until the mass of the meteor is completely consumed by ablation.

- 2) Larger objects can reach what is called “the point of retardation”; velocity drops to less than 100 meters per second, too small to heat what is left of the meteor to incandescence. The meteor, now called a meteorite, falls to earth at a constant velocity determined by its mass and drag.

Observations of 7 meteorites showed points of retardation varying from 4 to 42 kilometers in altitude, with a mean of 17 kilometers.^[2]

References

- 1) S. J. Edberg and D. H. Levy, *Observing Comets, Asteroids, Meteors, and the Zodiacal Light*, Cambridge University Press, 1994.
- 2) F. Heide, *Meteorites*, 1891. Translated by Edward Anders, 1964.
- 3) T. Shimizu, *Fireworks, The Art, Science, and Technique*, Pyrotechnica Publications, 1981.

Guidance for Authors (Continued from page 25)

Format:

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

There needs to be a short abstract at the start of the article. (An abstract is a brief summary of the article; it is not a listing of areas to be addressed.)

Include 3 to 5 keywords to be used in a reference database. Note that multi-word names and phrases constitute only one keyword (e.g., potassium nitrate or heat of reaction).

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

Figures, Photos, and Tables are numbered separately; each type starts with 1 and is then numbered consecutively. For submission, place

them at the end of the text or as separate files. During page composition, they will be inserted into the text as appropriate. For graphs, please also submit “raw” X–Y data.

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

Editing:

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

Studies on the Use of Epoxy Resin Binder in Small Rockets

R. I. Grose

Environmental and Chemical Systems Department, Royal Military College of Science,
Shrivenham, Swindon, Wiltshire, SN6 8LA, United Kingdom

ABSTRACT

A propellant suitable for use in small firework rockets has been developed. The binder used in the composition is an epoxy resin. The composition can be mixed while wet, thus reducing safety hazards. The propellant has been evaluated using a simple lab-built thrust measurement apparatus, and has been shown to have superior performance to Black Powder.

Keywords: rocket, epoxy, thrust measurement

Introduction

The production of pyrotechnic mixtures is an inherently dangerous process, due to the possibility of a rapid violent highly exothermic reaction occurring. Several factors affect the probability of initiation of such a reaction. Examples of such factors are particle size and shape of the components, the possibility of electrostatic spark generation and the presence of moisture. Jennings-White and Kosanke^[1] have outlined the hazards of some specific chemical combinations, and the pyrotechnic literature is filled with examples and good advice on how to avoid accidents.^[2-6]

Most production processes are still carried out by hand and are therefore good candidates for mechanisation. The majority of pyrotechnic mixtures require dry powder mixing at some point during the production process. Such mixtures are sensitive to initiation from several sources, such as friction and electrostatic spark. The inclusion of a liquid component to pyrotechnic mixtures would greatly reduce these hazards and would also facilitate automation of the production process.

Many large rocket systems use a polymer, such as hydroxy-terminated polybutadiene (HTPB), as a fuel/binder component.^[7,8] The production of the propellant grains is by an extrusion process.^[7] The main objective of the work described in this paper was to find an extrudable composition that would work in small firework rocket motors.

A suitable binder for use in such compositions would need to have several desirable properties. It would need to burn well in order to maintain the high reaction rate required in small rocket motors. It would need to be easily processable, which would restrict the choice to thermosetting resins. Compositions containing thermoplastic resin binders would need to be heated during the mixing stage, which is undesirable for safety reasons. Thermosetting resins can be processed at low temperatures, and then cured at relatively low temperatures. The candidate binder should retain good mobility at high solids loading, and it should have excellent dimensional stability on curing. This demanding range of properties should also be available in a polymer that is economically attractive.

Most commercially available thermoplastic materials have relatively high melting temperatures and were considered to be poorly suited to the requirements outlined above. Thermosetting resins tend to have better dimensional stability than thermoplastics, and this makes them attractive for use as a pyrotechnic binder. They are changed irreversibly during the curing process from flowable products into highly intractable cross-linked resins. Examples are phenol-formaldehyde resins, such as Bakelite™, and epoxy resins, such as Araldite™. Both types of resin have been used in large items.^[9,10]

Experimental

Epoxy resins were selected for use in rocket motors after it was found that phenol-formaldehyde (PF) resins were not suitable. It was found that a significant percentage (approximately 20%) of rockets made using a PF resin exploded shortly after ignition. This was attributed to the presence of voids in the composition, arising from the curing of the PF resin. The curing process produces water, which evaporates and leaves voids behind. Such a situation is catastrophic for any rocket motor and cannot be easily overcome using this PF resin system.

Epoxy resins undergo a crosslinking process, but no condensation products are formed and so the formation of voids should not occur. The chemistry of the formation of the resin is adequately described in most polymer chemistry textbooks; so will not be described here.

A propellant composition was developed that used potassium perchlorate as the main oxidiser component. Potassium benzoate and charcoal were used as the fuel components in a 2:1 ratio. The composition was arrived at by development of a whistling composition. Copper(II) oxide was incorporated into the mixture as a burn rate enhancer. Transition metal oxides are known to facilitate the decomposition of perchlorates,^[11,1b] and CuO was selected to be used. Manganese(IV) oxide, nickel(II) oxide and iron(III) oxide were evaluated, but none performed as well as CuO. The composition is given in Table 1.

Table 1. Composition of Rocket Propellant.

Component	Amount in parts	Amount in %
Potassium perchlorate	75.0	72.7
Copper(II) oxide	1.4	1.4
Potassium benzoate	11.2	10.9
Charcoal	5.6	5.4
Epoxy resin	9.9	9.6

The solid components all passed a 125-mesh sieve. The charcoal used was 60-dust grade (particle size of 60 microns to dust).

The resin used was Araldite 219, supplied by Ciba-Geigy Ltd. This consists of a bisphenol-A epichlorohydrin prepolymer and a modified aromatic amine hardener.^[12] If desired, a carboxylic acid may be added to accelerate the hardening process, as the acid catalyses the epoxy ring opening step. A small amount of acid (about 1% of the resin component by weight) was used to speed the curing process.

The solid components were sieved separately. The oxidiser components were then added to the resin and mixed thoroughly. The remaining ingredients were then added to this mixture. This produced a fairly stiff material, which was extrudable. The mixture was piston-extruded into the motors, a PTFE coated gallery spike was inserted and the motors were cured at 50 °C for 3 hours. The spike was then removed. The motors were made of rolled cardboard, twitched at one end to form a nozzle. The length of the tube was 90 mm, o.d. = 17 mm, i.d. = 12 mm, nozzle diameter = 4 mm. The spikes used had variable length, but all had a base diameter of 3 mm tapering to 2 mm at the top. The nozzle was positioned 14 mm from the end of the tube. The mass of composition used in each motor was kept as constant as possible, at 10 ± 1 g.

Other epoxy resins were tested for use in rockets, but none performed as well as 219 resin. Those evaluated were 751C (normal prepolymer + polyoxypropylenetriamine hardener), 672C (normal prepolymer + isophorone diamine + benzyl alcohol) and RX710C (prepolymer contains bisphenol-F).

The rockets were evaluated qualitatively using visual trials, but quantitative evaluation was available by using a simple home-built thrust meter. This apparatus has been more fully described elsewhere,^[13] but essentially it consists of an adapted strain gauge. Thrust data can be obtained easily, which is very useful for comparison and development purposes. However, visual tests are still an important part of evaluation due to the visual nature of the pyrotechnic art!

Table 2. Effect of Different Burn Rate Catalysts on Thrust.

Material	Thrust in		Normalised (CuO = 100)
	g	(lb.)	
Copper(II) oxide	1270	(2.80)	100
Manganese(IV) oxide	1080	(2.38)	85.0
Nickel(II) oxide	1080	(2.38)	85.0
Iron(III) oxide	630	(1.39)	49.6

Results and Discussion

Figure 1 is a trace of a small rocket (dimensions given in previous section) filled with the composition detailed in Table 1. A Black Powder model gave a similar trace, with a peak height of approximately 750 g (1.65 lb). It can be seen that the epoxy-bound composition develops a considerably higher thrust than the Black Powder model. It is noteworthy that the peak thrust is developed less than half a second after ignition, and does not last for more than 0.3 s.

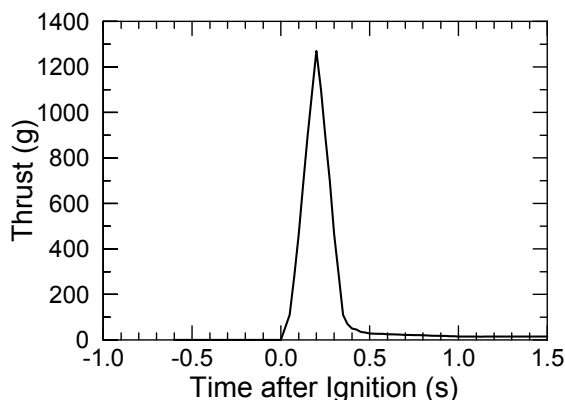


Figure 1. Thrust trace for epoxy-bound composition.

Visual tests showed that the epoxy-bound composition powered the motor to a greater height than the Black Powder. Both motors were filled using the same mass of powder, and contained the same gallery length. During the launch phase, several different observers noted that the epoxy-bound composition seemed to produce more “zip” than the Black Powder motors.

Table 2 contains data on the peak thrust obtained from compositions containing different burn rate catalysts. The compositions were the same as in Table 1, except that copper(II) oxide was replaced by the materials listed.

The length of the gallery spike also plays a large role in the burning of the propellant. (Figure 2 shows the design of a typical small rocket motor.) The dependence of thrust upon gallery length is given in Figure 3.

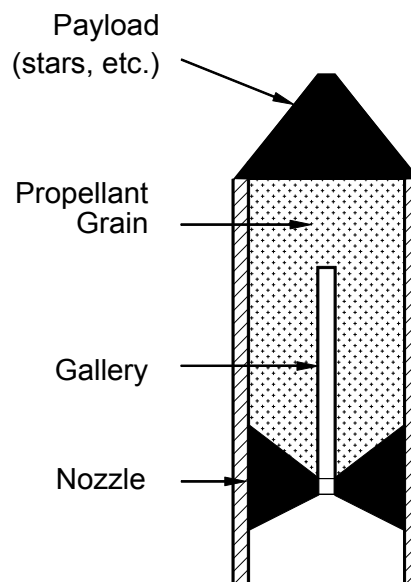


Figure 2. Design of a typical small rocket motor.

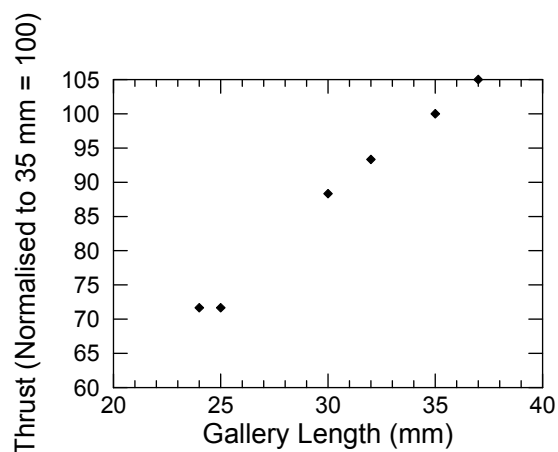


Figure 3. Effect of gallery length on thrust.

The data in Figure 3 has been normalised to 35 mm = 100. Although thrust increases as the gallery length increases due to an increase in surface area, the time of burn drops. "Burn through" is more likely with longer gallery lengths, and so 35 mm was set as a standard gallery length around which to optimise the composition.

Conclusion

An epoxy-bound propellant for small firework rocket motors has been developed, and has been shown to have superior performance to Black Powder. The composition can be mixed wet, which significantly reduces the risk of accidental ignition.

Acknowledgements

The financial assistance of Standard Fireworks is gratefully acknowledged, as is their permission to publish this paper.

References

- 1) C. Jennings-White and K. Kosanke, *Journal of Pyrotechnics*, Issue 2, 1995; [a] p 22; [b] pp 26–27.

- 2) J. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, 1985, pp 94 and 182.
- 3) R. Lancaster, *Fireworks: Principles and Practice*, Chemical Publishing Co., 2nd ed., 1992.
- 4) T. Shimizu, *Fireworks: The Art, Science and Technique*, Pyrotechnica Publications (reprint), 1986.
- 5) C. Jennings-White, *Pyrotechnica XVI*, 1995, pp 13–15.
- 6) J. C. Cackett, *Monograph on Pyrotechnic Compositions*, RARDE, 1965, Chapters 15 and 16.
- 7) E. M. G. Cooke, "The Manufacture of High Performance Composite Propellants and Novel Charges by Batch and Continuous Extrusion Processes", *Propellants, Explosives, Pyrotechnics*, Vol. 15, 1990, pp 235–242.
- 8) N. Kubota and S. Miyazaki, *Propellants, Explosives, Pyrotechnics*, Vol. 12, 1987, p 183.
- 9) H. L. Girdhar and A. J. Arora, *Journal of Spacecraft and Rockets*, Vol. 13, 1976, p 443.
- 10) H. W. Chatfield and P. M. Holmes, "Improvements in or Relating to Pyrotechnic Compositions", UK Patent 881 731, 8 Nov 1961.
- 11) K. Kishore et al., "Effect of Catalyst Concentration on Burning Rate of Composite Solid Propellants", *AIAA Journal*, Vol. 15, 1977, pp 1649–50.
- 12) Ciba-Geigy Hazard Data Sheet for 219 epoxy resin, 1995.
- 13) J. Akhavan, I. Grose, M. Williams and B. Cook, "A Device for Quantitative Evaluation of Thrust Produced By Small Rocket Motors", *25th International Conference of ICT*, Karlsruhe, FRG, 1995, pp 25-1–25-2.

Development of a Video Spectrometer

K. L. & B. J. Kosanke

PyroLabs, Inc., Whitewater, CO 81527 USA

ABSTRACT

A simple, low-cost visible light spectrometer, consisting primarily of a video camcorder and an inexpensive diffraction grating, was assembled and found to be of use in work to improve colored pyrotechnic flames. This instrument is all that is needed to collect and store useful, qualitative flame color information. With this simple instrument, the nature of color agents and the sources of interfering chemical species can be determined.

If semi-quantitative data is needed, a video frame grabber and personal computer can be employed. These allow more accurate identification of wavelengths of spectral features (lines and bands). It also makes possible the determination of relative intensities of spectral features. If quantitative intensity data is needed, a suitable calibration source is necessary and calibration corrections must be applied to the intensity data.

In a brief study using the video spectrometer, it has become clear that much of the difficulty in achieving high quality green and blue color flames is often the result of impurities present in the raw chemicals. Specifically, the presence of sodium and calcium can act significantly to shift green flame colors toward yellow and blue flame colors toward white.

Keywords: spectroscopy, flame color, video

Introduction

The quality and range of colors produced in fireworks has improved significantly in recent years. However, there continues to be considerable interest in further improving colored flame formulations. To date, most efforts have been hindered by the lack of a satisfactory and af-

fordable spectrometer. Without spectral information it is all but impossible to identify the sources of undesirable interferences acting to reduce color purity. Without information about the emitting species present and their relative spectral intensities, researchers are reduced to using little more than trial and error to guide their efforts. (For more information on the physics and chemistry of colored flames, see Modules 6 and 7 in reference 1.)

This article is one of a series being written to share information on the development of a simple and inexpensive, yet surprisingly effective, instrument to collect spectral data. The instrument not only produces reasonably high-resolution spectra, it simultaneously records a series of spectra from the base of a flame to its tips, and does so continuously throughout the period of burning. The apparatus is referred to as a "video spectrometer". The concept was developed and the work initiated at roughly the same time both by the Kosankes and by T. Wilkinson. Since that time, there has been collaboration; however, the development has proceeded along slightly different paths. The work being reported herein and in an earlier article^[2] is primarily that of the Kosankes, whereas the work of Wilkinson will be reported in a subsequent article.^[3]

The philosophy expressed in the design and application of the video spectrometer has cost, simplicity, and adequacy as central tenets. That is to say, almost everything in this article could be done better with greater expenditures of time and money. However, when adequate results could be achieved using inexpensive items, or using equipment that is already likely to be available, that is what was done. For example, the instrument is constructed using a standard video camcorder because it produces acceptable results, is compact, and is commonly available. Similarly, a very inexpensive diffraction grating

and standard home light sources are used because they are adequate to the task.

Occasionally in this article, alternatives in equipment or methodology are mentioned. For example, the use of a black and white video camera is recommended to overcome some of the problems associated with internal light filters in a color video camcorder. However, most times the reader is left to think of alternatives and ponder their relative merits.

The Instrument

The key components of the video spectrometer and their arrangement are illustrated in a plan view in Figure 1. Light from the calibration sources passes through a slit with a fixed-width of approximately 3 mm. The test source has a manually adjustable slit width ranging from 0 to 3 mm and can be adjusted to control the light intensity from the source. (Typically a width of approximately 1 mm is appropriate.) From there the light travels a distance of approximately 2 m, where it passes through an inexpensive transmission diffraction grating mounted to the lens of a home video camera (camcorder), with the grating aligned vertically (producing a horizontal dispersion).

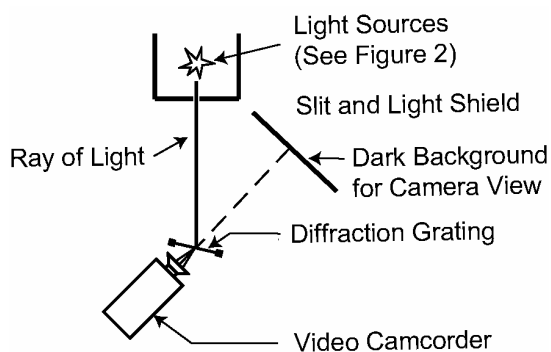


Figure 1. View of the elements comprising the video spectrometer in the horizontal plane (not to scale).

Spectral resolution is improved if the diffraction grating is positioned at an angle approximately midway between the camera and the sources. This angling of the diffraction grat-

ing is facilitated with a filter holder such as the "Cokin Creative Filter System",^[4] which is designed to accommodate multiple glass plate filters. The diffraction grating can be inserted somewhat diagonally into the filter holder by using the different grooves in the filter holder. The holder slips onto an adapter ring mounted to the camera lens, making it easy to remove when the camera is used for other applications. This mounting system also facilitates the vertical alignment of the grating because the whole filter assembly is designed to rotate somewhat freely on its adapter ring. (This is especially convenient for those video cameras where the whole lens rotates as the camera is focused.)

The physical arrangement of light sources in the vertical plane is shown in Figure 2. Uppermost is the test source, typically a burning pyrotechnic composition. Below the test source is a pair of calibration light sources. The bottom light source is a clear-glass, 60-watt incandescent light bulb with a vertical tungsten filament.^[5] This provides a continuous spectrum of colored light, probably best described as a "gray body" spectrum.^[6] Behind and above it is a small fluorescent bulb (Sylvania^[7] DULUX-S, CF1306/841). Figure 3 is an example set of spectra recorded with the video spectrometer. (For ease of reproduction in this article, all spectra have been rendered as negative black and white images.) Uppermost is the spectrum of a burning red star. Below that is the spectrum of the Sylvania fluorescent bulb. On the bottom is the continuous spectrum from the incandescent light.

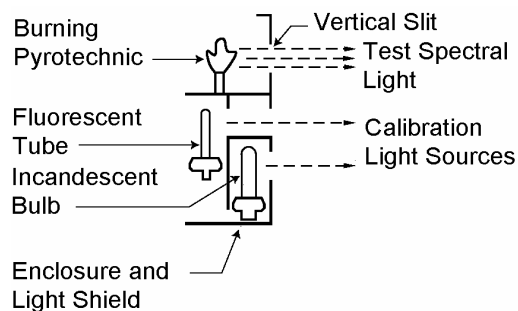


Figure 2. Vertical cut away view, illustrating the arrangement of light sources for the video spectrometer (two calibration sources plus a pyrotechnic flame).

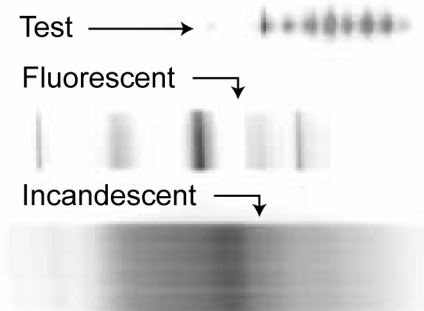


Figure 3. Example of a video spectrometer image (red star plus two calibration spectra) presented as a negative black and white image (3 mm slit widths).

The calibration light sources are useful, but not essential for most purposes. The fluorescent source can provide wavelength calibration information. But since colored light spectra contain sufficiently prominent and well identified features (atomic lines and molecular bands), the spectra themselves could be used for approximate wavelength calibrations. The incandescent source can provide intensity calibration information. However, for most investigations with the video spectrometer, intensity calibration is not necessary. Beyond their potential use for calibrations, the lamps do provide a convenient light source for setting up and adjusting the video camera.

Figure 4 is a reproduction of the fluorescent light spectrum provided by the manufacturer. Table 1 is the authors' attempt to quantify the wavelength and intensity of the spectral features for use as a calibration reference. Table 2 has been included as an aid to the reader in correlating the spectral wavelengths reported in this article with perceived color.

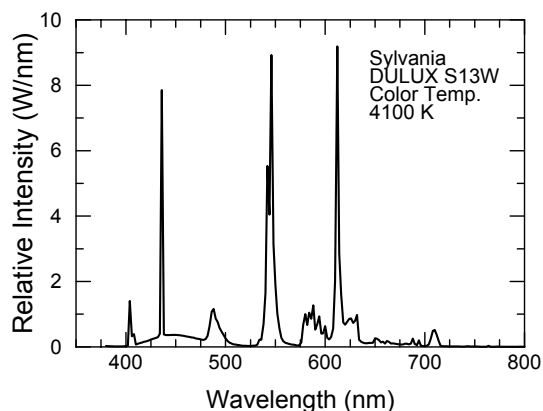


Figure 4. Light spectrum provided by Sylvania for their DULUX-S, CF 13 DX/841 fluorescent light.

Table 1. Wavelength and Relative Intensity of the Major Spectral Features in Figure 3.

Wavelength (nm) (a)	Peak Power (W/nm) (a)	Total Power (W) (b)	Total Intensity (Relative) (c)
404	1.4	7.0	11
436	7.9	15.3	37
487	1.2	9.4	20
546	8.9	51.4	100
612	9.2	31.0	54
708	.5	3.4	5

- (a) As reported by Sylvania for the spectral resolution seen in Figure 4.
- (b) Areas under the curve for the spectral features.
- (c) Relative peak areas corrected for energy (wavelength), using $E \propto 1/\lambda$, and normalized to 100 for the 546 nm peak.

Table 2. Approximate Wavelengths Associated with Various Colors of Light.^[6]

Perceived Color	Approximate Wavelengths (nm)
Red	700 to 610
Orange	610 to 590
Yellow	590 to 570
Green	570 to 490
Blue	490 to 450
Violet	450 to 400

The slit was located in the vicinity of the source for several reasons. With the slit a long distance from the camera, it can be opened much wider than if it were near the camera. This makes it easier to adjust its width and to have separate test and calibration slits. If the slit were too near to the camera, it would not be possible to focus the camera on it as required, and only a small portion of the grating and camera lens would be used. Further localized imperfections in the grating and lens could degrade spectrometer performance. Most importantly, with the slit attached to the holder of the test flame source, it is trivially easy to control its orientation so that light from the central portion of the flame is directed to the grating and camera.

To collect spectral data with usable accurate intensities, one must not overload the charge coupled device (CCD) of the video camera with an over bright image. Apparent source brightness should be controlled by adjusting the test source slit width, the distance between the source and slit, the distance from the slit to the camera, or any combination of the three. Also the video camera's iris control should be set to manual and adjusted to control the apparent source brightness.

The resolution achieved by the video spectrometer is determined by the convolution of the slit width and the characteristics of the diffraction grating and video system. For any given camera, narrowing the slit and "zooming in" for a close-up view increases the resolution up to some value that is limited by the quality of the diffraction grating. The grating used in this case has a moderately high number of lines (530 lines per mm) but is quite inexpensive (<\$2).^[8] The resolution achieved is more than adequate for use in pyrotechnics. As a test of resolution, a neon discharge tube was used as the test source with a slit width of 1 mm. A spectral resolution of 2–3 nm at a wavelength of 600 nm was achieved, see Figure 5. (Note that the top portion of Figure 5 is an expanded view of the neon spectrum, accomplished by using the video camera's telephoto capability to zoom in on just the red portion of the neon spectrum.) This resolution is sufficient to allow the identification of fairly narrowly spaced atomic lines, whereas most pyrotechnic spectral intensity will

appear as much broader molecular bands. (For more information on spectral types and pyrotechnic spectra see Modules 6 and 7 of reference 1.)

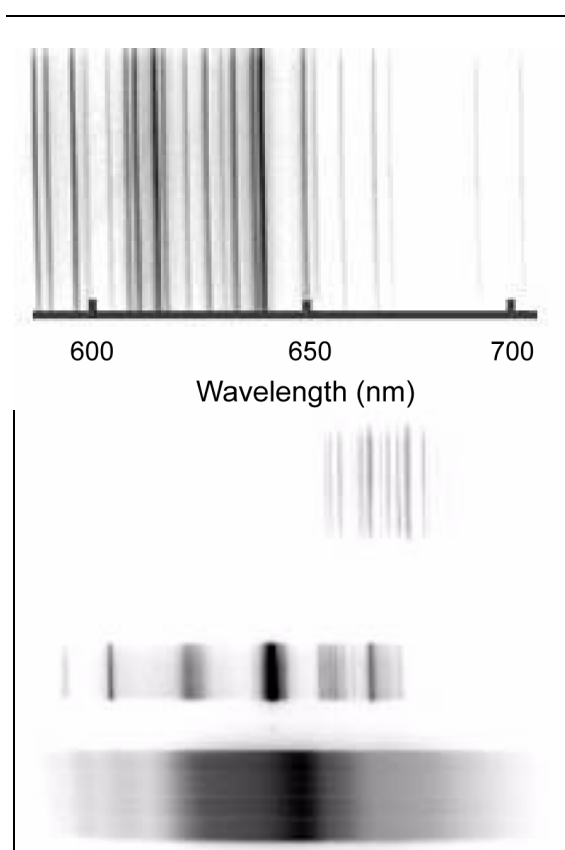


Figure 5. Lower: A collection of the two calibration spectra plus the neon spectrum. Upper: View with video camera "zoomed in" on the neon spectrum (1 mm slit width).

Not shown in Figure 1 is a large screen video monitor connected to the video camcorder. While it is possible to set up and use the video spectrometer using only the small eyepiece monitor on the camera, it is much more convenient to have a large screen monitor that can be seen throughout the work area. Although colored spectra are attractive, the intrinsic resolution of the chromance (color) signal is significantly less than that for the luminance (black and white intensity) signal. Accordingly, fine tuning the video spectrometer (and data processing) is facilitated by operating the video monitor in a black and white (gray scale) mode.

Data Capture

Preparation for the collection of spectral data requires some adjustment of the instrument. First set up the video camcorder with the diffraction grating in place and aim the camera directly at the light source slit(s). With the work area moderately dark and an operating light source located directly behind the slit, set the focus control to manual and adjust the focus for a sharp image of the slit. Then aim the camera to the side (pan) just enough for the spectral image to be visible. At this time, using the wide angle/telephoto ("Zoom") control, adjust the size of the image so that the spectrum from the incandescent light nearly fills the width of the image area. (If a light source that produces reasonably narrow features is used, such as a fluorescent bulb, fine tune the camera's focus for the sharpest spectral image.) Finally, if the camera has an electronic iris control, set it to manual and adjust it such that the brightness of the image is not excessive. The light produced by pyrotechnic flames is quite bright, and it may be necessary to fine tune the iris adjustment or narrow the test source slit to keep the camcorder CCD from being overloaded. Also, the exposure should be set for 1/60 second (in the US); this will eliminate potential problems with flickering of the electric lamps.

The bulk data capture mechanism is the video recorder of the camcorder itself. As a test sample of pyrotechnic composition is burned, an essentially continuous collection of flame spectra (60 video fields per second), including any audio commentary by the experimenter, is preserved for later reproduction and processing. In addition, because the slit can be oriented along the length of the flame from its base to its tip, a series of spectra at varying distance along the flame are also recorded. This is potentially useful because of possible differences in the chemical species and temperatures present at various points in the flame.

As always it is necessary to follow all safety procedures, such as limiting the presence of combustible materials in the work area and employing air handling equipment to remove combustion products from the burning compositions.

Qualitative Data Processing

If only qualitative spectral information is needed, then simply playing back the recorded spectra may be sufficient, possibly using the pause capability of the recorder to hold the video image for more thorough examination. For this type of data interpretation, generally only approximate wavelengths are determined, and no correction is made for the sensitivity of the camera as a function of wavelength. Figure 6 presents two examples, a red and a blue color flame spectrum. (Note that calibration spectra have been removed from Figure 6 for simplicity of presentation, and a nanometer wavelength scale has been added.) The red flame spectrum is the same as that presented in Figure 3, and it obviously dominates in the longer wavelength (red) end of the spectrum. The color of the blue flame is not as pure. In the blue flame spectrum there are strong bands in the short wavelength (violet-blue) end of the visible spectrum. However, there are also strong bands near 500 nm (green) and even features near 600 nm (orange). It is the non-blue features in this blue flame that act to seriously reduce the purity of its color.

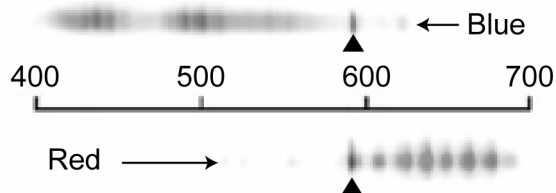


Figure 6. Examples of red and blue flame spectra, with the calibration spectra removed, a wavelength scale (in nm) added, and the Na-line annotated (▲).

In Figure 6, the wavelength scale was established using the known spectral features from the fluorescent light, specifically the peaks at 436 and 612 nm. The accurate positioning of the wavelength scale was then accomplished using the very narrowly spaced sodium doublet lines (▲) at 589 nm, clearly visible in the test spectra. The sodium doublet lines are present in es-

entially all pyrotechnic flames due to trace amounts of sodium in the chemicals used.

An acceptable alternative wavelength calibration method is to use the prominent known spectral features present in the test spectra themselves. To facilitate use of this, Table 3 was compiled. It lists the wavelengths and relative intensities of prominent features in pyrotechnic colored flame spectra.^[9-11] In addition, many other spectral features are possible, most notably features from various oxides. However, in typically formulated colored flame compositions, they are relatively weak features.

Table 3. Identification of Some Major Spectral Features Grouped by Chemical Species and Band Group.

Source (a)	Wavelength (nm) (b)	Relative Intensity (c)
SrCl	689	<1
	674–676 (d)	5
	661–662 (d)	10
	649	4
	636	10
	624	2
SrOH	608–611 (d)	10
Sr (e)	461	10
CaCl	633–635 (d)	1
	621–622 (d)	10
	618–619 (d)	10
	605–608 (d)	1
	593	10
	581	4
CaOH [Ref. 10]	644	2
	622	10
	602	2
	554	5
Ca (e)	442–445 (d)	10
Na	589	10
BaCl	532	3
	524	10
	521	1
	517	2
	514	10
	507	1

Table 3. (continued)

Source (a)	Wavelength (nm) (b)	Relative Intensity (c)
BaOH [Ref. 10]	513	10
	488	8
Ba (e)	554	10
CuCl (f, g)	538	2
	526	4
	515	2
	498	4
	488	8
	479	5
	451	1
	443	6
	435	9
	428	7
CuOH [Ref. 10]	421	4
	537	10
	530	9
	524	9
	505	6
Cu (e)	493	5
	522 (d)	10

- (a) Unless otherwise indicated, these data are taken from reference 9.
- (b) Wavelengths are only reported to the nearest nm.
- (c) The reported relative intensities are normalized to 10 for the strongest emission within a group of features from each chemical species. Different band groups for the same chemical species are separated by a single solid line in the table. Because intensities are normalized within each group and because the manner of excitation for the spectra in the literature is generally different than that for pyrotechnic flames, it cannot be assumed that the intensities listed in the table will be those observed in pyrotechnic flames.
- (d) When two or more spectral features are within about 2 nm of each other, they are listed as a single feature showing a range of wavelengths and with the combined intensity of the features.
- (e) Other weaker atomic lines occurring in the visible range are not reported.
- (f) Pearse and Gaydon report six groups of bands for CuCl; however, the bands in only three of the groups were seen in flame spectra examined for this article. Also they appear to have collectively

normalized the intensities of the bands (i.e., the strongest band in each group is not set to 10).

(g) Shimizu^[11] reports a total of 31 bands for CuCl, only the 10 strongest of those correspond to wavelengths reported by Pearse and Gaydon.

Figure 7 is a comparison of the spectra of two burning orange stars. The lower spectrum is from a standard formulation based on a calcium salt, and the upper spectrum is from a formulation producing a visibly more attractive orange flame. In the lower spectrum, the emission bands observed are those characteristic of calcium monochloride, a band from calcium monohydroxide and the sodium doublet lines at 589 nm. The same features are present in the upper spectrum; however, also visible are three features near 520 nm, which are the strongest bands from barium monochloride. Obviously then, the improvement in the orange color was accomplished by using a small amount of a barium salt to shift the composite calcium color point from reddish orange to orange. (A similar approach is described in reference 12; a discussion of color mixing and composite colors in Module 6 of reference 1.)

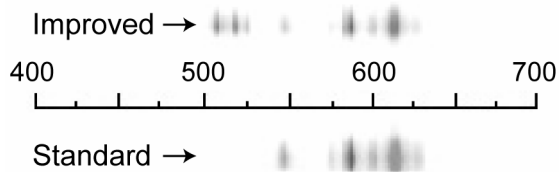


Figure 7. Comparison of spectra from two orange stars. The upper spectrum has green bands to improve the orange color.

Semi Quantitative Data Processing

If more quantitative spectral information is desired, one can capture the video data using a personal computer. The spectra for this article were collected with the inexpensive (but quite effective) Snappy® software/hardware system.^[13] Computer capture allows hard copy printouts of the spectral images to be produced, such as those presented in this paper. Also disk files of the video images can be created for use in data processing or for archival purposes.

To identify unknown spectral features, fairly precise identification of their wavelengths is helpful. Because the relationship between wavelength and screen location is essentially linear, only two spectral features of known wavelength are needed to establish a scale factor (the wavelength in nm per millimeter separation on the printout). The peaks at 436 and 612 nm in the fluorescent calibration spectrum are convenient for this purpose. By simply measuring the physical distance in millimeters between the two features on a paper printout of the spectrum and dividing 176 nm (612 – 436) by the distance, one establishes the scale factor (nm/mm). This same scale factor applies to all spectra recorded, providing no changes are made to the camera setup. The most convenient method to locate oneself on the test spectrum is to use the sodium doublet lines at 589 nm. If the physical distance from the sodium line to an unknown feature in the test spectrum is measured, its corresponding wavelength can be determined by simply multiplying the distance just measured by the scale factor and adding to or subtracting from 589 nm, depending on whether the unknown feature lies to the higher or lower wavelength side of the sodium line.

This type of approximate wavelength calibration is illustrated in Figure 8. In this case, from the full size printout of the spectra, the distance between the 436 nm and 612 nm features in the fluorescent light spectrum was measured as approximately 60.5 mm. Thus the scale factor is 2.91 nm/mm (176/60.5). In the test spectrum, the distances from the sodium doublet line to two of the features are 29.5 and 20.0 mm. Thus they correspond to wavelength displacements of 86 nm (2.91×29.5) and 58 nm from the 589 sodium doublet, or wavelengths of

approximately 674 nm (86+589) and 647 nm. From Table 3, it is fairly obvious these must be the SrCl bands listed as 674–676 nm and 649 nm. As a practical matter, this method only allows identification of wavelengths to within a few nanometers. This is due to difficulty in visually determining the points of peak intensity for the features seen on the spectrum printout.

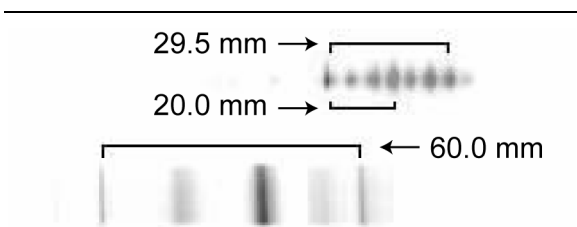


Figure 8. Example of approximate method for determining unknown wavelengths.

Adobe PhotoShop®^[14] is a popular digital image processing program. Although not its normal function, it offers the ability to produce intensity data from the spectra captured on a personal computer. One uses the “color-picker” (densitometer) intensity function, found on the Info Pallet, on the spectral areas of interest to generate, intensity versus image position data. This position data can then be used to determine screen position (wavelengths) more accurately. The procedure used is the same as suggested above; however, instead of making physical measurements with a ruler, the locations of screen pixels corresponding to the highest intensity for spectral features are used. In addition, although labor intensive, it is possible to use the Adobe intensity function to produce an intensity versus wavelength graph of the spectrum. Starting on one side of the screen image, intensity readings are recorded manually as one moves from pixel to pixel across the image. Then these data are plotted to produce a graph of intensity (density) versus screen location. By knowing the wavelengths of at least two features in the spectrum, one can convert the screen locations to wavelengths. In a trial of this method it took about 30 minutes to produce and graph the data from a single spectrum.

Un-Scan-It Gel®^[15] is a software package intended for computerized density scanning of

gel electrophoresis plates. However, it works wonderfully to digitize video spectrometer data captured on a personal computer. It also allows intensity calibration of the image, plotting the results, integrating peak (band) intensities, and

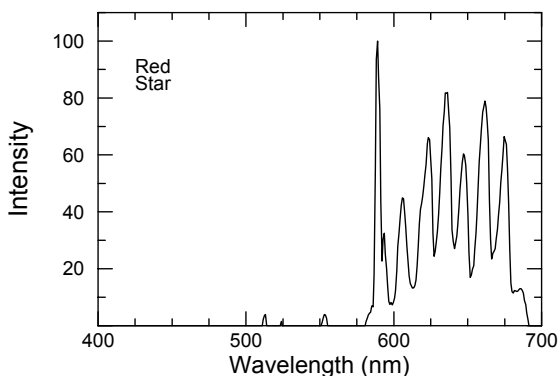


Figure 9. Example of the spectrum from a red test star.

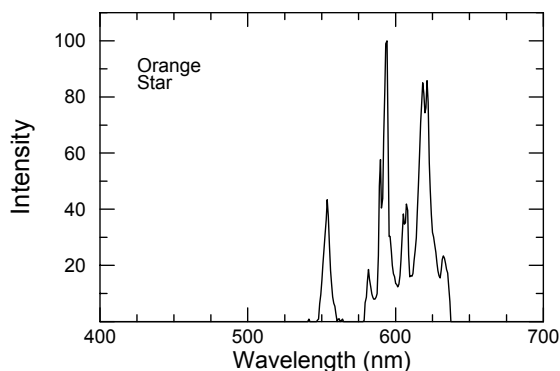


Figure 10. Example of the spectrum from an orange test star.

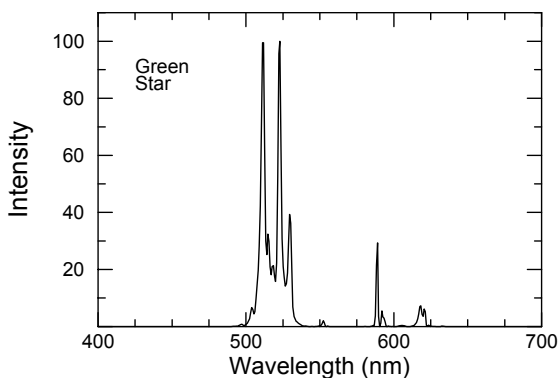


Figure 11. Example of the spectrum from a green test star.

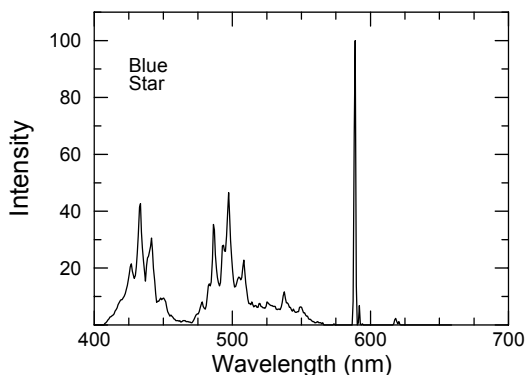


Figure 12. Example of the spectrum from a blue test star.

dividing the length of the flame into multiple separate spectra. With Un-Scan-It, the time to produce an intensity versus screen position graph and store the data is about one minute. Snappy and Un-Scan-It were used to produce the graphs in the remainder of this paper, including a series of example color flame spectra. The test stars^[16] used to produce these spectra are based on ammonium perchlorate, hydroxy-terminated polybutadiene (HTPB), and a color agent. The spectra are presented in Figures 9 through 12 with their peak intensities normalized to 100.

As an example of the utility of having the spectral data in graphical form, consider Figure 13. This presents two similar appearing green flame spectra. These spectra were produced as a test of the hypothesis that replacing some of the ammonium perchlorate with potassium perchlorate would improve the green flame color. Both formulations used the same chemical color agent, barium nitrate; however, the new (improved) formulation was prepared a couple of years after the first. The improvement to the

color was obvious, as perceived by a panel of viewers; the original formulation appeared noticeably more yellow. In Figure 13, the most obvious difference seen in the “Improved” spectrum is the presence of a weak continuum for the “Improved” formulation. The reason for this is not entirely clear, but presumably it is a result of the incandescence of liquid potassium chloride particles in the flame or from potassium ion recombination (see Module 6 and 7 of reference 1). Regardless of its source, the presence of the continuous emissions could only act to reduce flame color purity, contrary to what was observed. The second most obvious difference in the improved formulation is the increased intensity of the green bands (from BaCl, see Table 3). This is presumably the result of an increase in flame temperature. However, these greater intensities should only cause an increase in brightness and not an improvement in color, unless there is a perceived increase in the green intensities relative to interfering features (i.e., the line from sodium and bands from CaCl).

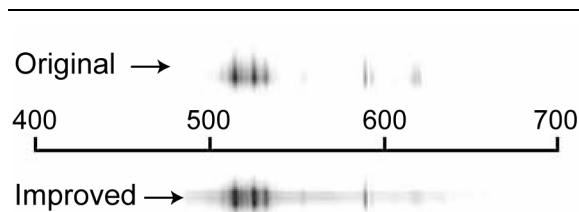


Figure 13. Comparison of the spectra from two green star formulations. The upper one appeared noticeably more yellow.

Figure 14 presents graphs of the spectra from Figure 13. The presence of the continuum and the increase in intensity noticed in Figure 13 are confirmed. Table 4 is a listing of intensities of

Table 4. Intensity of Key Spectral Features Seen in Figure 13.

Wavelength (nm)	Intensity (x 1/1000)		Normalized Intensity		Identification of Source	Perceived Color
	Original	Improved	Original	Improved		
507 – 532	61.2	98.3	≅ 100	≅ 100	BaCl	Green
589	3.7	5.6	6.0	5.7	Na	Yellow
593	1.5	1.3	2.5	1.3	CaCl	Orange
618 – 622	4.5	3.4	7.4	3.5	CaCl	Red

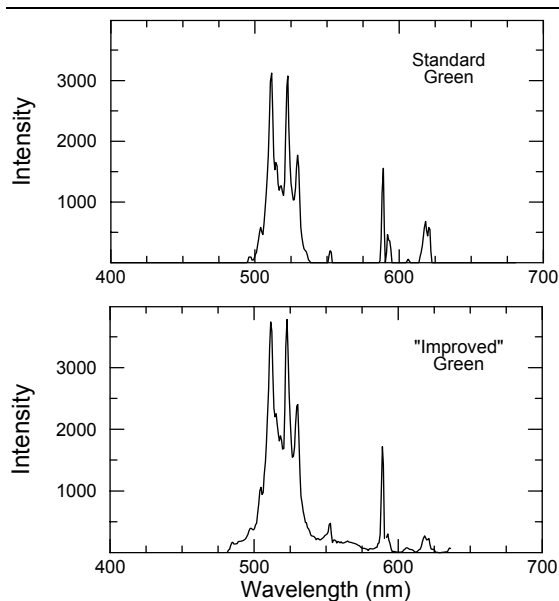


Figure 14. The two green spectra as in Figure 13, but rendered as graphs.

key spectral features. The presence of the continuum and the increase in intensity are confirmed. However, notice in the improved star formulation that the normalized intensity of the sodium doublet is reduced by about 5%, and the calcium monochloride bands are reduced by about 50% as compared with the original formulation.

Thus spectral analysis suggests that it is unlikely the visible improvement in flame color is the result of substituting potassium perchlorate for some of the ammonium perchlorate as hypothesized. It is more likely that, over the two year time span, chemicals from different lots (or suppliers) were being used and the different lots had differing amounts of interfering chemicals.

Quantitative Data Processing

The relative intensity data such as demonstrated in the green example can be very useful. However, when reasonably-accurate, absolute-intensity results are needed, an intensity calibration is necessary. The need for this calibration is a result of the way in which the camcorder prepares its composite color image. Internal light filters differentiate between the three primary video colors. These filters, in combination with

an internal infrared filter and the wavelength dependent sensitivity of the CCD, produce a wide deviation from constant light sensitivity across the color spectrum.

The needed calibration information might be acquired using the fluorescent light source and the spectral data provided by the lamp's manufacturer. However, there are not many useful spectral features in the light output, and there is no guarantee that each bulb produces spectra identical to that reported by the manufacturer. A somewhat better alternative is to use the spectrum from an incandescent bulb as shown in Figure 2. (Obviously, still better would be to use a black body source or a spectrally calibrated lamp.)

A 60 W tungsten filament is expected to produce a color temperature of approximately 2800 K.^[17] Figure 15 is a graph of radiant power as a function of wavelength for a color temperature of 2800 K.^[18] However, the spectrum recorded with the video spectrometer, Figure 16, is grossly different than that of Figure 15. Originally it had been hoped that the two spectra would be similar enough that the needed correction would simply require applying a set of wavelength-dependent correction factors. However, the magnitude of the correction required in the region from 650 to 700 nm is too extreme for this method. The gray-scale image captured using Snappy is only 8-bit data (intensities ranging from 0 to 255). With correction factors exceeding 50 being needed, the resulting intervals between successive values would be unacceptably large. Accordingly, another method was sought.

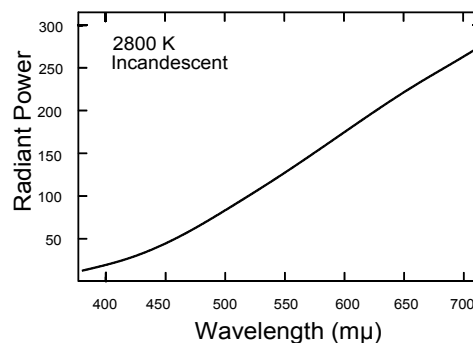


Figure 15. Spectral energy curve of typical 2800 K tungsten lamp.

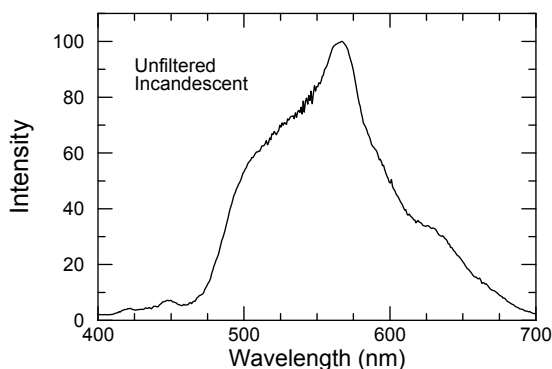


Figure 16. The observed spectrum of the incandescent calibration light source.

A more constant sensitivity as a function of wavelength would be obtained with a black and white video camera. However, that would be an additional purchase for many potential researchers and would probably require the use of a separate video recorder. Another alternative would be to use a still camera and black and white film. But for a short duration light source, only a few spectral images could be recorded, and because of the flame's flickering (movement behind the slit) they might not be typical of what is being produced. Another drawback of using film is the time delay in developing it, thus making set up and adjustment more difficult than with the video camera.

A coarse initial correction for intensity was attempted using externally mounted light filters. A pair of rose colored filters (GamColor^[20] polyester color filters #105 and #130) reduced the sensitivity in the green region and improved the observed continuous spectrum sufficiently to allow final correction using reasonably small numerical calibration factors. Figure 17 is the filtered continuous spectrum. Figure 18 is a graph of the intensity calibration factors which successfully reproduce the 2800 K spectrum (Figure 15).

As of this writing, no studies have been conducted using intensity-corrected spectra. However, studies to measure the temperature of glitter spritzel (dross particles) and flash temperatures will be initiated soon. For that work, fairly accurate spectral intensities will be needed.

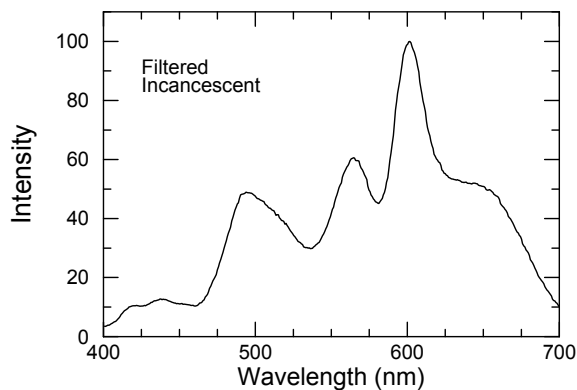


Figure 17. The filtered spectrum of the incandescent calibration light source.

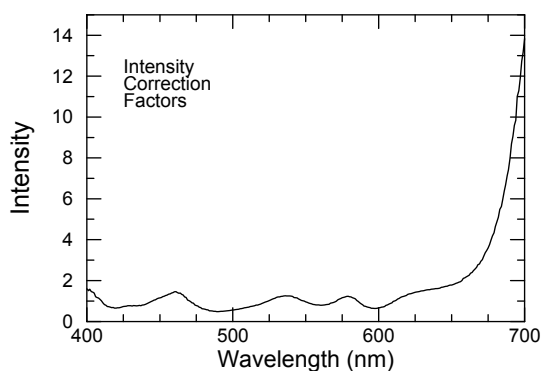


Figure 18. Intensity calibration factors for the filtered spectra.

Conclusion

Although still in an early stage of development, the video spectrometer has already proven useful. For example, a recent gathering of flame color researchers were able to conclude that many of the problems preventing the better colored flame formulations from producing high purity colors, stem from impurities in the chemicals used. (Most notably the presence of sodium and calcium caused problems.)

Probably the most significant advantage of a video spectrometer in studying flame color formulations is its relative low cost, assuming a camcorder and personal computer are already available. Also, its ability to continuously record very short duration spectra is ideal for pyro-

technic flames. Finally, the ability to look simultaneously at various points along the length of a flame is a feature generally absent from even high quality commercial spectrometers.

Clearly further improvements can be made in the hardware and operation of the video spectrometer. This work is shared in the hope that others would find the video spectrometer useful and would further develop the instrument.

Acknowledgments

The authors gratefully acknowledge the assistance of S. Anderson in the preparation of the test stars used in this article and J. La Marca for providing the GamColor filters. The authors wish to acknowledge the technical assistance of W. Meyerricks, S. Anderson, W. Smith, T. Wilkinson, L. Weinman, and D. Dolata.

References

- 1) K. L. & B. J. Kosanke and C. Jennings-White, *Lecture Notes for Pyrotechnic Chemistry*, Journal of Pyrotechnics, 1997.
- 2) K. L. & B. J. Kosanke, "A Video Spectrometer", *American Fireworks News*, No. 196, 1998.
- 3) T. Wilkinson, in preparation.
- 4) Cokin Creative Filter System, Cromofilter, France.
- 5) Central Scientific, Franklin Park, IL, USA. Item number 32945.
- 6) *The Illustrated Dictionary of Pyrotechnics*, Journal of Pyrotechnics, 1995.
- 7) OSRAM Sylvania, Maybrook, NY, USA.
- 8) Central Scientific, Franklin Park, IL, USA. Item number 86252.
- 9) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, John Wiley, 1976.
- 10) R. Herrmann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry*, Interscience Publications, 1963.
- 11) T. Shimizu, A collection of 7 articles originally in Japanese but recently translated by Shimizu into English. These articles are about to be republished by the Journal of Pyrotechnics under the title: "Studies of Colored Flame Compositions of Fireworks".
- 12) C. Jennings-White and S. Wilson, "The Best Oranges Don't Always Come from Florida", *Pyrotechnics Guild International Bulletin*, No. 71, 1990, p 32.
- 13) Play, Inc., Rancho Cordova, CA, USA, "Snappy Video Snapshot", version 2.0.
- 14) Adobe Systems, Inc. San Jose, CA, USA, "Adobe PhotoShop 3".
- 15) Silk Scientific, Inc. Orem, UT, USA, "Un-Scan-It Gel", version 4.1.
- 16) S. Anderson, personal communication and samples, 1992. Also an article accepted for publication in *Journal of Pyrotechnics*, Issue 8 titled "Colored Composite Stars".
- 17) H. Horenstein, *Color Photography, A Working Manual*, Little Brown, 1995, p 34.
- 18) C. B. Neblette, *Photography, Its Materials and Processes*, Van Nostrand, 1962, p 17.
- 19) GamColor light filters, The Great American Market, Hollywood, CA, USA.

Events Calendar

Pyrotechnics

29th International Annual Conference of ICT “Energetic Materials—Production, Processing and Characterization”

June 30–July 3, 1998, Karlsruhe, Germany

Contact: Ms Manuela Wolff

Phone: +49-7214-6401-21
FAX: +49-7241-6400-11
Web Site: <http://www.ict.fhg.de>

The Chemistry of Pyrotechnics & Explosives

July 19–24, 1998, Chestertown, MD, USA

Advanced Pyrotechnic Seminar: A Survey of Highly Reactive Systems—Explosives, Propellants, and Pyrotechnic Gas Generants

July 26–31, 1998, Chestertown, MD, USA

Contact: John Conkling
PO Box 213

Chestertown, MD 21620, USA

Phone: 410-778-6825
FAX: 410-778-5013
e-mail: John.Conkling@washcoll.edu

24th International Pyrotechnics Seminar

July 27–31, 1998, Monterey, CA USA

Contact: Allan J. Tulis, Seminar Chairman

IIT Research Institute
10 West Street

Chicago, IL 60616-3799

Phone: 312-567-4543
FAX: 312-567-4543
e-mail: atulis@hp.iitri.com
web:<http://intlpyro.org>

22nd Detonation Symposium

Aug. 30–Sept. 4, 1998, Snowmass, CO, USA

Contact: Dr. James Kennedy

Phone: 505-667-1468
FAX: 505-667-6301
e-mail: kennedy@lanl.gov

Pyrotechnicians International Convention

Sep. 21–22, Orlando, Florida, USA

Contact: Pyrotechnicians International
Route 4, Box 207
Rock Port, MO 64482, USA

American Pyrotechnics Association – 50th Anniversary – Convention

Sept 23–27, Orlando, Florida, USA

Contact: Julie Heckman
PO Box 213

Chestertown, MD 21620, USA

Phone: 301-977-3746
FAX: 301-977-7716
e-mail: julie@fireworksaftey.com

4th International Symposium on Fireworks

Oct. 8–13, 1998, Halifax, Nova Scotia, Canada

Contact: Ettore Contestabile
Canadian Explosives Research Lab., CANMET
555 Booth Street
Ottawa, Ont., K1A 0G1, Canada

Phone: 613-995-1363
FAX: 613-995-1230
e-mail: econtest@cc2smtp.nrcan.gc.ca

Pyrotechnic Chemistry Course—USA

Oct. 10–11, 1998, Purdue University,
W. Lafayette, IN USA

Contact: Ken Kosanke, PyroLabs
1775 Blair Road
Whitewater, CO 81527, USA

Phone: 970-245-0692
FAX: 970-245-0692
e-mail: ken@jpyro.com
Web Site: www.jpyro.com

**3rd International Autumn Seminar on
Propellants, Explosives and Pyrotechnics**

Oct. 5–8, 1999, Chengdu, China

Contact: Prof. Feng Changgen, Mech. & Engr.

Beijing Institute of Technology

PO Box 327

Beijing, 100081, China

FAX: +86-10-6841-2889

e-mail: cgfen@public.east.cn.net

Explosives

Computational Mechanics Assoc. Courses:

Fall 1998:

**Numerical Modeling of Explosives and
Propellants**

Detonation Physics

Introduction to Explosives

Connect: Computational Mechanics Associates

PO Box 11314

Baltimore, MD 21239-0314 USA

Phone: 410-532-3260

FAX: 410-532-3261

**1998 Insensitive Munitions & Energetic Ma-
terials Technology Symposium**

Nov. 16–19, 1998, San Diego, CA USA

Contact: ADPA/NSIA

Phone: 703-247-2582

FAX: 703-522-1885

e-mail: slevin@ndia.org

Web Site: www.adpansia.org

(Continued on Page 58)

Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures

Part 2. Stoichiometric Mixtures

D. Chapman, R. K. Wharton, J. E. Fletcher

Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom

and

G. E. Williamson

HM Explosives Inspectorate, Health and Safety Executive, St Anne's House, Trinity Road, Bootle, Merseyside, L20 3QZ, United Kingdom

ABSTRACT

The sensitiveness and thermal stability of stoichiometric sulfur/chlorate mixtures (approximately 30:70) have been investigated. The mixtures were found to be very sensitive to friction, with BAM limiting loads below 40 N. Some ignitions occurring at the lowest measurable level of 5 N result in limiting loads of ≤ 5 N. When the mixtures were heated slowly in cardboard fireworks tubes, they gave ignition temperatures in the region of 115–160 °C depending on the source and treatment of the sulfur.

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

Introduction

Part 1 of this series^[1] discussed the problems posed by the presence of sulfur/chlorate mixtures in fireworks compositions. In this second paper we report initial studies on stoichiometric sulfur/chlorate mixtures (approximately 30:70 S:KClO₃). The work has involved measurement of the acidity of the sulfur samples used to formulate the mixtures and determination of both the sensitiveness and thermal stability of the resulting mixes.

Experimental

Sulfur/chlorate mixtures were prepared from samples of potassium chlorate and sulfur purchased from laboratory suppliers or supplied by a United Kingdom (UK) manufacturer and importer of fireworks. The two potassium chlorate samples used were a high purity (AnalaR) laboratory material and a sample typical of that used by a Far Eastern manufacturer. Sulfur samples were standard laboratory grade (flowers of sulfur), and two samples representative of the materials used by a UK and a Far Eastern manufacturer. Additionally, samples of the oxidisers—potassium nitrate and potassium perchlorate—were included in the study for comparison.

Components were ground and sieved to obtain fractions for test that passed through a 0.5 mm mesh. Testing was performed on the sieved materials without further treatment and on samples dried at 100–105 °C, which were then stored in a desiccator. A series of mixtures was prepared from the oxidiser and sulfur samples. The components were weighed and then added to sample bottles where mixing took place, remotely, using a tilting roller mixer.

The mixtures produced were then subjected to thermal or sensitiveness testing.

Table 1. pH Measurement of Sulfur Samples.

Sulfur	Treatment	pH
Flowers	none	6.15–6.31
Flowers	dried 100 °C 2 hrs	5.76–6.05
Flowers	overnight heating at 105 °C	3.91–3.99
Far Eastern manufacturer's	none	5.92–6.36
Far Eastern manufacturer's	dried 100 °C 2 hrs	5.91–6.11
UK Manufacturer's	none	7.97
UK Manufacturer's	dried 100 °C 2 hrs	7.29–7.75

Acidity Measurement

Acidity of the sulfur samples was estimated from pH measurements. A portion of the sulfur, 5.0 g, was placed in a conical flask containing 250 cm³ distilled water with 1 drop of surfactant added. The mixture was placed in an ultrasonic bath and agitated for 30 minutes, then removed and allowed to cool to room temperature before measuring pH. Measurements were made using a combined electrode which had been calibrated at pHs of 4.01 and 7.01.

Thermal Stability

Cardboard fireworks tubes (70 mm × 10 mm id and 2 mm wall thickness) were prepared with a pressed clay plug (approximately 10 mm) at one end. To measure temperature of ignition, duplicate sets of 2 g samples of the sulfur/chlorate mixtures were placed in cardboard tubes, thermocouples (type T) inserted into the samples and tissue paper plugs loosely inserted into the top. The filled tubes were placed into heated aluminium blocks set to give a temperature rise of 5 °C hr⁻¹. A similar thermocouple was placed in the metal block to monitor the block temperature. Temperatures were calculated to ±0.5 °C using a PICO TC-08 combination thermocouple amplifier and analogue-to-digital converter with electronic cold junction. Block temperature was calibrated against a platinum resistance thermometer, which in turn was calibrated and traceable to national standards. The digital data were collected every 10 s using the provided software.^[2] Ignition of the sample was recognised by a sharp increase

in the recorded temperature compared with that of the block.

Sensitiveness Measurement

The friction and impact sensitivenesses^[3] of sulfur/chlorate mixtures, in powdered form, were measured using standard BAM (Bundesanstalt für Material-forschung und -prüfung) apparatus and sample sizes.^[4] The criteria for positive events were a visible flash or audible crack for both impact and friction. In no case was there any difficulty in ascertaining a positive result. In the investigation of friction sensitiveness, a number of test samples did not initiate on the forward run but did so on the return; these were considered as giving a positive result. The method utilised to analyse the data was the conventional limiting energy or limiting load, either measured directly or via probit^{[5][a]} studies which involved determining the probability of reaction at a minimum of three points. These data points were usually evaluated from 16 events.

Results

Acidity Measurements

The acidities of the sulfur samples ranged from 3.91 for a sample that had been heated at 105 °C for a prolonged period to 7.97 for the UK manufacturer's sulfur in its "as received" state. Table 1 lists the measured pH for the samples.

Table 2. Ignition Temperatures (°C) for 30:70 Sulfur/Chlorate Mixtures Prepared from “As Received” Materials.

Material	Flowers of sulfur		Far Eastern manufacturer's sulfur		UK manufacturer's sulfur	
Potassium chlorate AnalaR	115.0	115.5	115.5	115.5	158.5	155.5
Potassium chlorate Far Eastern	116.5	115.5	115.5	115.5	152.5	155.5

Table 3. Ignition Temperatures (°C) for 30:70 Sulfur/Chlorate Mixtures Prepared from Dried Materials.

Material	Flowers of sulfur		Far Eastern manufacturer's sulfur		UK manufacturer's sulfur	
Potassium chlorate AnalaR	119.0	119.0	118.5	117.5	159.5	147.5
Potassium chlorate Far Eastern	117.0	118.5	115.0	114.5	149.0	149.5

Table 4. Friction Sensitiveness (Limiting Load, N) for 30:70 Sulfur/Chlorate Mixtures Prepared from “As Received” Materials.

Oxidiser	Type of sulfur		
	Flowers	Far Eastern manufacturer's	UK manufacturer's
Potassium chlorate AnalaR*	10	10	≤5
Potassium chlorate Far Eastern	10	10	≤5
Potassium perchlorate SLR*	60	—	—
Potassium perchlorate Far Eastern	60	—	—
Potassium Nitrate SLR	360	—	—

* AnalaR = analytical reagent.

SLR = specified laboratory reagent for general laboratory applications.

Thermal Stability

Ignition temperatures of slowly heated (5 °C hr⁻¹) sulfur/chlorate mixtures prepared from as received materials without drying are listed in Table 2.

Similar experiments were performed with sulfur and other oxidisers, however the heater system used could only achieve 180 °C, and this was insufficient to ignite these mixtures. Tests were also carried out after drying the materials at 100–105 °C. The ignition temperatures are listed in Table 3.

Sensitiveness Measurements

Friction sensitiveness of 30:70 mixtures of sulfur with the oxidisers was measured for the materials “as received”, the only treatment being sieving through a 0.5 mm sieve. The results are presented in Table 4.

Table 5. Impact Sensitiveness (Limiting Impact Energy, J) for Sulfur/Chlorate Mixtures Prepared from “As Received” Materials.

Oxidiser	Type of sulfur		
	Flowers	Far Eastern manufacturer's	UK manufacturer's
Potassium chlorate AnalaR	15	15	15
Potassium chlorate Far Eastern	20	25	20
Potassium perchlorate SLR	20	—	—
Potassium perchlorate Far Eastern	30	—	—
Potassium nitrate SLR	40	—	—

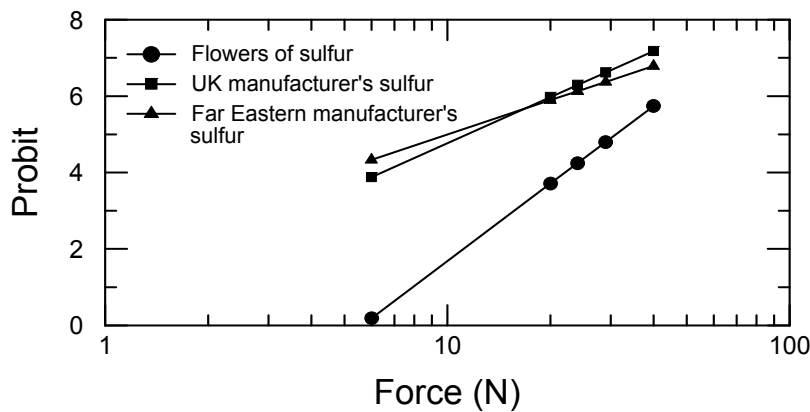


Figure 1. Typical probit plots for friction sensitiveness (mixtures made up from AnalaR potassium chlorate and the indicated sulfur).

Similarly, Limiting Impact Energies were measured and are reported in Table 5.

Dried samples were prepared and their sensitiveness determined by probit analysis. Typical probit lines generated from friction testing are shown in Figure 1.

The probit lines were used to calculate the limiting load applied in the BAM Friction test^[4] which corresponds to a 0.17 probability. Table 6 reports the results.

Table 6. Calculated BAM Friction Sensitiveness for 30:70 Sulfur/Chlorate Mixtures Prepared from Dried Materials.

Materials used in formulating mixture		Calculated Limiting Load (N)
Sulfur	Chlorate	
Flowers	AnalaR	40
UK	AnalaR	10
Far Eastern	AnalaR	10
Flowers	Far Eastern	10
UK	Far Eastern	20
Far Eastern	Far Eastern	10

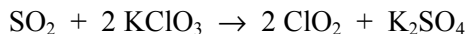
Similarly, the probit lines generated from impact data were used to calculate the limiting impact energies from the BAM Fallhammer test, Table 7.

Table 7. Calculated BAM Impact Sensitiveness for 30:70 Sulfur/Chlorate Mixtures Prepared from Dried Materials.

Materials used in formulating mixture		Calculated limiting impact energy (J)
Sulfur	Chlorate	
Flowers	AnalaR	5
UK	AnalaR	15
Far Eastern	AnalaR	15
Flowers	Far Eastern	10
UK	Far Eastern	20
Far Eastern	Far Eastern	20

Discussion

Tanner^[6] has cited the acidity of sulfur in the form of polythionic acids as one cause of the instability of sulfur/chlorate mixtures. He has suggested the reaction



to be the initiation step for a chain reaction leading to ignition. The release of sulfur dioxide from the polythionic acids by the action of heat or friction was proposed as the “trigger” for the reaction. Storey^[7] has shown that sulfur and potassium chlorate held at 80 °C spontaneously ignite when sulfur dioxide is blown into the mixture. Additionally, Weingart^[8] has reported that the thermal stability of sulfur/chlorate mixtures is increased by the addition of base. The samples of sulfur used in our study had pH values between 3.91 and 7.97. With this large range in acidity it was anticipated that there would be an effect on both thermal stability and sensitiveness of mixtures formed with potassium chlorate.

Ignition temperatures for the sulfur/chlorate mixtures indicate a difference between the UK manufacturer’s sulfur and the other samples for both “as received” and dried materials. The alkaline pH measured from extracting the UK manufacturer’s sulfur with water suggests that this type of sulfur may contain a small amount of base, possibly intended as an anticaking agent. The addition of base to sulfur is reported as being required in UK military pyrotechnics to stabilise sulfur/chlorate mixtures.^[9] Interestingly, heat treatment when drying the sulfur reduces the ignition temperature of sulfur/chlorate mixtures produced from the UK manufacturer’s sulfur while for the other sulfur samples the ignition temperature increases with heat treatment. With the acidic samples it would appear that the acidity as measured by pH is not the critical factor. As the sulfur is heated, acidity in the form of sulfuric acid is increased but the weaker, less stable polythionic acids will be decomposed in the heat treatment, removing or reducing the sulfur dioxide-producing material from the reaction until oxidation of the sulfur produces sufficient sulfur dioxide for the reaction to be triggered.

It may be possible that two ignition mechanisms could operate. The sulfur samples which were acidic formed sulfur/chlorate mixtures, which ignited at or below the melting temperature of 119 °C for orthorhombic sulfur, S_α .^[10] On the other hand, the sulfur which was found to be slightly alkaline formed sulfur/chlorate mixtures which had higher ignition temperatures (approaching 160 °C). At lower temperatures the action of sulfur dioxide on chlorate has been suggested as the trigger mechanism.^[6] An alternative mechanism at temperatures above 140 °C has been proposed by McLain:^[11] this involves S_8 molecules breaking into smaller units which can penetrate the potassium chlorate lattice. The temperature at which this occurs is well above the Tammann temperature^[12] for potassium chlorate, and there will be significant diffusion of the sulfur fuel into the oxidiser lattice. Ignition should occur at, or before, 159.1 °C, which is the reported temperature for maximum rate of formation of S_3 fragments.^[11] This suggests that in our experiments the UK manufacturer’s sulfur is reacting by fragmenting its S_8 rings and suppressing any reactions due to sul-

fur dioxide. Conversely, the other sulfur samples are likely to be reacting via the formation of sulfur dioxide, initially from polythionic acids. If the polythionic acids have been decomposed prior to mixing then the reaction requires sulfur dioxide to be generated by oxidation.

The standard procedures for measuring impact and friction sensitiveness calculate the stimulus required for a single probability of initiation. For the BAM methods this is a limiting value corresponding to a level of approximately 0.17 (or less) probability of initiation. In the corresponding UK methods, 0.50 probability of initiation is found by a "Bruceton Staircase" method.^[13] Typically, 15–25 samples would be used for the BAM method and 50 samples for a "Bruceton Staircase" method. In this study we investigated the whole response curve by probit^[5] transformation and "standard" BAM methodology.

Storey^[7] has reported a Figure of Friction of 0.12 for an unspecified sulfur/chlorate mixture tested using the Rotary Friction apparatus.^[14] An approximate BAM limiting load of 6.6 N can be calculated from this value using the relationship for explosives reported by Wharton and Chapman.^[15] This limiting load falls within the range measured for the "as received" materials, which were below 10 N (Table 4). Acidity in the form of the sulfur pH does not seem to have a major influence on the sensitiveness of the materials. All samples had BAM limiting loads below 40 N which would correspond to a Figure of Friction of less than 1. Materials having Figures of Friction less than 3 are regarded as being "very sensitive" in the UK.^[16] Similarly, the mixtures were below the UN criterion of 80 N for transport in the form tested. Heat treated sulfur samples, which had more acidic pH, appear to be marginally less sensitive to friction. This is probably due to polythionic acid levels being reduced by heating. Further work will be carried out to investigate this.

Impact sensitiveness results for the 30:70 sulfur/chlorate mixtures were all above the 2 J threshold in the UN scheme, indicating that the main mechanical hazard posed by the mixtures is the response to friction stimuli.

Conclusions

Initial work with stoichiometric mixtures (30:70) of sulfur and potassium chlorate indicate that the material can be extremely friction sensitive depending on the source of the sulfur and its treatment. Sulfur/chlorate mixtures in cardboard fireworks tubes have been shown to ignite at temperatures below the sulfur melting temperature when subjected to slow heating. Added materials, of the type likely to be found in fireworks compositions, could affect the reactivity of sulfur/chlorate mixtures and this will form the basis for our next paper.

Acknowledgement

The authors are grateful to Standard Fireworks Limited for the supply of raw materials for test, together with cardboard tubes and clay for preparing the test specimens.

Notes

[a] Probit analysis is a statistical treatment used for quantal or all-or-nothing response systems and is particularly useful in extrapolating data to very low or very high probability where an S-shaped response curve is generated. For example, it has been used in studying biological systems to find the mortality rate from insecticide at different concentrations (see reference 5). The insects are either killed or survive. In our case the test sample initiates or does not.

References

- 1) D. Chapman, R. K. Wharton and G. E. Williamson, "Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 1. Introduction", *Journal of Pyrotechnics*, Issue 6, 1997, pp 30–35.
- 2) PICOLOG, MSDOS version, Release 3.07, Pico Technology Ltd., Cambridge, United Kingdom, 1995.
- 3) R. K. Wharton and D. Chapman, "The Use of the Term Sensitiveness to Describe the Response of Pyrotechnic Compositions to

Accidental Stimuli”, *Journal of Pyrotechnics*, Issue 7, 1998.

- 4) “Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria”, ST/SG/AC.10/11/Rev 2, 2nd rev. ed., United Nations, New York and Geneva, 1995, pp 105–6.
- 5) D. J. Finney, “Probit Analysis a Statistical Treatment of the Sigmoid Response Curve”, Cambridge University Press, London, 1952, p 2.
- 6) H. G. Tanner, “Instability of Sulfur–Potassium Chlorate Mixtures” *Journal of Chemical Education*, Vol. 36, 1959, p 58.
- 7) P. D. Storey, “Identification and Assessment of Hazardous Mixtures in Pyrotechnics”, *13th International Pyrotechnics Seminar*, Grand Junction, Colorado, USA, July 1988, p 765.
- 8) G. W. Weingart, *Pyrotechnics*, 2nd ed., Chemical Publishing. Co. Inc., New York, 1947, p 1.
- 9) A. Bailey and S. G. Murray, *Land Warfare: Brassey’s New Battlefield Weapons Systems & Technology Series Volume 2. Explosives, Propellants and Pyrotechnics*, Brassey’s (UK), London, 1989, p 119.
- 10) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Interscience Publishers, New York, 1972, p 424.
- 11) J. H. McLain, *Pyrotechnics*, The Franklin Institute Press, Philadelphia, 1980, p 73.
- 12) J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, New York, 1985, p 70.
- 13) Ref. 4 p 385.
- 14) Ref. 4 p 110.
- 15) R. K. Wharton and D. Chapman, “The Relationship between BAM Friction and Rotary Friction Sensitiveness Data for High Explosives”, *Propellants, Explosives, Pyrotechnics*, Vol. 22, 1997, p 71.
- 16) Sensitiveness Collaboration Committee, “Manual of Tests”, Procurement Executive, Ministry of Defence, Royal Armament Research and Development Establishment, October 1988.

© British Crown copyright, 1998.

Events Calendar

(Continued from Page 50)

Fireworks

Summer Fireworks Festival

Jul. 27–31, 1998, Auburn/Weedsport, NY, USA

Contact: Charles Hill

4533 Foster Valley Road

Endicott, NY 13760 USA

Phone: 607-748-0667

FAX: 607-748-0899

Pyrotechnics Guild International Convention

August 9–14, 1998, Gillette, WY, USA

Contact: Bruce Burns, Chairman

PO Box 6027

Sheridan, WY 82801

Phone: 307-674-7376

e-mail: bburns@cyberhighway.net

10th Western Winter Blast

Feb. 12–14, 1999, Lake Havasu, AZ, USA

Contact: Steve Rhodes

Phone: 906-685-2968

e-mail: remains4u@aol.com

web site: www.wpa.pyrotechnics.org

High Power Rocketry

LDRS XVII

Aug. 6–9, 1998

Contact: Neal Baker

5352 West 6600 South

West Jordan, UT, 84084, USA

Phone: 801-359-5544

FAX: 801-359-5544

e-mail: nbaker@lgcy.com

Web Site: www.urock.org/ldr/index.html

Model Rocketry

NARAM-41

For launch information visit the NAR web site at:
<http://www.nar.org>

Editorial Policy

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

Novel Powder Fuel for Firework Display Rocket Motors

NOTE: This article originally appeared in
Proceedings of the 21st International Pyrotechnics Seminar, 1995.

Barry Cook

Standard Fireworks Limited, Huddersfield HD4 7AD, England

ABSTRACT

An inexpensive, readily prepared and relatively insensitive powdered fuel suitable for the filling of small firework display rocket motors using a funnel and rammer technique is discussed.

Firework display rocket motors are typically cardboard or aluminium tubes filled with a gunpowder derivative. Consolidation is achieved by incremental filling and pressing or, as at Standard Fireworks, by a mechanically operated funnel and rammer system.

The objective was to provide a simple in-house method to prepare a free-flowing powdered fuel compatible with the available filling equipment. The raw materials are inexpensive and readily available.

The paper will discuss the following aspects: choice of binding agent for the powder, choice of raw materials and relative proportions, hazard data, and performance data.

Introduction

The largest majority of firework rockets are powered by gunpowder filled motors; for example, Standard Fireworks uses 40 tonnes per annum of gunpowder simply as a fuel for rocket motors. In addition to the bulk purchase of this gunpowder, there are associated costs involved in both storage and transport.

This paper describes the work done towards providing an alternative fuel that can be readily manufactured at Standard Fireworks, when required, thus reducing the overall amount of gunpowder that needs to be held in store for the manufacture of fireworks.

The following information is the subject of a Patent Application. G.B. 2,274,480 A.

1. Rocket Motor (Description)

The motor tube is a small open-ended cardboard tube having a choked aperture (ventura) at one end, produced either by crimping the tube or by pressing into place an internal clay washer. The tube is filled with gunpowder, which is compressed around a tapered brass insert, thus providing a cone-shaped gallery in order to increase initial burn rate and produce the required thrust.

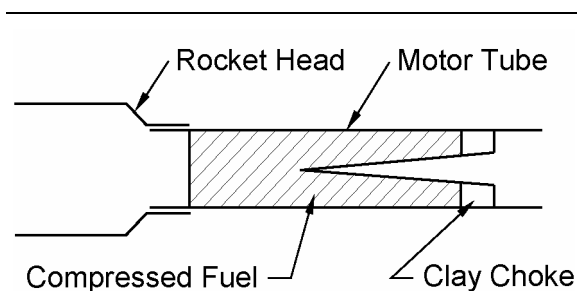


Figure 1. Schematic diagram of small rocket motor.

The tube is open-ended, allowing the final 'burn through' to ignite the effects enclosed within the attached rocket head.

2. Replacement Rocket Powder

Requirements

- 1) Safety considerations during manufacture, use and storage (i.e., impact and friction sensitiveness).
- 2) Physical Nature: free-flowing, non bridging powder/granules.
- 3) Quick and simple on site method of manufacture (i.e., prepared as required) and thus eliminating the problems associated with storage and transport of large mounts of explosives.
- 4) Readily available, multi-sourced, relatively inexpensive, non-toxic raw materials.

3. Background

From past experience, using a simple blend of the ingredients of gunpowder does not produce a rocket motor with the required burn properties. The gunpowder, currently in use at Standard Fireworks, has the chemical composition shown below:

Ingredient	%
Potassium nitrate	68±1.5
Charcoal	9±1.0
Sulphur	23±1.0

However, it is well known that simple whistle-effect pyrotechnic admixtures have properties which are suitable for use as a propellant for small rockets. A typical mixture is a blend of potassium perchlorate with a metal salt of an aromatic carboxylic acid and a liquid binder; such an example is shown below:

Ingredient	Parts
Potassium perchlorate	60
Potassium benzoate	40
Polystyrene binder soln.	2

With this background knowledge, it was decided that an attempt would be made to adapt the whistle mixture and to give it suitable flow characteristics to be used with the powder filling equipment at Standard Fireworks.

4. Development Work

It was decided initially to keep the oxidant as potassium perchlorate and the aromatic acid as potassium benzoate, as currently used at Standard Fireworks.

4.1. Binder

The desired properties of the binder are:

- (i) Solid.
- (ii) Relatively low melting (<100 °C).
- (iii) Easily oxidised to produce mainly oxides of carbon as the major gaseous product.
- (iv) Readily available and moderately priced.

With the above properties in mind the binder of choice was selected from aromatic compounds either unsubstituted or substituted with OR or NR₁R₂, where R, R₁, R₂ = hydrogen, low alkyl or an aromatic ring. Especially those having carbon to hydrogen weight ratios ≥ 13:1. Examples of such materials are given in Table 1.

The compositions used for the initial trials were based upon whistle effect signal mixtures used at Standard Fireworks (i.e., admixtures of potassium perchlorate and potassium benzoate). Such mixtures, upon ignition, proved to be too violent for use as a rocket motor composition. However substitution of part of the potassium perchlorate with potassium nitrate eventually gave satisfactory results. Examples of experimental mixtures are given in Table 2.

The tests were carried out using a small rocket with a loaded plastic head (Net Explosive Content [N.E.C.] of motor = 10 g).

The composition of choice was No. 9 (Code WPR 40). This was made after consideration of performance test results, chemical hazard data and availability of raw materials. The composition compares favourably with the currently used gunpowder in all aspects of performance, cost and ignition sensitivity.

Table 1. Examples of Chosen Binders.

Binder	Formula	C/H Weight Ratio	Melting Point °C
Naphthalene	C ₁₀ H ₈	15:1	80–82
2-Methoxy-naphthalene	C ₁₁ H ₁₀ O	13:1	73–75
Diphenylamine	C ₁₂ H ₁₁ N	13:1	52–54
Diphenylether	C ₁₂ H ₁₀ O	16.5:1	26–30
Biphenyl	C ₁₂ H ₁₀	14.5:1	69–72
2-Hydroxybiphenyl	C ₁₂ H ₁₀ O	14.5:1	57–59
Stearic acid *	C ₁₈ H ₃₆ O ₂	6:1	67–69

* control

It is prepared *simply* by tumble mixing of the weighed and sieved ingredients. The motors retained their effectiveness after storage through two cold and damp English winters in an unheated magazine.

5. Performance and Sensitiveness Tests

Comparison of the performance of WPR 40 with gunpowder (R81) is shown from the trace given by measurement of the thrust output from identical size of motors. See Figure 3.

The thrust measurements were made on equipment developed in conjunction with Royal Military College of Science, Shrivenham, a diagrammatic representation of which is shown in Figure 2.

Table 2. Experimental Mixtures.

No.	Constituent Parts				Flight Results
	Potassium Perchlorate	Potassium Nitrate	Potassium Benzoate	Binder (parts)	
1	60	—	40	Naphthalene (10)	50% motors exploded upon ignition
2	60	—	40	Biphenyl (10)	50% motors exploded upon ignition
3	60	—	40	2-Methoxy Naphthalene (10)	All motors exploded upon ignition
4	45	15	40	Biphenyl (5)	Good vigorous flight
5	45	25	30	Diphenylamine (5)	Weak flight
6	50	20	30	Diphenylamine (5)	Vigorous flight
7	35	35	30	2-Hydroxy Biphenyl (5)	Weak launch
8	40	30	30	2-Hydroxy Biphenyl (5)	Improved on No. 7
9	45	25	30	2-Hydroxy Biphenyl (5)	Vigorous launch
10	45	25	30	Stearic acid (1)	No launch

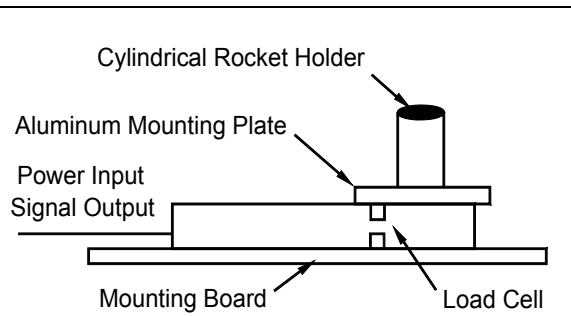


Figure 2. The thrust meter device.

The Thrust Measurement Device

The device consists of an adapted load cell. The load cell is a beam arranged so that an applied load will result in a proportional strain along that beam. The strain so produced is detected using an array of strain gauges, which convert the strain into an electrical signal, the magnitude of which is related to that of the applied strain.

The load cell is mounted on a flat metal plate, which provides extra overload protection for the device.

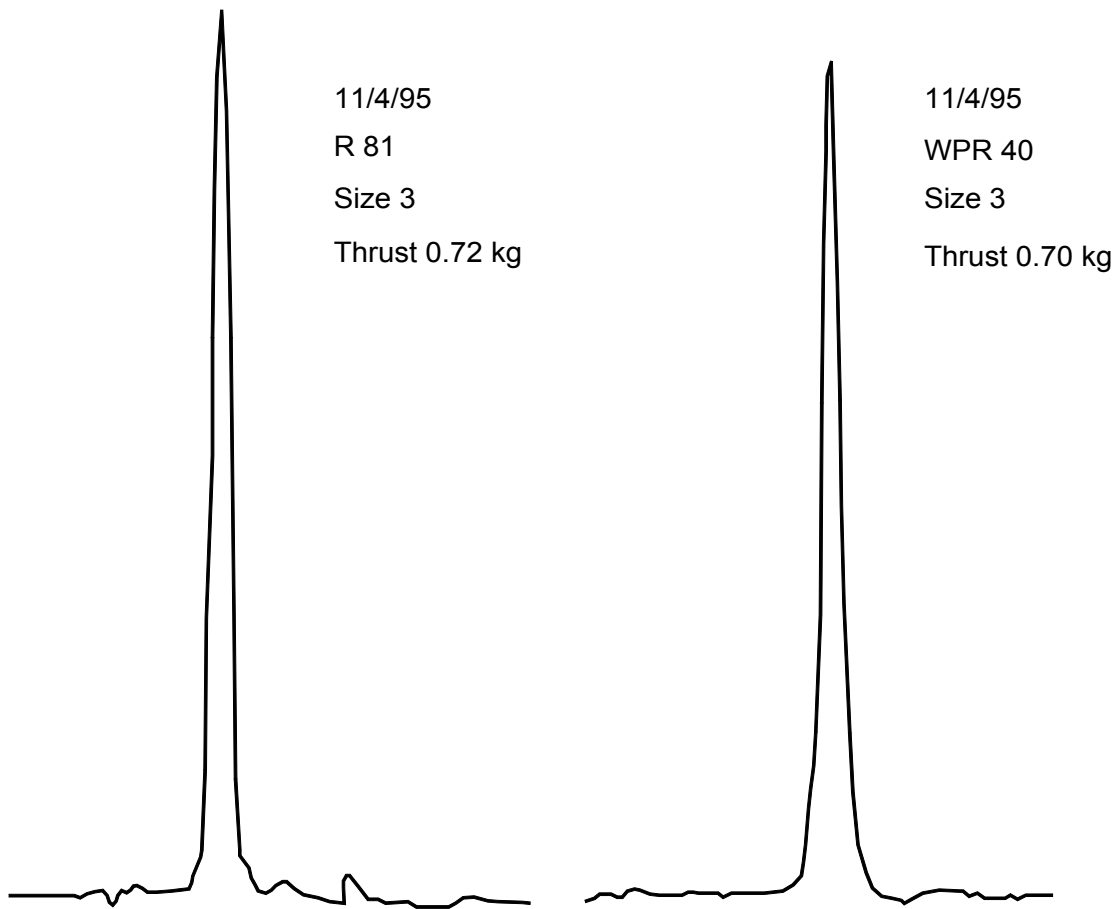


Figure 3. Comparative thrust measurements.

Table 3. Mallet Friction Test Results.

Composition: White Powder Rocket 81

Part number: WPR40

Mallet →	Rock Maple			Nylon	Steel	
Anvil →	Yorkstone	Hard Wood	Soft Wood	Mild Steel	Mild Steel	
1	x	x	x	x	x	E
2	x	x	x	x	x	x
3	x	x	x	x	x	x
4	x	x	x	x	x	x
5	x	x	x	x	x	x
6	x	x	x	x	x	x
7	x	x	x	x	E	x
8	x	x	x	x	x	x
9	x	x	x	x	x	x
10	x	x	x	x	x	x
Total E	0	0	0	0	2	
%E	0%	0%	0%	0%	50%	

x = non event

E = event

6. Ignition Sensitiveness Testing

6.1 Mallet Friction Test

In this test a small sample of explosive is spread onto an anvil and struck a glancing blow with a standard wood or steel-tipped or nylon-tipped mallet held in the operator's hand.

The combinations used are:

Steel-tip mallet on steel anvil;

Nylon-tip mallet on steel anvil;

Wood mallet on: softwood
hardwood
and Yorkstone.

An ignition is judged to have occurred if the observer detects any of the following:

- a) sparks or flame,
- b) a crack as some or all of the trace reacts,
- c) for the all-wooden mallet only, a smell of burning.

Results are reported as the number of ignitions occurring during ten cycles. For the steel-on-steel combination therefore, the number of

ignitions from twenty cycles is divided by two and rounded up to the nearest integer and quoted as the equivalent number of ignitions from ten cycles.

For Hazard Data Sheet purposes results are rounded for each surface combination as follows:

- | | |
|---------------------------------------|------|
| No ignition in ten cycles | 0% |
| Up to six ignitions in ten cycles | 50% |
| More than six ignitions in ten cycles | 100% |

Comparative results are given in Tables 3 and 4.

6.2 B.A.M. Fallhammer Test

The BAM Fallhammer Test [Bundesanstalt für Materialforschung und -prüfung] involves dropping a range of standard weights from known heights onto an explosive sample and observing an "explosion" or a "no reaction". The height at which a decrease of 10 cm of drop height causes a change in sample response from "explosion" to "no reaction" for six consecutive trials is determined. This value is then converted into an energy value (in joules) and

Table 4. Mallet Friction Test Results.

Composition: Gunpowder Rocket 81

Part number: 16050

Mallet →	Rock Maple			Nylon	Steel	
Anvil →	York-stone	Hard Wood	Soft Wood	Mild Steel	Mild Steel	
1	x	x	x	x	x	x
2	x	x	x	x	x	x
3	x	x	x	x	x	x
4	x	x	x	x	x	x
5	x	x	x	x	x	x
6	x	x	x	x	x	x
7	x	x	x	x	x	x
8	x	x	x	x	x	x
9	x	x	x	x	x	x
10	x	x	x	x	x	x
Total E	0	0	0	0	0	
%E	0%	0%	0%	0%	0%	

x = non event

E = event

this value is termed the Limiting Impact Energy (LIE). The detection of a positive event is by an explosion.

Results:

Limiting Impact Energy	(L.I.E.)
Rocket 81 (Gunpowder)	10.0 J
WPR 40	<30 J

6.3 Ignition Temperature

The ignition temperatures obtained from a Differential Scanning Calorimeter trace are shown below:

Material	Ignition Temperature
Rocket 81	350 °C
WPR 40	480 °C

7. Conclusions

The composition of choice (i.e., WPR 40) has proved to be a relatively safe and cost effective replacement for gunpowder in small rocket motors. It is anticipated that further work, chiefly involving modification of the granular form of this material, will make it acceptable for use in all the rocket motors currently in production.

Obvious advantages of this composition are ease of manufacture, readily available and multi-sourced raw materials and reduced problems associated with gunpowder storage.

Use of the Term Sensitiveness to Describe the Response of Pyrotechnic Compositions to Accidental Stimuli

Roland K. Wharton and David Chapman

Health and Safety Laboratory, Harpur Hill,
Buxton, Derbyshire, SK17 9JN, United Kingdom

ABSTRACT

This paper clarifies the differences between the terms sensitivity and sensitiveness, highlights the adoption of the latter by the United Nations, and proposes that sensitiveness could usefully be employed in describing certain hazard characteristics of pyrotechnic compositions.

Keywords: sensitiveness, sensitivity, hazard, pyrotechnic

Introduction

The Sensitiveness Collaboration Committee of the United Kingdom Ministry of Defence has produced a manual^[1] that describes the standard test procedures and apparatus used to assess the safety of “energetic materials” (in this context, high explosives, propellants and pyrotechnics) for Service use. The manual defines a number of hazard parameters and uses the terms sensitiveness and explosiveness for characterising the response of explosive systems in accident situations. In a different sense, sensitivity is used to describe the deliberate application of a stimulus.

Sensitiveness, as used in the United Kingdom (UK), can be defined as a measure of the relative probability of an explosive being ignited or initiated by a prescribed stimulus. The stimuli are those considered relevant to accident situations and include impact, friction and electric spark. The word sensitiveness is therefore used in relation to assessing the hazard characteristics of the explosive material.

Sensitivity, on the other hand, is used in the UK to designate a measure of the stimulus required to cause reliable functioning of an explosive material in its designed mode. Detonators provide a good example, since the conditions for reliable initiation are specified in terms of a minimum current. Similarly, for pyrotechnic compositions, it is likely that the sensitivity to flame is considered at the design formulation stage.

Whereas the UK uses the terms as described above, other countries adopt a different approach. In Japan,^[2,3] Canada^[4] and Croatia,^[5] for example, sensitivity is used in the same sense as sensitiveness in the UK.

United States (US) usage of the term sensitivity has recently been defined^[6] for pyrotechnics but it is not clear whether the stimuli are in relation to design mode or accidental functioning.

Cook^[7] proposes a different terminology in which the term precariousness is used to refer to “hazard sensitivity” (i.e., sensitiveness, as defined above) and “sensitiveness” is used to designate “performance sensitivity”.

Clearly, the wide-ranging use of similar words to describe different characteristics of explosives creates the potential for confusion.^[8] The latest edition of the Manual of Tests and Criteria^[9] relating to the United Nations (UN) scheme for the transport of dangerous goods has almost universally used the term sensitiveness which is helpful, although some inconsistencies remain.

The areas of inconsistent terminology in the UN manual appear to be largely editorial in origin (e.g., whereas Test Series 3 refers to type (a) tests as being for determining the sensitiveness to impact and type (b) for determining the sensitiveness to friction, the descriptions of the boxes in the flow chart assessment scheme (ref. 9, p. 21) refer to impact sensitivity and friction sensitivity). Another anomaly relates to test methods 3 (a) (vi) and 3 (b) (iv) which are titled impact and friction sensitivity tests, respectively, but from their introductory descriptions are clearly used to measure mechanical sensitiveness.

Discussion

Although the UN manual provides the first global test scheme for explosives, it strictly relates only to transport situations and is part of the process by which packaged explosives goods and articles are classified. However, since it provides well accepted and widely used explosives test methods, the test procedures have been adopted for other uses.

Examples are the use of sensitiveness information obtained from the UN-recommended, German Bundesanstalt für Materialforschung und -prüfung (BAM) tests in relation to the notification, supply and use of bulk chemicals under European Community (EC) legislation,^[10] and the inclusion of BAM mechanical sensitiveness tests in the harmonised European Committee for Standardisation [Comité Européen de Normalisation (CEN)] test methods^[11] that are currently being developed as a means of assessing whether commercial sector explosives meet the essential safety requirements of the European Civil Uses Directive.^[12] Other examples are the use of the BAM tests in the classification of explosives substances under the Chemical (Hazard Information and Packaging for Supply) Regulations 1994 (CHIP 2) and for the categorisation of explosives under the draft Control of Major Accident Hazards involving Dangerous Substances Directive (COMAH)^[13] as part of large scale hazard evaluation.

Quantification of the sensitiveness of pyrotechnic compositions is needed for UN purposes (i.e., transport classifications) but the information can also be valuable in assessing hazards involved in handling (e.g., dropping) and manufacturing (e.g., pressing).

Surveys of accidents involving pyrotechnics^[14] and, more generally, explosives^[15] have indicated that they are often caused by mechanical stimuli, particularly friction.

The Health and Safety Laboratory provides a support service to the UK Explosives Inspectorate and one of its functions is to provide laboratory assistance to the technical investigation of accidents involving explosives. Studies in recent years have clearly demonstrated the role that mechanically sensitive pyrotechnic compositions have had in certain accidents and have highlighted the importance of measuring sensitiveness.^[16]

Examples are provided by: the initiating pyrotechnic material involved in the explosion of 800 kg of mixed explosives and detonators at Peterborough in March 1989;^[17] accidents during the pressing of titanium/blackpowder mixtures for gerbs;^[18] and the ignition during processing of a thiourea/chlorate white smoke mix.^[19]

When evaluating the hazards posed by explosive materials, the explosive response in a defined system should be considered as well as the likelihood of the initiation occurring as a result, for example, of a given mechanical stimulus.

While sensitiveness covers the latter, in the UK the term explosiveness is defined as “the degree of violence shown by an explosive material when it responds to a prescribed stimulus relevant to an accident situation”.^[1]

The plot of sensitiveness against explosiveness, Figure 1, is useful in illustrating the hazards posed by traditional types of explosives, but for certain modern materials the regions of correlation no longer apply.^[20] For this reason it is advantageous to measure explosiveness together with sensitiveness. Pyrotechnic compositions exhibit a range of explosiveness and sensitiveness (“some can be sensitive enough to be classed as primary explosives”^[1]) and they can occur throughout the sensitiveness/explosi-

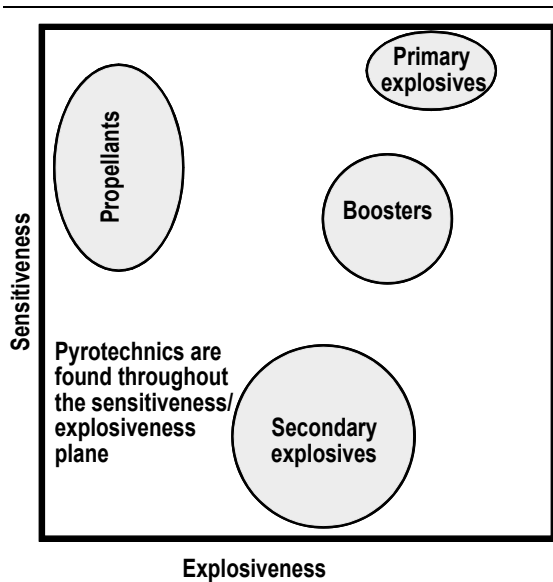


Figure 1. The relationship between sensitiveness and explosiveness for different types of explosives.

veness plane illustrated in Figure 1. The existence of this variable behaviour reinforces the need to undertake practical measurements since there are no other means of accurately predicting the hazard.

Conclusion

This short paper advocates use of the UN-accepted term sensitiveness to describe the response of pyrotechnic compositions to accidental stimuli.

Evaluation of the sensitiveness of pyrotechnics (particularly to friction and impact) is important since the results can provide a means of assessing the hazards involved in different manufacturing and handling processes.

References

- 1) Sensitiveness Collaboration Committee, *Manual of Tests*, Ministry of Defence, Royal Armament Research and Development Establishment, October 1988.
- 2) T. Yoshida, Y. Wada and N. Foster, "Safety of Reactive Chemicals and Pyrotechnics", *Industrial Safety Series*, Vol. 5, Elsevier, 1995, p 86.
- 3) K. Hara, M. Kanazawa and T. Yoshida, "Evaluation of Fire and Explosion Hazards for Non-Azide Gas Generant", *Journal of Pyrotechnics*, No. 4, 1996, p 15.
- 4) R. Bowes, "Hazard Analysis of Pyrotechnic Compositions", *Proceedings of the 2nd International Symposium on Fireworks*, Vancouver, Canada, 1994, p 17.
- 5) M. Suceška, *Test Methods for Explosives*, Springer-Verlag, 1995, p 21.
- 6) K. L. and B. J. Kosanke, *The Illustrated Dictionary of Pyrotechnics*, Pyrotechnic Reference Series No. 1, p 107, Journal of Pyrotechnics, 1995.
- 7) M. A. Cook, *The Science of Industrial Explosives*, Ireco Chemicals, 1974, p 235.
- 8) H. J. Yallop, "Explosion Investigation", *Forensic Science Society and Scottish Academic Press Ltd.*, 1980, p 21.
- 9) *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, ST/SG/AC.10/11/Rev 2, second revised edition, United Nations, New York and Geneva, 1995.
- 10) *Official Journal of the European Communities*, L383, Directive 92/69, 1992.
- 11) CEN/TC 321, *Explosives for Civil Use*.
- 12) Council Directive 93/15 EEC, 5 April 93, Harmonisation of Provisions on the Placing on the Market and Supervision of Explosives for Civil Use.

- 13) "Control of Major Hazards involving Dangerous Substances". *Com* (94) 4 final, 26 Jan 1994, 94/0014 (SYN).
- 14) F. L. McIntyre, "Incident/Accident Survey of Pyrotechnic Compositions", *Proceedings of the 6th International Pyrotechnics Seminar*, Denver, Colorado, 1978, p 392.
- 15) A. Bailey, D. Chapman, M. R. Williams and R. Wharton, "The Handling and Processing of Explosives", *Proceedings of the 18th International Pyrotechnics Seminars*, Breckenridge, Colorado, 1992, p 33.
- 16) R. K. Wharton, "Observations on the Sensitiveness and Reactivity of certain Pyrotechnic Mixes That Have Been Involved in Ignition Accidents", *Proceedings of the 1st International Fireworks Symposium*, Montreal, Canada, 1992, p 339.
- 17) R. K. Wharton and R. J. Rapley, "Technical Investigation of the Explosion on 22 March 1989 at Peterborough, England", *Propellants, Explosives, Pyrotechnics*, Vol. 17, 1992, p 139.
- 18) R. K. Wharton, R. J. Rapley and J. A. Harding, "The Mechanical Sensitiveness of Titanium/Blackpowder Pyrotechnic Compositions", *Propellants, Explosives, Pyrotechnics*, Vol. 18, 1993, p 25.
- 19) R. K. Wharton and A. J. Barratt, "Observations on the Reactivity of Pyrotechnic Compositions containing Potassium Chlorate and Thiourea", *Propellants, Explosives, Pyrotechnics*, Vol. 18, 1993, p 77.
- 20) Ref. 1 p 5.

© British Crown copyright, 1998.

Some Measurements of Glitter

K. L. and B. J. Kosanke

PyroLabs, Inc., 1775 Blair Road, Whitewater, CO,
USA

C. Jennings-White
Salt Lake City, UT, USA

ABSTRACT

A brief series of measurements was made on the flashes produced by a simple glitter formulation. In part this was done as a test of one theory for the chemistry of glitter. However, this was also done to produce some intrinsically interesting data that have not been previously reported. It was observed that both increasing the percentage of aluminum in the formulation and decreasing the particle size of the aluminum, decreased the delay time before the appearance of the glitter flashes. Both the size and duration of glitter flashes increased for flashes with greater delay. It was also observed that there was a rapid increase in temperature just prior to the onset of the flash event.

Introduction

Glitter effects are one of the most attractive in fireworks. Several theories have been proposed for its chemistry and are discussed in a review article by one of the authors.^[1] One reason for conducting the work reported in this article was to collect some information to test one of those theories; however that discussion is left to the review article. For the most part, this article simply presents the results of the study without an attempt to interpret them.

Experimental

To keep the chemistry simple and make the results unambiguous, a fairly simple glitter formulation was used. The basic formulation is given in Table 1 and is similar to one suggested by Fish.^[2]

Table 1. Basic Test Glitter Star Formulation.

Component	Parts
Potassium nitrate	54
Charcoal (air float)	11
Sulfur	18
Sodium bicarbonate	8
Dextrin	4
Aluminum (a)	(a)

(a) Various types and amounts of aluminum were used.

The mixture of ingredients without aluminum was prepared in sufficient quantity to make many small batches of test stars. Each batch of composition was dampened with 10% distilled water. The stars were made as cylinders $\frac{1}{4}$ inch (6 mm) in diameter and approximately $\frac{1}{2}$ inch (12 mm) in length using a compacting force of approximately 50 psi. A relatively small diameter was chosen for the test stars to limit the number of glitter flashes produced per unit time, which facilitated their observation and counting. On average approximately 550 glitter flashes were observed for each test star burned.

One series of test stars was made with a spherical atomized aluminum having an average particle size of approximately 12 microns (Alcoa S-10). For these stars, the percentage of aluminum in the composition was either 5, 7 or 10 percent. For another series of test stars, the aluminum was held constant at 7 percent, but the average particle size of the atomized aluminum was either 3, 12 or 30 microns (using Valimet H3, Alcoa S-10 and Valimet H30, respectively).

The test stars were burned under one of two conditions. In some instances they were burned

at a height of approximately 11 feet (3.3 m) and the dross droplets allowed to fall vertically under the influence of gravity. However, in most cases the test stars were burned in a horizontal air stream moving at approximately 40 mph (65 kph), causing the dross droplets to be carried down wind. The air stream was allowed to diverge shortly after the point where the star was burned. Thus the wind speed gradually fell to an average of approximately 25 mph (40 kph) over the range of the observed glitter flashes. The air temperature was relatively cool, approximately 45 °F (7 °C) for the gravity driven tests and 35 °F (2 °C) for the wind driven tests.

Under either test condition (gravity or wind) glitter flashes occurring at greater distances from the test star correspond to greater delay times. However, for simplicity in reporting the results of this study, for the most part, only delays in terms of distances are given. For a given delay distance, this is the distance from the burning star to the center of a one foot (0.3 m) interval over which observations were made. For example, flash events reported for a down wind distance of 4 feet (1.3 m) are those occurring between 3.5 and 4.5 feet (1.1 and 1.4 m) from the star.

The percent of flashes versus down wind distance curves were produced using a cubic spline. This method was chosen because the level of precision of the data is not great and because the intrinsic shape of the curves is unknown. Accordingly, it is not intended to imply that any undulations seen in the graphs are real.

Results

The effect of varying aluminum concentration (5, 7, and 10 percent) is shown in Figure 1. For this formulation, increasing aluminum concentration decreased the typical delay of the glitter flashes. This is seen in both the down wind distance at which the maximum number of flashes occurs and in the average distance traveled before the flash reaction, see Table 2. The effect of varying the particle size of the atomized aluminum (3, 12 and 30 micron) is also shown in Figure 2. For this test, increasing particle size increased the typical delay of the glitter flashes. It is possible to interpret both

sets of data (effects of concentration and particle size) as glitter delay increasing as the result of decreasing the total surface area of aluminum in the composition.

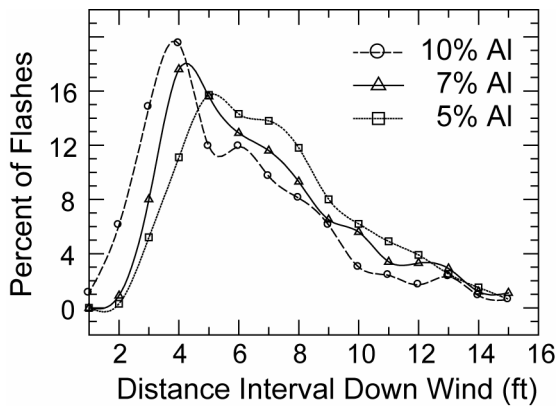


Figure 1. Graph of the percent of glitter flashes occurring as a function of down wind distance, for various aluminum concentrations.

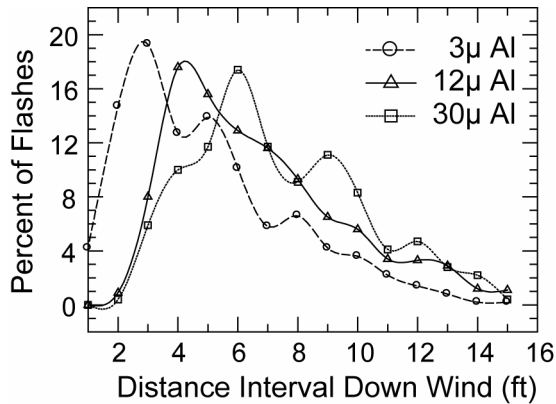


Figure 2. Graph of the percent of glitter flashes occurring as a function of down wind distance, for various aluminum particle sizes.

Table 2. Summary of Approximate Glitter Flash Distance Information for Variations in Formulation.

Formulation	Glitter Flashes	
	Peak (ft.)	Average (ft.)
5 percent	5.1	7.1
7 percent	4.3	6.7
10 percent	3.8	5.8
3 micron	2.9	5.0
12 micron	4.3	6.7
30 micron	6.0	7.3

Although not the primary purpose of these measurements, some other interesting observations were made. Considering the likely droplet velocities in the air stream, it is possible to estimate the time elapsed before the glitter flashes occur, based on the distance they traveled. In this case it was simply assumed that droplet speed during the first foot traveled was half that of the air stream. Thereafter, droplet speed was assumed to equal that of the air stream at each point. Accordingly, for the formulations tested, it is estimated that the peak number of glitter flashes are typically occurring roughly 0.1 second after leaving the burning star. Similarly the average time to the occurrence of the glitter flashes is roughly 0.2 second.

There appears to be a relationship between the time interval before flash occurrence and the physical size and duration of the flash. The size relationship is demonstrated in Figure 3, which presents 1/60 second negative black and white images of typical glitter flashes. Here the flashes are organized by distance from the burning star (using 7 percent of the 12 micron aluminum) in a gravity driven test. (As in the air stream driven case, there is a functional relationship between increasing distance and increasing time.) In Figure 3, the actual size of each image area is approximately 10 inches (0.25 m); thus the size of the flashes ranges from about 1 to 3 inches (25 to 75 mm) depending on the distance from the star.

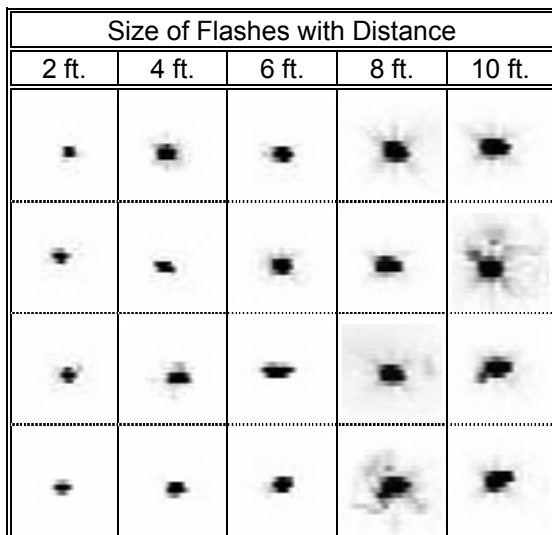


Figure 3. Examples of typical glitter flashes as a function of distance from the star (negative black and white images).

There also appears to be a correlation between the observed duration of the glitter flashes and the distance from the burning star (delay time). This was established by observing the number of successive video fields (each 1/60 second) during which individual flashes were visible. For each down wind distance from test stars, 25 observations of the duration of flashes were made, and an average duration was calculated. These data are listed in Table 3 and graphed in Figure 4. Using a statistical model wherein a glitter flash can initiate at any time during the 1/60 second image interval, it can be estimated that

$$D = \frac{N - 1}{60}$$

where D is the approximate average flash duration and N is the average number of video fields over which glitter flashes are seen. Using this relationship, average flash durations were calculated as a function of distance in the air stream from the burning star. These flash durations ranged from approximately 3 to 13 ms (see Table 3).

Table 3. Average Glitter Flash Duration as a Function of Down Wind Distance.

Distance (ft)	Ave. No. Fields	Ave. Flash Duration (ms) (a)
4	1.20	2.8
6	1.20	3.8
8	1.32	5.5
10	1.48	7.5
12	1.52	10.2
14	1.86	13.3

(a) Values were calculated using curve fitted flash durations from Figure 4.

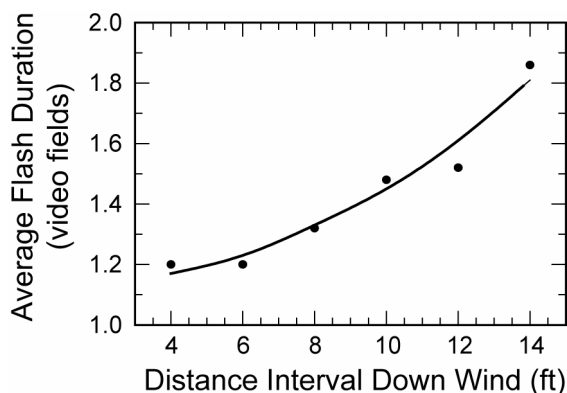


Figure 4. Graph of the average number of video fields for glitter flashes as a function of distance.

Figure 5 is a composite negative black and white image of a glitter droplet traveling to the left, until the time when it is just beginning to flash. Figure 5 is composed of a series of individual 1/60 second (17 ms) video fields; however, to help identify the passage of time and the progress of the droplet, only every other video image was included. Note that the intensity of the emitted light is roughly constant until about the last three images, where its intensity (darkness) noticeably increases. Figure 6 is a graph of this droplet's image intensity prior to the onset of the flash reaction. In Figure 6, all of the video images were captured and analyzed, not just the half presented in Figure 5. The light intensity at first remains fairly constant and then rapidly increases just prior to the flash.



Figure 5. Composite image of a glitter dross droplet just prior to the start of the flash reaction. Note the droplet is moving from right to left.

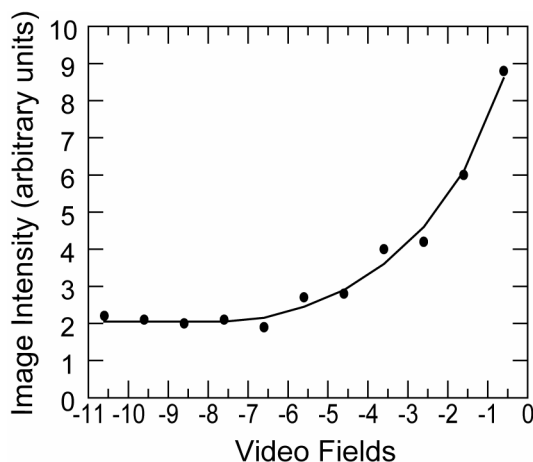


Figure 6. Graph of video image intensity of the dross droplet from Figure 5.

Light intensity is a function of temperature, thus the temperature of the glitter dross droplet is increasing just prior to the flash reaction. However, at this time, the response function (intensity versus wavelength) of the video camera is not known. Thus it is not possible to assign temperatures to the dross droplet. (There are plans to make such measurements in the future.)

Conclusion

The results reported in this article are somewhat interesting on their own. They also provide a basis to draw an inference regarding the chemistry operating in the glitter phenomenon. However, the discussion of glitter chemistry is left for another article by one of the authors.^[1]

The results presented are based on only a limited amount of data and for only one type of formulation. Further, in some cases, assumptions and approximations have been made. Thus a good measure of caution is warranted before drawing firm conclusions from these results.

Acknowledgments

The authors wish to acknowledge D. Tygett of Valimet for providing samples of their H3 and H30 aluminum. The authors are also grateful to S. Anderson for providing technical and editorial comments on this article.

References

- 1) C. Jennings-White, "Glitter Chemistry", *Journal of Pyrotechnics*, Accepted for publication in Issue 8, 1998.
- 2) T. Fish, "Glitter Stars Without Antimony," *Pyrotechnics Guild International Bulletin*, No. 24, 1984.

Another Fog Study

Monona Rossol

181 Thompson St., No. 23
New York, NY 10012, USA

A two page summary of research done by Dr. Jacqueline M. Moline from the Mount Sinai-Irving J. Selikoff Center for Environmental and Occupational Medicine^[1] investigated the health complaints of 25 pit musicians at the *Beauty and the Beast*. These musicians are exposed nightly to pyrotechnic emissions, glycol fog mists, and other air pollutants.

A questionnaire was used to determine which symptoms the musicians attributed to fumes and fog. The percentages of musicians that listed runny or stuffy noses, cough, shortness of breath, tearing or strained eyes, and sore or dry throats ranged between 41 and 59 percent. These are very similar to the percentages claimed by performers in the other two major studies,^[2,3] and they support those results.

Dr. Moline's initial medical investigation on October 23, 1996 included a physical examination and spirometry (measurement of lung capacity) before and after a matinee performance. A follow up study three weeks later included repeat post-performance spirometry and physical examination. Dr. Moline reported her findings as follows:

An analysis of the pulmonary function tests showed that there was a statistically significant decrease in forced vital capacity from pre- to post-performance. In addition, there was evidence of a decrease in measurement of small airway function ... in 16 of 25 (64%) individuals. When current smokers were excluded (smoking is the most common cause of decrement in small airway function), 13 of 22 (59%) of musicians exhibited abnormalities in their small airway function. Of the fourteen musicians who were present on both screening days, 10 of 14 showed small airway dysfunction.

The conditions for the musicians in the music pit at "Beauty and the Beast" are unhealthy. A large percentage of the musicians are suffering from symptoms related to the irritative effects of the work environment. Several musicians now require medical care and medication to treat their symptoms which have developed or worsened since taking part in this production.

Clearly special effects are harming the musicians. The same also is true for the singers, dancers, and anyone else who is exposed repeatedly. A coordinated effort is needed to protect these people. Producers must plan to use special effects only in venues with ventilation systems capable of drawing fog and smoke away from audiences and music pits. Manufacturers must be sure their fog machines control and minimize the temperature of vaporizers. Special effects directors must choose the least toxic effects and use the least amounts necessary. Stage directors must block the performers' actions away from heavily fogged areas.

References

- 1) Letter Report: "Beauty and the Beast", Jacqueline M. Moline, MD, MSc., Mount Sinai-Irving J. Selikoff Center for Environmental and Occupational Medicine, New York City, January 17, 1997.
 - 2) Study begun in 1990 for Actor's Equity and the League of American Theaters and Producers. The report went through four versions. The Final Report was released in August 1994. (HETA 90-355-2449).
 - 3) "Health effects of glycol based fog used in theatrical productions", Harry H. Herman, Jr., report to Actor's Equity Association, July 1995.
-

Possible Applications for Computer Codes in the Development of Pyrotechnic Compositions

Rutger Webb

Kruisbeklaan 14, NL 37 22 TH Bilthoven,
Netherlands
e-mail: rwebb@pi.net

The following letter contains some comments on the possible applications for computer codes in the development of pyrotechnic compositions. It is hoped to stimulate more discussion on the practical applications of thermodynamic computer codes in the development of pyrotechnic compositions. (For example, for modeling colored compositions).

In brief, if one has the possibility to choose from various fuels and oxidizers, and wants to predict possible pyrotechnic reactions, simple balanced stoichiometric equations may, in some cases, be reasonably fine. But in other situations, one wishes to have more information, such as the reaction products that can be formed, and at what temperature. Certain thermodynamic computer codes can calculate these for you. (They give you reaction products and temperatures—and more—from given compositions. Most modern PC's require a very short runtime, and it is often possible to feed large numbers of compositions to them in one run.) These codes were originally developed for rocket propellants.^[1,2] There are a number of different codes; two are listed in the Table. The idea of using the output from a thermodynamic code for theoretical modeling of pyrotechnic illumination compositions was apparently first described by Dr. Bernard Douda.^[3] Theoretical modeling of pyrotechnic color compositions has also been described by Arno Hahma.^[4] Ramohalli^[5] described modeling gas generators. Vladimiroff^[6] calculated flame temperatures of propellants.

Name	Comments
NASA Lewis CEA	Computer code from NASA Lewis ^[1]
PROPEP	A version of the NWC Propellant Evaluation Program (PEP) that was provided by the NSWC during 1988. This program is basically the PEP program written by D. R. Cruise at NWC described in NWC TP 6037 titled "Theoretical Computations of Equilibrium Compositions, Thermodynamic Properties, and Performance Characteristics of Propellant Systems". ^[2]

CEA = Chemical Equilibrium with Application

NWC = Naval Weapons Center

NSWC = Naval Surface Weapons Center

It is important, for this application, to use the results of such a 'tool' with proper care, before attempting to derive conclusions from it. One has to be aware of various limitations. Some examples of limitations are:

- The output often does not tell anything about kinetics (rate at which the chemical reactions take place).
- Calculations are based on minimization of free energy; equilibrium is assumed.
- Programs have difficulty converging when many solids are present.
- Flames have many different shapes, which are not modeled, influencing their radiative performance.^[7]
- Accurate input data for fireworks binders/fuels may not always be available.

The 'useful' output, for this situation, is the predicted reaction products and temperatures. In case one is interested in modeling a colored-fire composition, the output can be used to calculate a ratio between 'desired emitters' and 'undesired emitters' of a color composition. Arno Hahma named this a 'quality factor' (Q). For example, for an imaginary barium magnesium flare, a simple Q could be calculated by:

$$Q = \frac{a[\text{BaCl}]}{b[\text{BaO}] + c[\text{MgO}]}$$

in units of mole per mole.

Calculating less simplified Q 's would seem more appropriate, but it is beyond the scope of this letter. Gradual changes in composition lead to new values of Q , which allows one to optimize it. If the trend of Q as a function of composition does not correlate with what one sees in real life, one has to go back to the 'drawing table' on how to calculate more accurate Q 's. At the moment work on this is ongoing.

The effort to predict radiated spectra from combustion of energetic materials appears to overlap with more than just one military application. For example, the radiation emitted from exhaust plumes of solid rocket propellants has been modeled since the 1960's and probably earlier.^[8,9,10] Also other related combustion phenomena have been modeled.^[11,12]

In conclusion, I would like to emphasize that this approach is not new, and that it is not my idea. These codes have advantages and disadvantages. Interested readers are encouraged to react.* (This letter has been kept short and, needless to say, there is much more to it.) I am greatly indebted to Arno Hahma, Dr. Bernie Douda, and Bonnie McBride for providing their help.

* Arno Hahma added to this "the codes are still much better than back of the envelope calculations. You can get close to the optimum quickly and do the fine tuning with traditional methods (i.e., experimentation)."

References

- 1) S. Gordon and B. J. McBride, "Computer Program for Calculating Complex Chemical Equilibrium Compositions and Applications. I. Analysis", NASA Reference Publication 1311, October 1994.
- 2) E. D. Brown, "An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers", *Journal of Pyrotechnics*, Issue 1, 1995.
- 3) B. E. Douda, "Radiative Transfer Model of a Pyrotechnic Flame", AD-769237, NAD/RDTR-258, September 1973, pp 14-15.
- 4) A. Hahma, "Theoretical Modeling of Some Pyrotechnic Mixtures", *International Symposium on Energetic Material Technology, ADPA Proceedings*, September 24-27, 1995, Phoenix, Arizona, USA.
- 5) T. Vladimiroff et al., "Flame Temperature Calculations at High Temperature and Pressure", *Propellants, Explosives, Pyrotechnics*, Vol. 19, 1994, pp 281-285.
- 6) K. Ramohalli, "Combustion Modeling of Explosive Pyrotechnics", paper 12, *Proceedings of the International Annual Conference ICT 1988, "Combustion and Detonation Phenomena"*, Karlsruhe, Germany, 1988.
- 7) A.G. Gaydon and H.G. Wolfhard, *Flames, Their Structure, Radiation and Temperature*, Chapman and Hall, 4th ed., 1979.
- 8) E. J. Beiting, "Predicted Optical Characteristics of Solid Rocket Motor Exhaust in Stratosphere", *Journal of Spacecraft and Rockets*, Vol. 34, No. 3, May-June 1997.
- 9) L. Deimling et al., "Radiation Emitted from Rocket Plumes", *Propellants, Explosives, Pyrotechnics*, Vol. 22, 1997, pp 152-155.
- 10) Victor Technology's page on the Internet <http://members.aol.com/victec>
- 11) Chang Eun Choi et al., "Numerical Analysis of a Gray Combustion with Nongray Radiation Using Weighted Sum of Gray Gases Model", *Combustion Science and Technology*, Vol. 115, 1996, pp 297-315.
- 12) W. Eckl et al., "Spectroscopic Investigation of Nitromethane Flames", *Propellants, Explosives, Pyrotechnics*, Vol. 22, 1997, pp 180-183.

Review of Ian von Maltitz's *Black Powder Manufacture Methods and Technique*

John Bergman

5438 E. Rotamer Rd., Milton, WI 53563, USA

In this book, Mr. von Maltitz has compiled a wealth of historical data about black powder, descriptions of commercial and amateur production methods, equipment, ingredients, formulae, and even comparative performance data. Probably nowhere else is so much basic information about this most fundamental of pyrotechnic mixtures, and many of its relatives, available in a single volume. Please note, however, that this is mainly a practical guide for the amateur. Those seeking scholarly analyses of the chemistry, physics, or thermodynamics of black powder should look elsewhere.

The book opens with an introductory chapter on safety, and this responsible approach is very welcome. Specifically directed toward the hobbyist, many of the suggestions are still good reminders for all who handle pyrotechnic mixtures in any capacity. The emphasis on keeping batches small, sticking to the safer methods, equipment, and procedures, and giving forethought to the possible consequences of an accident is wise counsel. If followed, this advice should help to reduce both the physical and social dangers inherent in this sort of experimentation. Despite these cautions, however, it is rather disappointing to see references later in the book to methods that involve heating mixtures “on a kitchen stove”. The author does suggest that

they be done outdoors, but the point deserves greater emphasis. For many reasons, both legal and practical, operations of this sort ought never to be conducted in a residence.

The author’s discussion of methods for the small-scale production of black powder is particularly useful to the hobbyist, for these methods provide an economical route to lift powder for shells and other applications. The descriptions of these processes—some of which are rather complex—are as exhaustive as the processes themselves are varied. Test results, by which the products’ performance may be compared, are provided for many of the methods. Detailed descriptions of several easy tests are also provided for those who may wish to make their own comparisons.

One chapter is largely devoted to black powder substitutes and related compositions. Few, if any, of these oddities will be useful to the serious pyrotechnist, and some of them—as the author warns—should definitely be avoided. However, their inclusion does provide interesting insights into the wide variety of mixtures devised, improvised, and used over the years for various purposes, and with varying degrees of success.

A number of appendices detail several historic processes for producing military black powder, describe a trip through Goex’s Moosic, Pennsylvania plant, provide specifications for commercial black powder, and give useful data on lift charges for various types of aerial shells.

All in all, this book is a readable and useful compendium which should be of interest to a wide audience. It is a worthwhile addition to any pyrotechnic library.

Journal Sponsors

The *Journal of Pyrotechnics* wishes to offer a special Thank You to the following Individual and Corporate Sponsors for their support.

Individual Sponsors:

Ed Brown

P.O. Box 177
Rockvale, CO 81244, USA
Phone: 719-784-4226

John and Karin Driver

2382 NW 30th Road
Boca Raton, FL 33431, USA
Phone: 561-483-7737
FAX: 561-483-4198
e-mail: JWDriver@worldnet.att.net

Corporate Sponsors:

Action Lighting, Inc.

Hugh Reid
P.O. Box 6428
Bozeman, MT 59715, USA
Phone: 800-248-0076
FAX: 406-585-3078
e-mail:
action_lighting@gomontana.com

Allied Specialty Insurance

Ed Schneider
10451 Gulf Blvd.
Treasure Island, FL 33706, USA
Phone: 800-237-3355
FAX: 813-367-1407

American Fireworks News

Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: 717-828-8417
FAX: 717-828-8695
e-mail: amerfwknws@aol.com
Web: www.barrettwebs.com/afn

Astro Pyrotechnics

Dan Hyman
2298 W. Stonehurst
Rialto, CA 92377, USA
Web: www.astropyro.com

Black Sky Research Assoc.

Scott Bartel
3179 Roosevelt Street
Carlsbad, CA 92008, USA
Phone: 760-730-3702
FAX: 760-730-3704
e-mail: blacksky@earthlink.net

Boom Boom Productions

Fred May
P.O. Box 1234
Hayfork, CA 96041, USA
Phone: 530-628-4436
FAX: 530-628-3023

Canadian Explosives Research Laboratory

Ron Vandebeek
CANMET, 555 Booth St.
Ottawa, ONT K1A 0G1, Canada
Phone: 613-995-1275
FAX: 613-995-1230
e-mail: rvandebe@nrcan.gc.ca
Web: www.nrcan.gc.ca

Daveyfire, Inc.

Alan Broca
7311 Greenhaven Dr. - Ste. #100
Sacramento, CA 95831, USA
Phone: 916-391-2674
FAX: 916-391-2783
e-mail: daveyfire@msn.com

Delcor Industries Inc.

Sam Bases
19 Standish Ave.
Yonkers, NY 10710, USA
Phone: 914-779-6425
FAX: 914-779-6463

Fire One

Dan Barker
863 Benner Pike
State College, PA 16801, USA
Phone: 814-238-5334
FAX: 814-231-0950
e-mail: rjc@fireone.com
Web: www.fireone.com

Firefox Enterprises, Inc.

Gary Purrington
11612 N. Nelson
Pocatello, ID 83202, USA
Phone: 208-237-1976
FAX: 208-237-1976
e-mail: firefox@pcaxxess.net
Web: www.pcaxxess.net/firefox

Fireworks

John Bennett
68 Ridgewood Gardens
Bexhill-in-Sea, East Sussex
TN40 1TS, United Kingdom
Phone: +1424-219-259
FAX: +1424-733-050
e-mail: JFBen@netcomuk.co.uk
Web: www.fireworks.co.uk/
fireworks-journal

Fireworks Business

Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: 717-828-8417
FAX: 717-828-8695
e-mail: amerfwknws@aol.com
Web: www.barrettwebs.com/afn

Fireworks and Stage FX America

Kevin Brueckner
P.O. Box 488
Lakeside, CA 92040-0488, USA
Phone: 619-596-2800
FAX: 619-596-2900
e-mail: go4pyro@aol.com
Web: www.fireworksamerica.com

Firework Professionals Ltd.

Anthony Lealand
PO Box 17-522
Christchurch, 8030
New Zealand
Phone: +64-3-384-4445
FAX: +64-3-384-4446
e-mail: firewxch@firework.co.nz

Fullam's Fireworks, Inc.

Rick Fullam
P.O. Box 1808 CVSR
Moab, UT 84532, USA
Phone: 801-259-2666

Goex, Inc.

Mick Fahringer
PO Box 659
Doyline, LA 71023-0659, USA
Phone: 318-382-9300
FAX: 318-382-3903
e-mail: BPMick@aol.com
Web: www.shooters.com/goex

High Power Rocketry

Bruce Kelley
PO Box 96
Orem, UT 84059, USA
e-mail: 71161.2351@compuserve.com

Industrial Solid Propulsion

Gary Rosenfield
1955 S. Palm St. - Ste. 6
Las Vegas, NV 89104, USA
Phone: 702-641-5307
FAX: 702-641-1883
e-mail: GaryR@power.net
Web: aerotech-rocketry.com

Iowa Pyro Supply

Mark Mead
1000 130th St.
Stanwood, IA 52337, USA
Phone: 319-945-6637

Island Fireworks Co., Inc.

Charles Gardas
N735 825th St.
Hager City, WI 54014, USA
Phone: 715-792-2283
FAX: 715-792-2640

**Kastner Pyro. & Fwks.
Mfg.**

Jeri Kastner
Rt 3, 938 Logtown Rd.
Mineral Point, WI 53565, USA
Phone: 608-943-6287
FAX: 608-943-6287

Lantis Fireworks & Lasers

Ken Lantis
P.O. Box 491
Draper, UT 84020, USA
Phone: 801-571-2444
FAX: 801-571-3516
e-mail: info@fireworks-lasers.com
Web: www.fireworks-lasers.com

Luna Tech, Inc.

Tom DeWille
148 Moon Drive
Owens Cross Rds, AL 35763, USA
Phone: 205-725-4225
FAX: 205-725-4811
e-mail: PyropakUSA@aol.com

**Marutamaya Ogatsu Fwks
Co. Ltd.**

1-35-35 Oshitate Fuchu
Tokyo, 183-0012, Japan
Phone: 81-423-63-6251
FAX: 81-423-63-6252
e-mail: moff@za2.so-net.or.jp

MP Associates, Inc.

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

OXRAL, Inc.

Tom DeWille
P.O. Box 160
Owens Cross Rds, AL 35763, USA
Phone: 205-725-4225
FAX: 205-725-4811
e-mail: Pyropak@juno.com

Precocious Pyrotechnics

Garry Hanson
4420 278th Ave. N.W.
Belgrade, MN 56312-9616, USA
Phone: 320-346-2201
FAX: 320-346-2403
e-mail: ppinc@midstate.tds.net

Pyro Shows, Inc.

Lansden Hill
P.O. Box 1406
LaFollette, TN 37766, USA
Phone: 800-662-1331
FAX: 423-562-9171

Pyrodigital Consultants

Ken Nixon
1074 Wranglers Trail
Pebble Beach, CA 93953, USA
Phone: 408-375-9489
FAX: 408-375-5225
e-mail: pyrodig@aol.com

PyroLabs, Inc.

Ken Kosanke
1775 Blair Road
Whitewater, CO 81527, USA
Phone: 970-245-0692
FAX: 970-245-0692
e-mail: kosankes@compuserve.com

RES Specialty Pyrotechnics

Steve Coman
4785 Dakota Street SE
Prior Lake, MN 55372, USA
Phone: 612-447-7976
FAX: 612-447-0065
e-mail: respyro@minn.net

Service Chemical, Inc.

Marvin Schultz
2651 Penn Avenue
Hatfield, PA 19440, USA
Phone: 215-362-0411
FAX: 215-362-2578

Skylighter, Inc.

Harry Gilliam
PO Box 480
Round Hill, VA 20142-0480, USA
Phone: 540-554-2228
FAX: 540-554-2849
e-mail: custservice@skylighter.com
Web: www.skylighter.com

Stresau Laboratory, Inc.

Mike Pesko
N 8265 Medley Rd.
Spooner, WI 54801, USA
Phone: 715-635-2777
FAX: 715-635-7979
e-mail: mpesko@syslan.net
Web: www.stresau.com

Sunset Fireworks Ltd.

Gerald Walker
10476 Sunset Drive
Dittmer, MO 63023, USA
Phone: 314-274-1500
FAX: 314-274-0883

Sunset Fireworks, Omaha

Jack Harvey
2335 South 147th Street
Omaha, NE 68144-2047, USA
Phone: 402-681-5822
FAX: 402-333-9840

Syd Howard Fwks. Int'l

Syd Howard
420 Halcrows Road, Glenorie
Sydney, NSW 2157, Australia
Phone: 61-2-9652-2244
FAX: 61-2-9652-1581

Theatre Effects, Inc.

Nathan Kahn
642 Frederick St.
Hagerstown, MD 21740, USA
Phone: 301-791-7646
FAX: 301-791-7719
e-mail: nathan@theatreffx.com
Web: www.theatreffx.com

Tri-Ess Sciences, Inc.

Ira Katz
1020 W. Chestnut St.
Burbank, CA 91506, USA
Phone: 818-848-7838
FAX: 818-848-3521

Western Pyrotechnics, Inc.

Rudy Schaffner
2796 Casey Road
Holtville, CA 92250, USA
Phone: 619-356-5426
FAX: 619-356-2051

Table of Contents from Prior Issues

Issue No. 1, Summer 1995:

Observations on the Heights Attained by Spherical Fireworks Shells	1
Observations on the Behaviour of Seamed Steel Mortar Tubes	6
An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers	11
Introductory Chemistry for Pyrotechnists Part 1. Atoms, Molecules, and Their Interactions	19
Concussion Mortar Internal Pressure, Recoil and Overpressure as Functions of Powder Mass	26
Prediction of Flame Temperatures Part 1. Low Temperature Reactions	37

Issue No. 2, Winter 1995:

The Semiconductor Bridge (SCB) Igniter	1
Modern Rack and Mortar Designs for Professional Fireworks Displays	6
Introductory Chemistry for Pyrotechnists Part 2. The Effect of Electrons	15
Hazardous Chemical Combinations: A Discussion	22
Bullet Impact Sensitivity Testing of Class B Fireworks and Ingredients and Detonability Testing of Flash Powder	36

Issue No. 3, Summer 1996:

Electric Spark Sensitivity of Reductive Element - Oxidizer Mixtures	1
Health Effects from Theatrical Pyrotechnics	14
Observation on the Perceived Burst Size of Spherical Aerial Shells	22
Aerial Shell Drift Effects: (A) The effect of Long Mortars (B) The Effect of Capsule-Shaped Shells	30
Ammonium Perchlorate Composite Basics	35

Issue No. 4, Winter 1996:

SEM Studies on a Strobe Star Composition	1
Flash Powder Output Testing: Weak Confinement	5
Evaluation of Fire and Explosion Hazards for a Non-Azide Gas Generant	15
Progress in Developing a Fuel-Air Salute	25
Pyrotechnic Whistles	37

Issue No. 5, Summer 1997:

Model Rocket Motors, Theory and Design	1
Flow Agents in Pyrotechnics	8
Hazard Analysis for the Manufacture of a UN Gas Generant	11
Techniques for the Quantitative Analysis of Sulfur and Chlorate in Fireworks Compositions	25
A Survey of Concussion Powders	33
The Nitrous Oxide Hybrid Rocket Motor	47
Correspondence: Comments on "Flash Powder Output Testing: Weak Confinement" from Issue No. 4	60

Issue No. 6, Winter 1997:

Thermal Hazards from the Accidental Ignition of Pyrotechnic Compositions	1
Methods for Calculation of Thrust Coefficients	9
Pyrotechnic Ignition and Propagation: A Review	17
Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 1. Introduction	30
Hydrazinium Nitroformate: A High Performance Next Generation Oxidizer	36
A Thermodynamic Properties Estimation Method for Isocyanates	43
A Severe Human ESD Model for Safety and High Reliability System Qualification Testing	57
Correspondence: Consideration of Alternate Whistle Fuels	65
Frequency Stabilization of Large Diameter Strobe Flares	68
Estimating the Distribution of Molecular Energies	70
Further Comment on "Flash Powder Output Testing"	70
Comment on "Model Rocket Engines, Theory and Design"	71
Review of Lecture Notes for Pyrotechnic Chemistry	71
Review of Introductory Practical Pyrotechnics	72

KEYWORD INDEX

The following list of keywords refers to articles that have appeared in Issues 1–7 of the *Journal of Pyrotechnics*. The bold number refers to the issue where the article appears; the unbold number after the dash refers to the page within the Issue, for example “fireworks display 3-22” means Issue 3, page 22. We hope that you find this useful.

- | | | |
|---|--|---|
| accidents 6-30 | formulating 7-15, 7-74 | propagation model 6-17 |
| accidental ignition 6-1, 2-22 | frequency stabilization 6-68 | propellant |
| activation energy 1-19, 6-17 | friction sensitiveness 7-51, 7-59 | evaluation 1-11, 7-59 |
| aerial shell | fuel 3-1, 7-15 | thermodynamics 1-11 |
| detonation 2-6 | fuel-air salutes 4-25 | pyrotechnics 3-14, 5-8, 6-1, 6-71 |
| diameter 1-1 | gas generant 4-15, 5-11 | pyrotechnic whistles 4-37 |
| drift 3-30 | glitter | qualitative analysis 5-25 |
| height 1-1 | delay 7-68 | reactivity 6-30 |
| mass 1-1 | flash size 7-68 | recoil force 1-26 |
| perceived size 3-22 | grain geometry 3-35 | reduction 2-15 |
| shape 3-30 | hazard | reductive element 3-1 |
| air bag 4-15, 5-11 | analysis 5-11 | risk profile 5-11 |
| aluminum oxide 5-8 | evaluation 4-15 | rocket |
| ammonium perchlorate 3-35 | sensitiveness 7-65 | propellant 1-11, 4-47, 6-36, |
| atomic theory 1-19 | hazardous chemical combinations ... 2-22 | 7-33, 7-59 |
| Benson group 6-43 | health effects 3-14, 7-73 | propulsion theory 5-1, 6-9, 6-71 |
| binder 7-59 | heat | safety 3-14, 4-25, 6-30 |
| Black Powder 5-1, 7-76 | capacity 1-37 | salute 4-5, 4-25 |
| blast | of reaction 1-19, 1-37, 6-17 | scanning electron microscope 4-1 |
| pressure 1-26, 4-5, 4-25 | high | SCB 2-1 |
| wave 5-33, 5-60 | nitrogen compositions 7-11 | semiconductor bridge igniter 2-1 |
| bullet impact sensitivity 2-36 | power rocketry 5-47 | sensitiveness 7-51, 7-65 |
| burn injury 6-1 | speed photography 4-37 | sensitivity 7-65 |
| burst size 3-22 | HNF 6-36 | silica 5-8 |
| carbon black 5-8 | HTPB 3-35 | smoke 3-14 |
| chain fusing 2-6 | human ESD model 6-57 | low 7-11 |
| chamber pressure 3-35, 5-1, 6-9, 6-47 | hybrid rocket motor 5-47 | sound pressure level 4-5, 5-33 |
| chemical | hydrazinium nitroformate 6-36 | specific |
| bonds 2-15 | hydroxyl-terminated polybutadiene.. 3-35 | heat ratio 6-9, 6-47 |
| energetics 1-19 | ICBM 7-26 | impulse 3-35, 5-1, 6-47 |
| equations 1-19 | ignition | spectator viewing distance 3-22 |
| equilibrium 1-11 | accidental 2-22 | spectroscopy 7-37 |
| formulas 1-19 | spontaneous 2-22, 6-17 | spontaneous ignition 2-22, 6-17 |
| nomenclature 1-19 | temperature 6-17, 7-51, 7-59 | stoichiometry 1-19 |
| chemistry 1-19, 2-15, 6-71, 7-15 | theory 6-17 | strobe |
| chlorates 5-25, 6-30, 7-51 | igniter (SCB) 2-1 | flare 6-68 |
| colored flame 2-15 | impact sensitiveness 7-59 | model 4-1 |
| spectra 7-37 | incompatibility, chemical 2-22 | star 4-1 |
| composite propellant 3-35, 6-36, 7-33 | internal pressure 1-26 | sulfur 5-25, 6-30 |
| concussion | isocyanate 6-43 | acidity 7-51 |
| mortar 1-26 | lift | /chlorate admixture 5-25, 7-51 |
| powder 1-26, 5-33 | charge 1-1 | test methods 4-15 |
| cook-off 6-17 | mass 1-1 | ESD 3-1 |
| delay, glitter 7-68 | loudness 4-5, 5-33 | spectroscopy 7-37 |
| dense pack 2-6 | low smoke 7-11 | theater 3-14 |
| detonability testing 2-36 | matrix rack 2-6 | thermal |
| dihydrazino-tetrazine 7-11 | meteor, artificial 7-26 | energy distribution 6-70 |
| diisocyanate 6-43 | microscopy (SEM) 4-1 | hazard 6-1 |
| dust explosions 4-25 | missile, ballistic 7-26 | radiation 6-1 |
| electric spark sensitiveness 3-1 | model rocketry 5-1 | run-away 6-17 |
| electrons 2-15 | monopropellant 6-36 | stability 7-51 |
| electrostatic discharge 6-57 | mortar | thermodynamics 1-11, 1-37 |
| entertainment | length 3-30 | computer codes 7-74 |
| pyrotechnics 1-26, 3-14, 5-33 | placement 3-22 | thrust 6-9 |
| enthalpy of formation 6-43 | pressure 5-33 | coefficient 6-9 |
| epoxy 7-33 | seamed 1-1 | measurement 7-33 |
| expansion ratio 6-9 | steel 1-1 | toxicity 3-14 |
| finale rack 2-6 | NFPA 3-22 | urazole 4-15, 5-11 |
| fireworks 4-25, 5-25, 6-30 | nitrogen, high 7-11 | urethane 6-43 |
| display 3-22 | nitrous oxide 5-47 | vacuum thrust coefficient 6-9 |
| mortar 1-6 | nozzle expansion ratio 3-35 | video spectrometer 7-37 |
| flame color temperature | overpressure 1-26, 2-6 | weak confinement 4-5 |
| 1-37, 6-26, 7-37 | oxidation 2-15 | whistle |
| flash powder 1-26, 2-36, 4-5, | oxidizer 3-1, 6-36, 7-15 | frequency 4-37 |
| 5-33, 5-60, 6-71 | oxygen exchange 7-15 | fuel 6-65, 7-59 |
| flow | PEP 1-11 | intensity 4-37 |
| ability 5-8 | periodic table 2-15 | music 7-1 |
| agents 5-8 | phthalates 6-65 | |
| fog study 7-73 | positive phase 4-5, 5-33 | |