

Journal of Pyrotechnics

Issue 10, Winter 1999

Policy Board Members:

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

Gerald Laib, Code 950X
Naval Surface Warfare Center
Indian Head Div.
101 Strauss Avenue
Indian Head, MD 20640-5035 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

Copy Editor:

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

Technical Editors for this issue:

Per Alenfelt, Hansson Pyrotech AB
Billdal, Sweden

Scot Anderson
Conifer, CO, USA

Ed Brown
Rockvale, CO, USA

Ettore Contestabile
Canadian Explosive Research Lab

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

Arno Hahma, Dept. of Chemistry
Univ. Turku, Turku, Finland

Will Meyerriecks
Tampa, FL, USA

Barry Sturman
Victoria, Australia

Rutger Webb, TNO-PML
Rijswijk, The Netherlands

Larry Weinman
Huntsville, AL, USA

Marc Williams, Night Musick
Aurora, CO, 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 10 Winter 1999

Burst Process of Spherical Aerial Shells Y. Takishita, H. Shibamoto, T. Matsuzaki, K. Chida, F. Hosoya, and N. Kubota ...	1
Six Methods for Estimating the Formation Enthalpy of Organic Compounds Will Meyerriecks	7
High-Nitrogen Fuels for Low-Smoke Pyrotechnics David E. Chavez, Michael A. Hiskey and Darren L. Naud	17
Measurement of the Effectiveness of Various Mitigation Methods at Reducing the Projectile Hazards from Fragmenting Steel Firework Mortar Tubes S. G. Myatt and M. R. Edwards	37
Combustion of Ti/C Pyrolants Michinori Takizuka, Toshio Onda, Takuo Kuwahara, and Naminosuke Kubota	45
Effect of Differing Charcoal Types Upon Handmade Lift Powder Charles Wilson	49
Communications:	
Peak In-Mortar Aerial Shell Accelerations by K. L. and B. J. Kosanke	56
Letter to the Editor from N. Kahn about "Fog" review article in Issue 7, with reply from M. Rossol, author of review article	60
Review by B. Sturman of R. Lancaster's book <i>Fireworks Principles and Practice</i>	61
Review by L. Weinman of P.W. Cooper's book <i>Explosives Engineering</i>	64
Review by B. Sturman of T. Shimizu's English translation of <i>Selected Pyrotechnic Publications of Dr. Takeo Shimizu, Part 3: Studies on Fireworks Colored-Flame Compositions</i>	65
Review by J. Bergman of the Confederation of British Industry's <i>Hearing Protection A Guide for Those Who Manufacture, Test, or Use Explosives</i>	68
Review by K. Kosanke of J. Akhavan's <i>The Chemistry of Explosives</i>	69
Review by B. Sturman of J. Akhavan's <i>The Chemistry of Explosives</i>	71
Errata	16, 55
Events Calendar	73
Sponsors	75
Author Instructions	78

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.

Burst Process of Spherical Aerial Shells

Y. Takishita, H. Shibamoto, T. Matsuzaki, K. Chida, F. Hosoya, and N. Kubota*

Hosoya Kako Co., Ltd., 1847 Sugao, Akiruno, Tokyo 197-0801, Japan

* Mitsubishi Electric Corporation, Kamimachiya 325, Kamakura 247-8520, Japan

ABSTRACT

The burst process of spherical fireworks shells has been examined experimentally and presented as a simplified physical model. The pressure in a shell was measured with a strain-type pressure transducer, which was inserted into the center of the shell. After the ignition of the bursting powder, pressure increased exponentially and the pressure also decreased exponentially, when the shell burst. The analysis of the pressure-versus-time curve indicated that the acting force on the stars in the shell was found to be dependent on various physical parameters: 1) the shape and material of the shell, 2) the characteristics of the bursting charge, and 3) the stars in the shell. The bursting process proposed in this study was confirmed by the observed ejection process of the stars in a Japanese-style, "warimono"* spherical shaped shell.

*A spherical shaped shell containing stars and bursting charge that produces a chrysanthemum-flower shaped display in sky. ^[1]

Keywords: spherical aerial shell, burst process, pressure impulse, star acceleration

Introduction

The Japanese-style shells are known to be completely spherical in shape,^[1] ranging from 70 to 900 mm in diameter as shown in Figure 1. A typical example of the biggest shell, 900 mm in diameter, is also shown in Figure 2. The shell is made of a relatively thick paper that consists of several pasted layers. The thickness of the shell wall is dependent both on the spherical size of the shell and the mass of the bursting charge. In general, the thickness of the shell wall increases as the size of the shell increases and as



Figure 1. Examples of typical Japanese-style spherical shells.



Figure 2. One of the biggest spherical shells in Japan.

the mass of the bursting charge increases. Figure 3 shows a cut-away model of a typical Japanese-style spherical warimono. A number of stars are set inside of the shell wall and held in

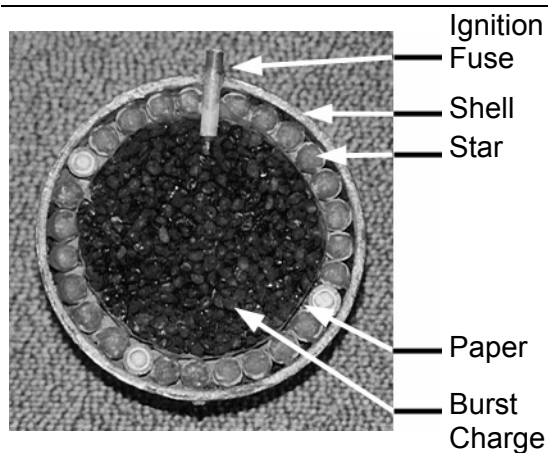


Figure 3. A typical cut-away model of a warimono (Japanese-style spherical display shell).

place with a spherical sheet of paper. A bursting charge is stuffed inside of the spherical sheet of paper. The ignition fuse is inserted into the center of the shell from the outside of the shell wall.

The design of the warimono shells is based on the long-term experience and skill of the technicians. Theoretical analysis and experimental

data related to shell design have not been previously reported. In this study, experimental measurements on the process of bursting shells have been conducted to evaluate the force acting on the stars and the initial velocity of the stars ejected from the bursting shell.

Experimental

To measure the force acting on the stars, which are placed inside of the spherical shell, the internal pressure generated by ignition of the bursting charge was measured using a pressure transducer. A warimono shell containing no stars was used as shown in Figure 4. The pressure was measured using a small stainless tube that was placed at the center of the shell. The tube was 8 mm in diameter, and the pressure transducer was mounted on the stainless tube outside the casing. The pressure measurement setup is shown in Figure 5. The time response of the transducer was approximately 4 μ s. That was considered short enough to measure the burning process of the bursting charge and the pressure decay process of the shell burst.

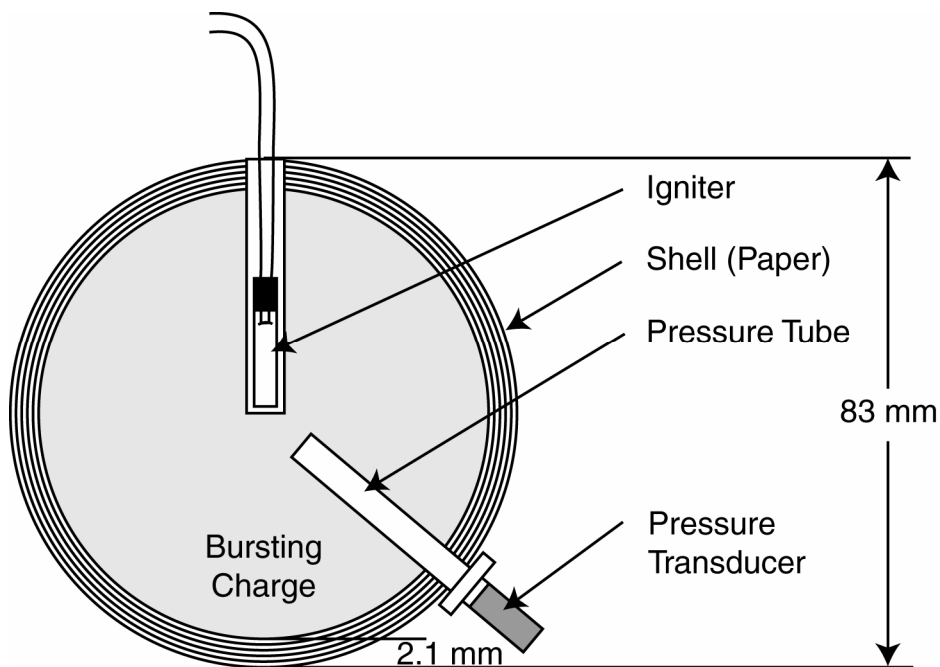


Figure 4. The warimono used for the measurements of pressure and shell fragments.

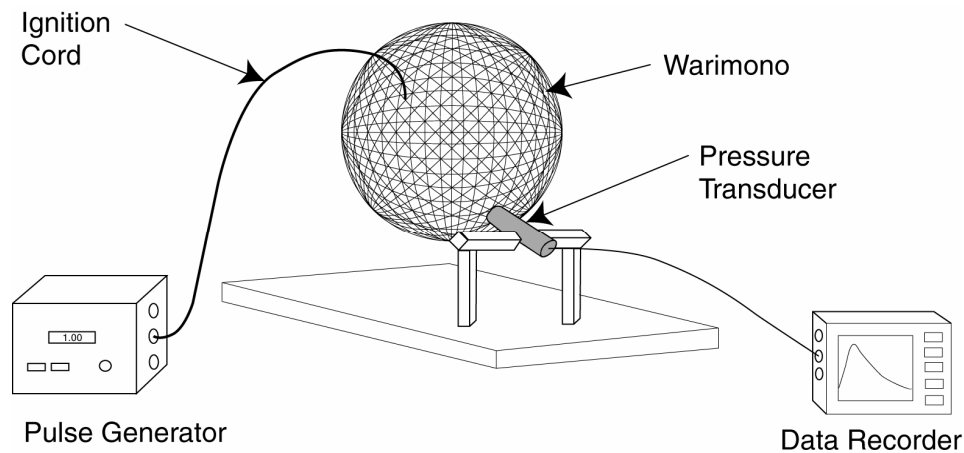


Figure 5. The experimental setup used for the measurements of pressure and shell fragments.

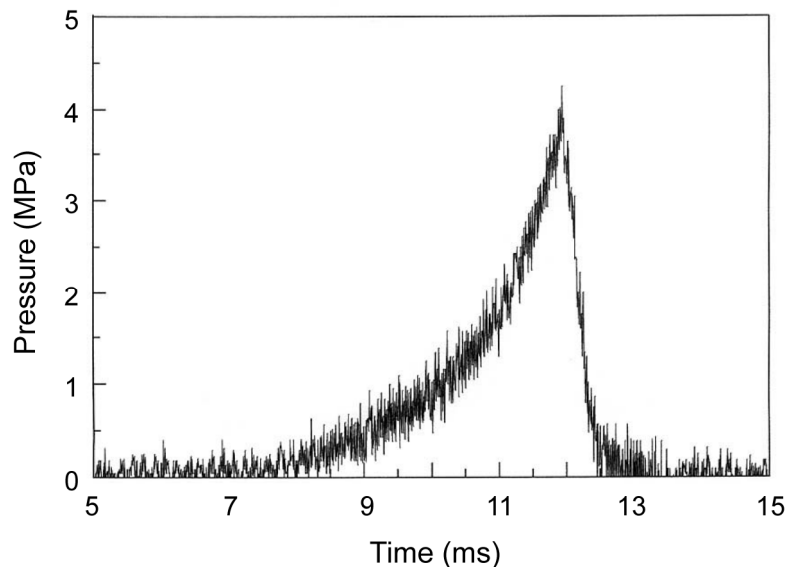


Figure 6. A typical pressure-versus-time curve during the process of a bursting warimono shell.

The bursting charge used was 100 g of potassium nitrate-based powder. The charge was ignited electrically through an ignition charge (0.3 g) of B/KNO₃ powder. The ignition signal and pressure were recorded by a DL708 Digital Scope. The chemical composition of the bursting charge is shown in Table 1.

Table 1. Chemical Composition of the Bursting Charge Used in this study.

Chemical Composition	% (mass)
Potassium nitrate	70
Sulfur	9
Hemp charcoal	14
Cooked rice powder	4
Chaff	3

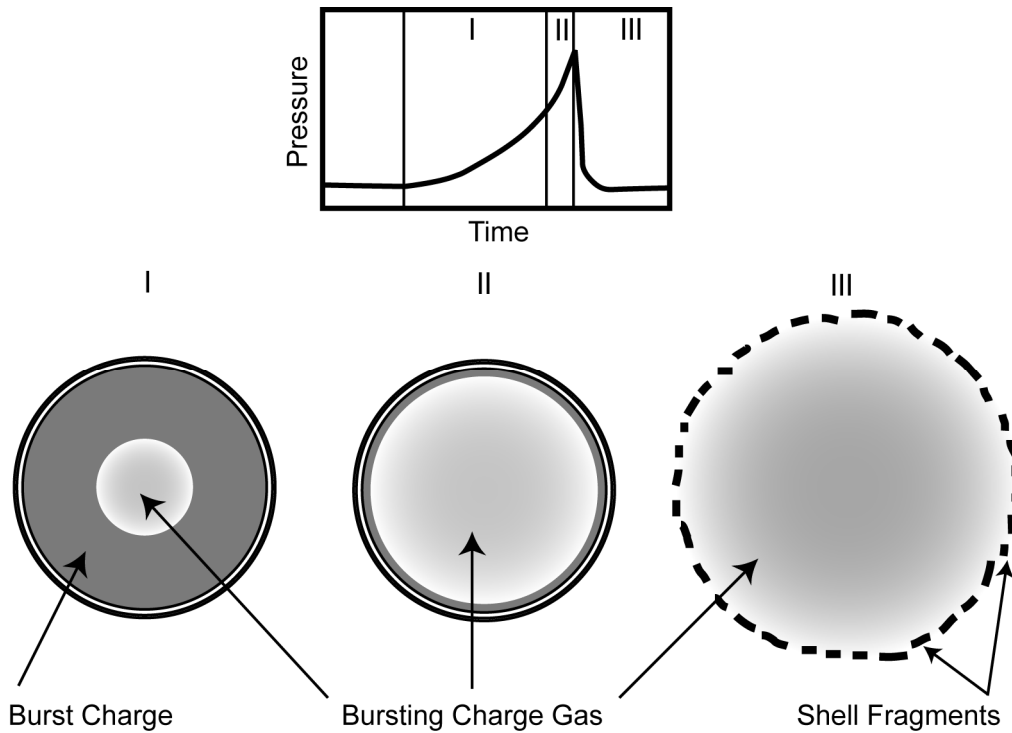


Figure 7. The bursting model of a warimono shell proposed in this study.

Results and Discussion

Figure 6 shows a typical example of the pressure-versus-time curve. No pressure rise was seen until 7 ms after the ignition signal. The pressure started to increase relatively smoothly at 10 ms then increased rapidly and reached its maximum of 4.4 MPa at 11.9 ms. The pressure decreased rapidly after reaching the maximum

and returned to the initial atmospheric pressure within 0.5 ms.

The combustion gas generated in the shell, due to the rapid burning of the bursting charge, raises the pressure in the shell. Since the initial pressure wave, generated at the center of the shell, propagates at the speed of sound of the burned gas (approximately 600 m/s), it passes before the pressure rises uniformly in the shell

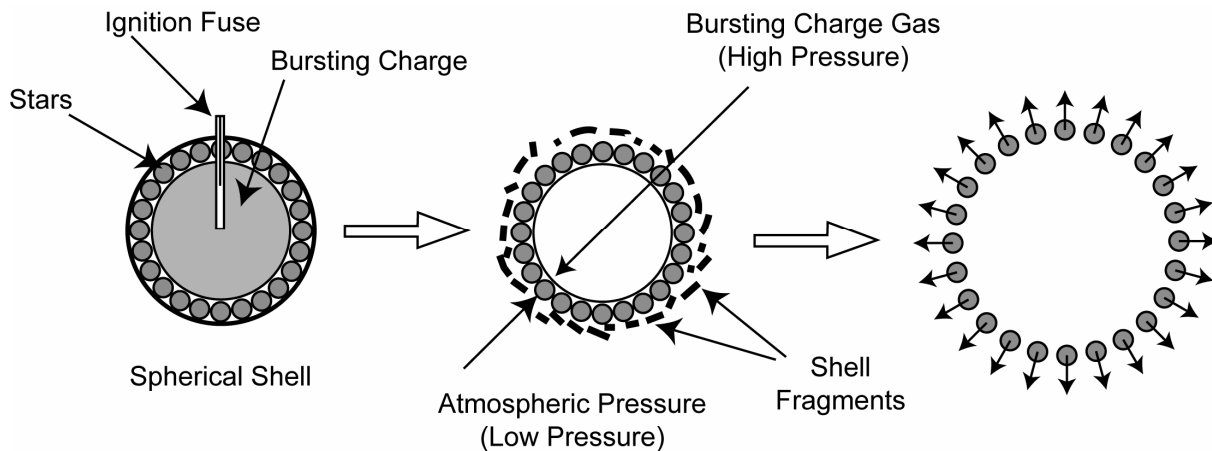


Figure 8. The ejection process of stars from a burst shell.

during the burning of the bursting charge. The pressure reaches its maximum when the shell bursts. The pressure is released, and the burned gas is ejected radially (i.e., to the atmosphere). This process is illustrated in Figure 7. No significant change in the shape of the shell is seen in Zones I and II during pressure build up. A large number of tiny fragments of the burst shell casing are created in Zone III, which are also ejected radially, and the pressure in the shell rapidly decreases. This process is illustrated in Figure 8. Figure 9 is a photograph of typical fragments of a burst shell. The tiny fragments are the result of the brittle fracture nature of the paper shell casing.

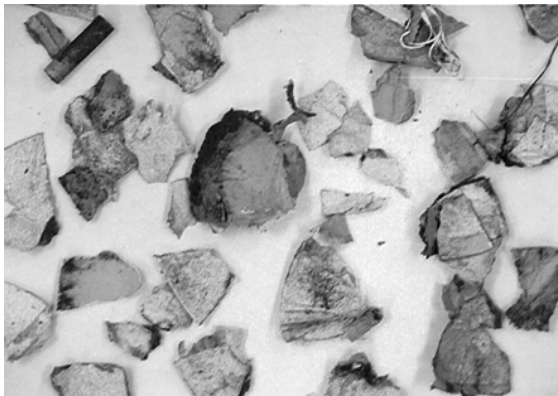


Figure 9. A photograph of the typical fragments of a burst shell.

Since the pressure difference between the gas generated by the burning bursting charge and

the atmosphere is large where the shell bursts, a pressure difference is created between the inner surface and the outer surface of each star.

It is evident that the pressure difference generated at the shell surface acts to force the stars outward in a radial direction when the shell bursts. If one assumes that the pressure difference between the inner surface and the outer surface of a star in the shell is p_s , and the surface area of the shell is a_s , the acting force on the star, F_s (illustrated in Figure 10), is given by

$$F_s = \int p_s da_s \quad (1)$$

The impulse acting on the star caused by the pressure difference, I_s , is given by

$$I_s = \int F_s dt \quad (2)$$

Substituting equation 1 into equation 2, one gets

$$I_s = \iint p_s da_s dt \quad (3)$$

Since the pressure acting on the star surface is dependent on the pressure decay process when the shell is burst, the force acting on the star is also dependent on the pressure decay process. It is also assumed that the pressure created in the shell acts on the inner-hemisphere of the shell and the atmospheric pressure acts on the outer-hemisphere of the shell. The effective pressure surface area of the star A_s is given by

$$A_s = \frac{1}{4}\pi d_s^2 \quad (4)$$

where d_s is the diameter of the star. Thus, the impulse is given by

$$I_s = (\frac{1}{4}\pi d_s^2) \int p_s dt \quad (5)$$

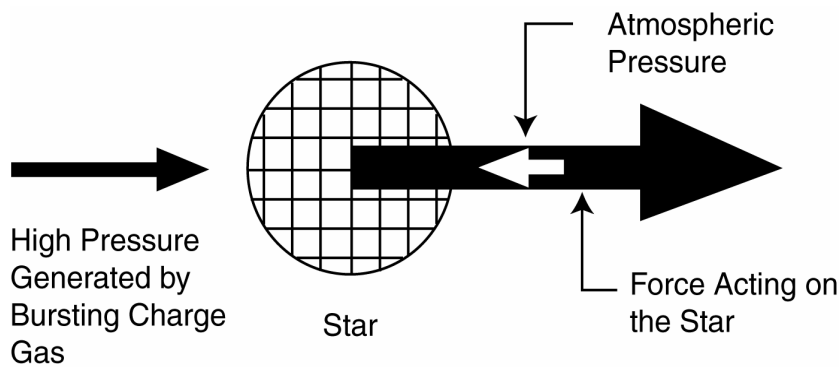


Figure 10. The impulse acting on a star surface due to the high pressure generated by the bursting charge.

This impulse is converted to the momentum change of the star as

$$I_s = m_s v_s \quad (6)$$

where m_s is the mass of the star and v_s is the initial velocity of star toward the outward radial direction. Using equations 5 and 6, v_s is represented by

$$v_s = \left(\frac{1/4\pi d_s^2}{m_s} \right) \int p_s dt \quad (7)$$

Since the real star ejection velocity v_s is considered to be reduced by aerodynamic and mechanical losses caused by gas movement and shell fragment formation process, the pressure efficiency η_b is defined as

$$v_s = \eta_b \left(\frac{1/4\pi d_s^2}{m_s} \right) \int p_s dt \quad (8)$$

The ejection model indicates that the pressure decay process occurring at the shell burst is an important parameter for the determination of the star ejection velocity.

In order to evaluate the validity of the star ejection model represented by equation 8, a model calculation was done at the following condition:

$$d_s = 11 \text{ mm}$$

$$m_s = 1.0 \times 10^{-3} \text{ kg}$$

Using the pressure curve $p_s(t)$ shown in Figure 6, the ejection velocity was determined to be $v_s = 95 \text{ m/s}$ in case of $\eta_b = 1.0$.

The experimental results obtained by photographic observation^[2] showed that the star ejection velocity ranged from 34 to 95 m/s. Using

equation 8 and the observed results, the pressure efficiency was determined to be $\eta_b = 0.36$ to 1.0. Though the experimental values are scattered in the data and the star ejection model is a simplified one, the ejection process of stars from spherical aerial shells can be understood.

Conclusions

The experiments conducted in this study revealed the ejection process of the stars in a spherical shell. The shell wall is burst by the pressure created by the burning of the bursting charge. The pressure difference between the inner-side and the outer-side surfaces of each star in the shell is converted to the impulse given to each star. The impulse gives the ejection velocity of each star toward the outward radial direction.

It is important to note that a large number of fragments are created when the shell wall is made of paper. This indicates that the spherical shell bursts uniformly along the shell surface, and the impulse acts on each star in a radial direction. The ejection velocity of each star is dependent on the maximum burst pressure created by the bursting charge and the inner spherical diameter, and the mass of each star.

References

- 1) M. Hosoya and F. Hosoya, *Science of Fireworks*, Tokai University Press, 1999.
- 2) T. Shimizu, "Conditions for Designing Japanese Fire-Display-Shells of Chrysanthemum Type", *Kogyo Kayaku Kyokaisi*, Vol. 18, No. 3, 1956.

Six Methods for Estimating the Formation Enthalpy of Organic Compounds

Will Meyerriecks

702 Leisure Avenue, Tampa, FL 33613-1835, USA

ABSTRACT

Finding published enthalpy of formation values for organic compounds is not always possible. Six methods are outlined for estimating this property, each utilizing different data that is generally readily available in one form or another. Additionally, a dozen different references for published thermodynamic data are provided.

Keywords: enthalpy of formation, heat of combustion, higher heating value, HHV, Benson group, flame temperature, free energy minimization

Introduction

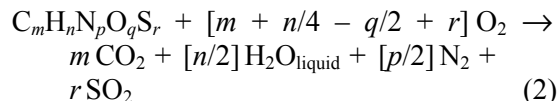
The *enthalpy of formation* ($\Delta_f H^\circ$) represents the energy required to form a molecule from its constituent elements in their standard states.^[1] It is required as part of the input data set for *free energy minimization* programs such as *PEP*^[2,3] or *CEA400*.^[4] Tabulated values may be found for various organic and inorganic compounds in a number of handbooks. The required value for a pure compound or complex mixture is sometimes not available. The different methods outlined in this article demonstrate ways of estimating the required value from information that is generally readily available, though sometimes from disparate or seemingly unrelated sources. All thermodynamic quantities are at standard conditions of 298.15 K and 1 bar pressure. All estimates of the $\Delta_f H^\circ$ in the following examples are for the solid phase.

Heat of Combustion

The *heat of combustion* ($\Delta_c H^\circ$) of a substance represents the heat evolved when that substance is completely converted to standard oxidation products by reaction with molecular oxygen.^[5] Equation 1 equates the $\Delta_c H^\circ$ to the sum of the $\Delta_f H^\circ$ of the products minus the sum of the $\Delta_f H^\circ$ of the reactants.^[1]

$$\Delta_c H^\circ = \sum \Delta_f H^\circ \text{ products} - \sum \Delta_f H^\circ \text{ reactants} \quad (1)$$

Equation 2 represents the ideal combustion of an organic compound composed of the elements C, H, N, O, and S:



The standard $\Delta_f H^\circ$ of the products, in kJ/mole, are found in Table 1.

Table 1. Standard Heats of Formation of Combustion Products at 298.15 K and 1 Bar.^[6]

Combustion Product	$\Delta_f H^\circ$ (kJ/mole)
CO ₂	-393.522
H ₂ O _(liquid)	-285.830
H ₂ O _(gas)	-241.826
O ₂	0.0
N ₂	0.0
SO ₂	-296.842

Tabulated values of the $\Delta_c H^\circ$ are sometimes found where the $\Delta_f H^\circ$ is not. To convert from

Example 1: The combustion enthalpy of *stearic acid*, $C_{18}H_{36}O_2$ (57-11-4), is -11280.4 kJ/mol.^[7]

$C_{18}H_{36}O_2$, $m = 18$, $n = 36$, $p = 0$ (no nitrogen present), $q = 2$, $r = 0$ (no sulfur present)

$\Delta_c H$	=	$\Sigma \Delta_f H^\circ$ (products)	-	$\Sigma \Delta_f H^\circ$ (reactants)
-11280.4	=	$m \Delta_f H^\circ CO_2 + [n/2] \Delta_f H^\circ H_2O_{liquid}$	-	$\Delta_f H^\circ C_{18}H_{36}O_2 + [m + n/4 - q/2 + r] \Delta_f H^\circ O_2$
-11280.4	=	$18 \Delta_f H^\circ CO_2 + [36/2] \Delta_f H^\circ H_2O_{liquid}$	-	$\Delta_f H^\circ C_{18}H_{36}O_2 + [18 + 36/4 - 2/2] \Delta_f H^\circ O_2$
-11280.4	=	$18 \Delta_f H^\circ CO_2 + 18 \Delta_f H^\circ H_2O_{liquid}$	-	$\Delta_f H^\circ C_{18}H_{36}O_2 + 26 \Delta_f H^\circ O_2$
-11280.4	=	$18 (-393.522) + 18 (-285.830)$	-	$\Delta_f H^\circ C_{18}H_{36}O_2 + 26(0.0)$
-11280.4	=	$-7083.40 + -5144.94$	-	$\Delta_f H^\circ C_{18}H_{36}O_2$

$C_{18}H_{36}O_2$, -947.94 kJ/mole

This compares favorably to a reference value^[7] of -947.7 kJ/mol.

one to the other, simply solve for the unknown in equation 1 using equation 2. See Example 1.

Note: because O_2 and N_2 are already *elements in their standard states*, their reference $\Delta_f H^\circ$ is 0.0 and thus can be ignored* in these computations. Generally, other elements present in many reactants, such as chlorine, are in trace quantities and do not influence the estimate significantly. If a reactant is considered that does include additional elements in non-trivial quantities, they would be handled in the same manner as described in example 1 for the CHONS system.

Higher Heating Value

Higher heating value, sometimes abbreviated *HHV*, or referred to as *caloric value*^[8] or *calorific value*,^[9] is actually the enthalpy of combustion in disguise; the sign is merely reversed by convention. It is usually used for complex or poorly characterized fuels such as coal and wood. The calculations made are the same as those described in example 1 for the $\Delta_c H^\circ$. The *lower heating value* is calculated in the same fashion as the higher heating value except that H_2O is in a *gaseous* rather than *liquid* form. It is usually preferable to convert the data from mass-based to formula-based so that the calculation of the product coefficients is simplified, and because many free energy minimization programs use formula-based data as input. This conversion requires the atomic weights of the elements involved. See example 2.

An equation^[10] that is sometimes used in estimating the HHV of biomass materials is:

$$HHV \text{ in MJ/Kg} = 0.63 + 0.39C \quad (3)$$

where C is the whole-number percentage of carbon. This equation was fit to 74 different fuels, and resulted in an r^2 (quality of fit) value of 0.894. It is valid for many biomass fuels that have low concentrations of waxes and oils. The effective range of carbon for this equation is between 33 and 55 percent.

* An additional correction may be made to account for the *change* in moles of *gaseous* species if the heat flow measurement were made in a constant-volume device such as a bomb calorimeter. It is not covered in this article due to this contribution typically only accounting for a correction of less than 0.5%.^[11]

Example 2: A charcoal manufactured from sawdust and pine bark, pyrolyzed at 400 °C, was shown to have a HHV of 12094 BTU/lb and an ultimate analysis of^[11] C 75.3%, H 3.8%, O 15.2%, N 0.8%, S 0.0%, and Ash 3.4%.

First, convert from BTU/lb to kJ/kg and HHV to $\Delta_c H$ (reverse sign):

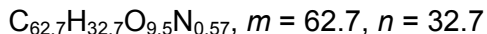
$$-28131 \text{ kJ/kg} = 12094 \text{ BTU/lb} \times 2.326 \times -1$$

Next, convert percent mass to moles per kilogram:

Element	% mass	g	Atomic ^[7] Weight (g/mol)	mol/kg
C	75.3	753	12.011	62.7
H	3.8	38	1.00794	37.7
O	15.2	152	15.9994	9.50
N	0.8	8	14.00674	0.57
S	0.0	0	32.066	0
Ash	3.4	34	NA	NA

Because the original form and composition of the elements that comprise the ash portion are unknown, it is assumed that it makes no significant contribution to the $\Delta_f H^\circ$. The resulting formula is $C_{62.7}H_{32.7}O_{9.5}N_{0.57}$. Since the molecular weight of this compound is 1 kg/mole, the $\Delta_c H$ of -28131 kJ/kg is also -28131 kJ/mole .

Using equations 1 and 2, solve for the reactant $\Delta_f H^\circ$:



$\Delta_c H$	=	$\Sigma \Delta_f H^\circ$ (products)	-	$\Sigma \Delta_f H^\circ$ (reactants)
-28131	=	$62.7 \Delta_f H^\circ \text{ CO}_2 + [32.7/2] \Delta_f H^\circ \text{ H}_2\text{O}_{\text{liquid}}$	-	$\Delta_f H^\circ C_{62.7}H_{32.7}O_{9.5}N_{0.57}$
-28131	=	$62.7(-393.522) + 16.35(-285.830)$	-	$\Delta_f H^\circ C_{62.7}H_{32.7}O_{9.5}N_{0.57}$
-28131	=	$-24674 + -4673$	-	$\Delta_f H^\circ C_{62.7}H_{32.7}O_{9.5}N_{0.57}$

$\Delta_f H^\circ$ for $C_{62.7}H_{32.7}O_{9.5}N_{0.57}$ is -1216 kJ/mol .

Benson Group Additivity

When the exact chemical structure of the compound is known, and it is composed of any of the elements *CHONS* or *halogens*, then a simple algorithm may be used to estimate the $\Delta_f H^\circ$ of the compound: the *Benson Group Additivity* method. Most “fragmentation” methods are limited to gas phase estimates. The method of Benson is an exception. It was extended to the liquid and solid phases by Domalski and Hearing,^[12] and is available in a software implementation.^[13] This method also estimates the heat capacity, entropy, entropy of formation,

Gibbs energy of formation, and the natural logarithm of the equilibrium constant for the formation reaction.^[12,13] This database was created from the analysis of 1512 different organic compounds.^[13]

First, the molecule is “broken down” into groups. A group generally defines the unique combination of the non-hydrogen atom of interest and the atoms that are immediately bonded to it. A few of the groups, such as the carboxyl that is present in carboxylic acids, are composed of two non-hydrogen atoms (carbon and oxygen in this case) instead of one. Next, after these groups have been identified, additional

correction groups are identified where applicable. These corrections account for such things as next-to-nearest-neighbor ring substitution interactions, ring strain corrections, etc. Lastly, the thermodynamic values assigned to each of

the selected groups are added, and the sum is the estimation of the properties for the molecule. The results are surprisingly accurate despite the simplicity of the method.

**Example 3: Estimate the $\Delta_f H^\circ$ of *cinnamic acid*
C₉H₈O₂ (621-82-9).**

In Figure 1, each group has been numbered to facilitate their identification. What is not shown, which is typical of molecular renderings, are the hydrogen atoms bonded to the carbon atoms. This method uses its own, simple nomenclature to describe the component groups. Figure 1 shows that atoms 2 through 6 are fundamentally the same: a benzene ring carbon bonded to two benzene ring carbons and a hydrogen atom (that is not shown). In Benson notation, this is C_B-(C_B)₂(H). Table 2 lists the component groups, including the $\Delta_f H^\circ$ values from reference 13.

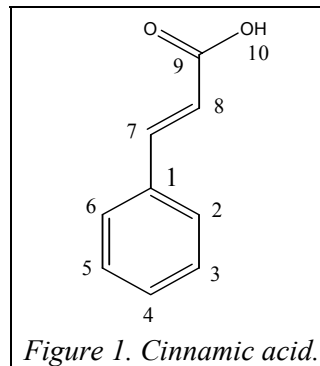


Table 2. Benson Groups and $\Delta_f H^\circ$ Values^[13] for Cinnamic Acid.

Group	Group Code	Qty.	Group $\Delta_f H^\circ$ (kJ/mol)	Total $\Delta_f H^\circ$ (kJ/mol)
1	C _B -(C _B) ₂ (C _D)	1	20.27	20.27
2-6	C _B -(C _B) ₂ (H)	5	6.53	32.65
7	C _D -(C _B)(H)	1	17.53	17.53
8	C _D -(CO)(H)	1	7.82	7.82
9	CO-(C _D)(O)	1	-134.10	-134.10
10	O-(H)(CO)	1	-282.15	-282.15
Total:				-337.98

This compares extremely well to a reference^[14] value of -337.23 kJ/mol.

Partial Benson Groups

Sometimes it is not convenient to “build from scratch” an entire molecule using Benson Groups. This may be due to the number of groups required to model the molecule, or, more likely, data for a required group does not exist and would render the estimate incomplete. It is certainly possible to create new groups—see reference 15 for how isocyanate groups were

evaluated. For “one-shot” estimates this may be more work than is necessary. A shortcut is to use what the author coined as a *Partial Benson Group* approach. This method relies on having the $\Delta_f H^\circ$ value for a molecule that is very similar in structure to the molecule with the unknown value. Subtracted from this “known” molecule are the groups and their respective $\Delta_f H^\circ$ values that do not belong, and then the ones required for the “unknown” molecule are added in yielding the estimate. See example 4.

Example 4: Estimate the $\Delta_f H^\circ$ of *cinnamic acid*, $C_9H_8O_2$ (621-82-9) using Partial Benson Groups. See Figure 1.

p-coumaric acid (Figure 2), $C_9H_8O_3$ (7400-08-0) $\Delta_f H^\circ$ -529.69 kJ/mol,^[16] is very similar in structure to cinnamic acid (see Figure 1). The only difference is the hydroxyl group at the “bottom” of the benzene ring. The group that is needed is $C_B-(C_B)_2(H)$, but instead there are two groups at that location: $C_B-(C_B)_2(O)$ and $O-(C_B)(H)$. By subtracting the two that are not needed, and adding the one required, the Partial Benson Group estimate is made. See Table 3.

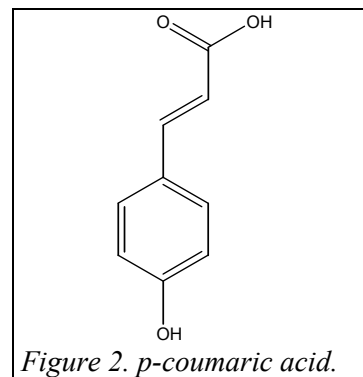


Table 3. Partial Benson Groups Estimation Method: Groups and $\Delta_f H^\circ$ Values.^[13]

Add/Subtract	Group Code	Qty.	Group $\Delta_f H^\circ$ (kJ/mol)	Total $\Delta_f H^\circ$ (kJ/mol)
<i>p</i> -coumaric acid $\Delta_f H^\circ$:		1	NA	-529.69
Add	$C_B-(C_B)_2(H)$	1	6.53	6.53
Subtract	$C_B-(C_B)_2(O)$	-1	1.00	-1.00
Subtract	$O-(C_B)(H)$	-1	-199.25	199.25
Total				-324.91

This compares favorably to a reference^[14] value of -337.23 kJ/mol.

Flame Temperatures

If the chemical formula of a compound is known (or calculated from an elemental analysis), but the structure is unknown, then using Benson Groups is ruled out. However, if a known pyrotechnic formulation using the compound has a measured flame temperature, then the $\Delta_f H^\circ$ may be “reverse-engineered” using a free energy minimization code. This assumes that

- The measured flame temperature is accurate.
- Chemical reactions proceed instantly (chemical kinetics are ignored).
- Combustion is complete at the temperature measurement location and does not include artifacts such as air entrainment cooling or afterburning that might alter the measured flame temperature and composition.
- The free energy minimization code can accurately model the product composition at the specified temperature and pressure, and includes all species that would realistically

be expected to be present in significant quantities.

- Gas/particle kinetic energy, condensed species velocity-lag, loss of energy by thermal radiation, etc. are all ignored.

In an ideal, adiabatic flame, where no heat is gained or lost, the enthalpy of the products equals that of the reactants.^[9] The free energy minimization code provides output of the combustion products present, their molar quantities, and the sum of their respective enthalpies at the stated conditions of temperature and pressure. Subtracting the sum of the $\Delta_f H^\circ$ of the reactants from the sum of the known $\Delta_f H^\circ$ of the products yields a useful (and optimistic) $\Delta_f H^\circ$ value for the unknown reactant. Due to the assumptions outlined above, this $\Delta_f H^\circ$ may be better regarded as a practical value than as an absolute one. See example 5.

Example 5: Estimate of $\Delta_f H^\circ$ based on flame temperature.

Shimizu^[17] has measured the flame temperatures of many colored flames. *Shellac* (9000-59-3) was used as the fuel/binder. Its formula is $C_6H_{9.6}O_{1.6}$.^[17] Estimate the $\Delta_f H^\circ$ based on the following formulation at a measured temperature of approximately 2475 K.^[17]

Ingredient	Formula	Percent	$\Delta_f H^\circ$ (kJ/mol)
Ammonium perchlorate	NH_4ClO_4	71	-295.3 ^[7]
Shellac	$C_6H_{9.6}O_{1.6}$	14	NA
Strontium carbonate	$SrCO_3$	10	-1220.1 ^[17]
Sodium oxalate	$Na_2C_2O_4$	5	-1317.96 ^[18]

Reviewing the results of the author's free energy minimization code,^[19] see Table 4, the difference in enthalpy between the products and the reactants is -52.30 kJ for 0.1304 moles of shellac. Thus, for this particular run, the $\Delta_f H^\circ$ per mole of shellac is $-52.30 \div 0.1304$, or -401.07 kJ/mole. This same procedure was used to evaluate 15 other data sets, and the overall "reverse-engineered" average was -440 kJ/mole. The tabulated results will appear in "Organic Fuels: Composition and Formation Enthalpy Part II: Resins, Charcoal, Pitch, Gilsonite, and Waxes".^[20]

Table 4. CEQ58 Specified Flame Temperature Run.

Propellant Composition:

Ingredient	Percent	moles	$\Delta_f H^\circ$ (kJ/mol)	Molecular Weight
Ammonium perchlorate	71.00%	0.6043	-295.3000	117.4888
Shellac	14.00%	0.1304	0.0000	107.3413
Strontium carbonate	10.00%	0.0677	-1220.1000	147.6292
Sodium oxalate	5.00%	0.0373	-1317.9600	133.9991

Enthalpy of Reactants ($\Delta_f H^\circ$) = -310.278 kJ/100 g

Element	Mole Fractions
C	11.1092
O	47.6526
H	3.6985
N	8.4645
Cl	21.4245
Na	1.7157
Sr	5.9351

Convergence Tolerance = 1×10^{-6}

Table 4. CEQ58 Specified Flame Temperature Run (continued).

Species with mole fractions ≥ 0.00001 :

Product	Species	Mole %	Mass
Water	H ₂ O	0.42226	26.24791
Carbon Dioxide	CO ₂	0.15795	23.98440
Carbon Monoxide	CO	0.11011	10.64219
Hydrogen Chloride	HCl	0.10763	13.54075
Nitrogen	N ₂	0.08719	8.42716
Hydrogen	H ₂	0.04850	0.33735
Sodium Chloride	NaCl	0.02073	4.17942
Strontium Chloride	SrCl ₂	0.01946	10.64207
Hydroxyl	OH	0.00887	0.52065
Chlorine	Cl	0.00777	0.95088
Hydrogen	H	0.00496	0.01726
Oxygen	O ₂	0.00212	0.23392
Nitrogen Oxide	NO	0.00077	0.07987
Sodium	Na	0.00063	0.04979
Oxygen	O	0.00059	0.03251
Sodium Hydroxide	NaOH	0.00027	0.03727
Strontium Chloride	SrCl	0.00008	0.03348
Strontium Hydroxide	Sr(OH) ₂	0.00008	0.03461
Strontium Hydroxide	SrOH	0.00001	0.00453

Mass fractions: Gas = 100.000 Condensed = 0.000

$\Delta_f H^\circ$ Reactants	=	-310.278	Temperature	=	2475 K
$\Delta_f H^\circ$ Gas	=	-362.583	$\Delta_f H^\circ$	=	-52.3049
Total Mass	=	100 g	Gas Molecular Weight	=	28.982
$\Delta_f H^\circ$ All	=	-362.583	Pressure	=	1.0 Bar
$\Delta_f H^\circ$ Condensed	=	0			

General Equations

If all else fails, and the *only* information available is the formula or composition of the reactant of interest, and it is composed of a subset of the elements CHO and N, then a “one size fits all” approach may be used. The author fitted a 2-dimensional equation for compounds containing only C and H, and 3-dimensional equations for compounds containing CHO, CHN, and CHON, to 1029 published $\Delta_f H^\circ$ (kJ/kg) values.^[14] The resulting equations may be used

to estimate *tentative* $\Delta_f H^\circ$ values if this is the *only* option available. While the CHO equation provides reasonably accurate values, the quality of the fit (r^2 parameter) for the other equations is not as good. Care must be exercised to stay within the boundaries of the input parameters; the equations used are polynomials, which are not well-behaved outside of the ranges specified. Don't divide by zero in equation 6 either! The results of the curve-fits are summarized in Table 5, the equations follow, and their respective parameters are listed in Table 6.

Table 5. Generic Equations, Percent Mass Basis Ranges, and Properties for $\Delta_f H^\circ$ Estimation of CHON Compounds.

Elements	Data Points	Ranges (min above, max below)				r^2	equation
		% C	% H	% O	% N		
CH	141	84.12	4.79			0.713	4
		95.21	15.88				
CHO	337	25.54	1.77	3.99		0.941	5
		89.34	14.14	71.08			
CHN	121	14.12	0.00		4.87	0.701	6
		88.28	12.08		83.31		
CHON	430	7.95	0.00	4.70	5.20	0.672	7
		81.63	13.02	63.99	74.44		

Equations:

$$y = a + bx^2 + cx^4 + dx^6 + ex^8 + fx^{10} \quad (4)$$

$$z = a + bx + cx^2 + dx^3 + ex^4 + fx^5 + gy + hy^2 + iy^3 + jy^4 + ky^5 \quad (5)$$

$$z = a + b/x + c/x^2 + d/x^3 + e/x^4 + f/x^5 + gy + hy^2 + iy^3 + jy^4 + ky^5 \quad (6)$$

$$z = a + bx + cy + dx^2 + ey^2 + fxy + gx^3 + hy^3 + ixy^2 + jx^2y \quad (7)$$

Table 6. Coefficients for Equations 4 through 7.

Coefficient	Equation			
	4	5	6	7
a	-2.5167e+07	3917.458641	21587.57325	-14380.3534
b	15831.82837	-634.043083	-1.9311e+06	5609.81255
c	-3.97590273	-26.7411923	-4.1661e+07	800.7687216
d	0.000498100	1.271410128	3.68535e+09	-670.056188
e	-3.1124e-08	-0.01593669	-7.0368e+10	-13.7322841
f	7.75955e-13	6.58264e-05	4.1961e+11	-197.843919
g		234.1069658	417.5059918	24.58584338
h		-5.30220462	-15.8927766	0.080091831
i		0.236528783	0.785609498	1.364527331
j		-0.00345384	-0.01411732	9.700068352
k		1.05262e-05	8.5484e-05	
x	% C	% C	% C	% O
y	$\Delta_f H^\circ$	% O	% N	% H
z	—	$\Delta_f H^\circ$	$\Delta_f H^\circ$	$\Delta_f H^\circ$

Curiously, equation 7 had the best r^2 value when O and H were used as opposed to any other combination or ratio of C, H, O, and N.

Conclusion

As illustrated, if a published $\Delta_f H^\circ$ value is not readily available, a value may be estimated using a variety of different methods. In addition to the cited references for published $\Delta_f H^\circ$ data, the reader may find the following titles of value:

- *Selected Values of Chemical Thermodynamic Properties, Part I. Tables, Circular 500*, F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and J. Jaffe, United States Department of Commerce, 1952.
- *Thermodynamic Constants of Inorganic and Organic Compounds*, M. Kh. Karapet'yants and M. L. Karapet'yants (translated from Russian by J. Schmorak), Ann Arbor Humphrey Science Publishers, 1970.
- *Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*, J.B. Pedley and J. Rylance, Sussex University, 1977.
- *Thermodynamic Data for Mineral Technology*, L. B. Pankratz, J. M. Stuve, and N. A. Gokcen, *Bureau of Mines Bulletin 677*, United States Department of the Interior, 1984.
- *NIST WebChem*, National Institute of Standards and Technology, 1998
<http://webbook.nist.gov>.

Acknowledgments

The author gratefully acknowledges the technical assistance of K. Kosanke, R. Kuzma, D. Meyer, and D. Wilson.

References

- 1) W. L. Masterson and E. J. Slowinski, *Chemical Principles*, 4th ed., W. B. Saunders Company, 1977.
- 2) *MicroPEP* computer program, Martin Marietta Corporation, 1987.
- 3) E. D. Brown, "An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers", Issue 1, *Journal of Pyrotechnics*, 1995, pp 11–18.
- 4) S. Gordon and B. J. McBride, *CEA400/600* computer programs, NASA Lewis Research Center, 1994.
- 5) R. P. Danner and T. E. Daubert, *Manual for Predicting Chemical Process Design Data*, American Institute of Chemical Engineers (DIPPR), 1983.
- 6) M. W. Chase Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., American Chemical Society, 1985.
- 7) *CRC Handbook of Chemistry and Physics*, 75th ed., D. R. Lide, Ed., CRC Press, 1994.
- 8) M. Slessor, Ed., *Dictionary of Energy*, 2nd ed., Nichols Publishing, 1988.
- 9) R. Lewis, Sr., *Hawley's Condensed Chemical Dictionary*, 12th ed., Van Nostrand Reinhold Co., 1993.
- 10) B. M. Jenkins, "Properties of Biomass", *Biomass Energy Fundamentals*, Volume 2: Appendices, G. A. Wiltsee, Jr., Ed., Electric Power Research Institute, 1993.
- 11) D. A. Tilman, *Wood as an Energy Resource*, Academic Press, 1978.
- 12) E. S. Domalski and E. D. Hearing, "Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K", Vol. 22, No. 4, *J. Phys. Chem. Ref. Data* (1993), and E. S. Domalski and E. D. Hearing, "Erratum: Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K", Vol. 23, No. 1, *J. Phys. Chem. Ref. Data*, 1994. [See Reference 13.]
- 13) *THERM, NIST Estimation of the Chemical Thermodynamic Properties of Organic Compounds at 298.15 K* computer program Version 5.2, NIST Standard Reference Database 18, U.S. Department of Commerce, 1994. [See Reference 12.]
- 14) J. B. Pedley, R. D. Naylor, S. P. Kirby, *Thermochemical Data of Organic Compounds*, Chapman and Hall, 1986.
- 15) W. Meyerriecks, "A Thermodynamic Properties Estimation Method for Isocyanates", Issue 6, *Journal of Pyrotechnics*, 1997.

- | | |
|---|--|
| <p>16) D R. Stull, E. F Westrum, Jr., G. C. Sinke, <i>The Chemical Thermodynamics of Organic Compounds</i>, John Wiley and Sons, 1969.</p> <p>17) T. Shimizu, <i>Fireworks From a Physical Standpoint</i>, Pyrotechnica Publications, 1983.</p> <p>18) D. D. Wagman, W. H. Evans, V. B. Parker, R. L. Nutall, <i>Selected Values of Chemical Thermodynamic Properties, Technical Note</i></p> | <p>270-8, United States Department of Commerce, 1981.</p> <p>19) W. Meyerriecks, <i>CEQ58 Chemical Equilibrium</i> computer program, Version 58, 1998.</p> <p>20) W. Meyerriecks, "Organic Fuels: Composition and Formation Enthalpy Part II: Resins, Charcoal, Pitch, Gilsonite, and Waxes", <i>Journal of Pyrotechnics</i>, No. 9, 1999.</p> |
|---|--|

(5/98)

Errata

Issue 9, Summer 1999 – corrected words are listed in **bold** type to help the reader locate them.

Page 16, Reference 11, first line should read: "(11) H. H. Finlayson, "**Examination of the**"

Page 21, authors' names – last name [Ellis] should have 3 asterisks: "and S. Ellis***"

Page 34, column 2, paragraph 2, 2nd line delete "is" should read: ".the second object **is** approaches"

Page 34, column 2, paragraph 2, 4th line should read: "When the second object is only a tiny amount **less** massive than the first, **the second object** will take an extremely ..."

Page 38, column 1, just above the middle should read: "This range of volumes is divided into **100** equal parts."

Page 40, column 2, paragraph 2, 4 lines from the bottom should read: "For example, for a temperature change from a starting temperature of T_1 to a final **temperature** T_2 , the change of ..."

Page 41, column 2, 2/3's way down page equation should read: " **$\Delta(PV) = P\Delta V$** , and"

Page 42, column 1, 10 lines from bottom should read: "All that is required is to measure the heat emitted **or absorbed** when a known amount of the compound..."

Page 42, column 2, 5 lines from the bottom 283.0 should be: " $x - \mathbf{283.0}$ kJ/mol = -393.5 kJ/mol"

Page 57, column 2, paragraph 2, line 17 should read: "solutions are sprayed into a **flame** or into an inductively ..."

Errata continued on page 55

High-Nitrogen Fuels for Low-Smoke Pyrotechnics^[1]

David E. Chavez, Michael A. Hiskey and Darren L. Naud*

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

ABSTRACT

It has been demonstrated that the high-nitrogen compound, 3,6-dihydrazino-s-tetrazine (DHT), can be utilized as a pyrotechnic fuel requiring small amounts of metal salts for coloring the flame. In addition, DHT pyrotechnic formulations using non-metallic oxidants, specifically ammonium perchlorate and ammonium nitrate, produce little smoke when burned. In light of this application of high-nitrogen compounds, we have determined that two other high-nitrogen fuels, bis-(1(2)H-tetrazol-5-yl)-amine monohydrate (BTAw), 5,5'-bis-1H-tetrazole (BT) and their salts are likely candidates for low-smoke pyrotechnic fuels. The various characteristics of these fuels have been examined in some detail; these include impact sensitivity with and without oxidant ammonium perchlorate, spectra of colored flames, and thermal analyses of their hydrates and salts.

Keywords: high nitrogen fuel, low smoke, pyrotechnics, bis-(1(2)H-tetrazol-5-yl)-amine, 5,5'-bis-1H-tetrazole, 3,6-dihydrazino-s-tetrazine.

Introduction

Traditional pyrotechnic formulations are typically composed of carbonaceous fuels and metal salts. These salts are often used as both oxidant and flame colorant—for example, strontium nitrate. Such mixtures are known to burn with abundant smoke and often ash as well, which is attributed to partial combustion and the generation of non-gaseous products, particularly metal oxides. In addition, recent formulations have introduced chlorinated polymers for color enhancement, yet this has done

little to decrease the amount of noxious smoke. Here at the Los Alamos National Laboratory we have made progress in reducing smoke and the metal content in pyrotechnic formulations without sacrificing flame color. This work is an offshoot of our high-nitrogen synthesis program to synthesize high-nitrogen compounds for use as explosives and gas generants. It is our hope that this technology will alleviate the exposure of crew and audiences to potentially harmful smoke.

Previously, Chavez and Hiskey have reported^[2] that 3,6-dihydrazino-s-tetrazine (DHT) (Figure 1), when mixed with non-metallic oxidizers and 5 wt. % coloring agents, produces little smoke and ash when burned.^[3] These formulations needed no chlorinated polymeric binder since the preferred oxidant, ammonium perchlorate (AP), acted as both oxidizer and color enhancer. The authors were able to make strong compact stars by wetting the AP formulations with water, pressing them into shape and drying. Because of the hygroscopic nature of ammonium nitrate (AN), formulations containing AN were wetted with alcohol rather than water. These stars were protected from moisture by dipping in nitrocellulose lacquer. In addition, the authors have simplified the syn-

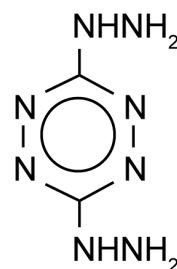


Figure 1. Structure of DHT.

thesis of DHT by bypassing the tedious hydrazinolysis of 3,6-diamino-*s*-tetrazine at elevated temperature.

Besides DHT, other high-nitrogen compounds have been studied for use as low-smoke pyrotechnic fuels. These compounds, bis-(1(2)*H*-tetrazol-5-yl)-amine monohydrate (BTaw) and 5,5'-bis-1*H*-tetrazole (BT) (Figure 2), are diprotic acids and can react with basic amines to form mono- and di-aminated salts, and with metal carbonates or hydroxides to form metal salts. Some of these salts are hydrates. By formulating these compounds with different ratios and compositions, it is now possible to achieve greater control and variability in burn rate and ignitability of high-nitrogen pyrotechnic formulations than with DHT alone.

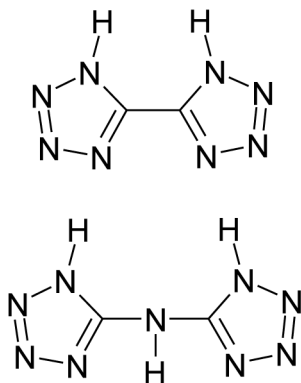
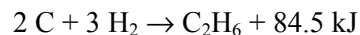


Figure 2. Structures of BT (top) and BTA (bottom). BTaw is the monohydrate of BTA.

Heats of Formation

A feature of these high-nitrogen fuels is their large positive heat of formation (ΔH_f), which is broadly described as the thermal change involved in the formation of one mole of fuel from its elements. Historically, because of the complexity of measuring absolute enthalpy, the elements have been assigned zero enthalpy of formation at standard temperature (25 °C) and pressure (1 atm). A compound having a negative heat of formation denotes that the reaction of its constitutive elements in the appropriate stoichiometric ratio is an exothermic reaction.

An example is the reaction of two moles of graphite (a form of pure carbon) with 3 moles of hydrogen gas to produce one mole of ethane gas, which would release 84.5 kJ of heat.



A compound with a positive heat of formation absorbs heat energy for its formation. The formation of one mole of DHT from its elements requires 535 kJ energy; thus its intrinsic chemical potential energy is comparably higher than that of ethane. However, it must be noted that the magnitude of a heat of formation *based on a mole of material* can be misleading.

A compound of large molecular weight can give the impression of having an unusually large heat of formation. This is because the heat of formation is dependent on the number and types of chemical bonds. Compounds with high molecular weights do, of course, have many bonds that contribute to the total heat of formation. The heat of formation of the hydrocarbon *n*-octane is -208 kJ/mol , which is more than twice that of ethane. This disparity could make one incorrectly believe that ethane has significantly more chemical potential energy than that of *n*-octane. For this reason it is usually best to compare the intrinsic enthalpies of different compounds by normalizing the heat of formation on a per mol·atom basis. Ethane has 8 atoms, so its normalized heat of formation is $-10.6 \text{ kJ/mol}\cdot\text{atom}$ (-84.5 kJ/mol divided by 8 atoms). The normalized heat of formation for *n*-Octane, with 26 atoms, is $-8.00 \text{ kJ/mol}\cdot\text{atom}$. Thus, it is seen that *n*-octane has an intrinsic enthalpy comparable to that of ethane gas.

In Table 1, the heats of formation of several traditional and high-nitrogen fuels are reported on a mole and mol·atom basis. Graphite and naphthalene have seemingly different heats of formation on a mole basis, but are similar when calculated on a per mol·atom basis. When compared on a mole basis, sucrose has a more negative heat of formation than that of potassium benzoate trihydrate. However, the benzoate salt has a more negative enthalpy than that of sucrose on a mol·atom basis. The large negative heat of formation of potassium benzoate is attributed to its being a salt and hydrated with three molecules of water.

Table 1. Heats of Formation, Heats of Reaction (balanced to CO₂ with AP as an Oxidizer), and Mol-Atom Normalized Values for Various Fuels.

Fuels	ΔH_f (kJ/mol)	ΔH_f (kJ/mol-atom)	ΔH_{rxn} (kJ/mol)	ΔH_{rxn} (kJ/mol-atom)
Graphite	0	0	-525	-58.4
Naphthalene	+60.2	+3.34	-6540	-57.4
Sucrose	-2220	-49.3	-6740	-47.8
K Benzoate·3H ₂ O	-1510	-62.9	-4020	-47.9
BTaw	+186	+10.9	-1940	-49.7
DHT	+536	+33.5	-2510	-57.0

Since pyrotechnic formulations are usually an intimate mixture of fuel and oxidizer, the heats of reaction of various fuels and AP have been calculated and are also included in Table 1. The calculations are based on one mole of fuel reacting with sufficient AP to oxidize all hydrogen to gaseous water and all carbon to carbon dioxide. Again, for the same reasons that the heats of formation were normalized, the heats of reaction were normalized on a mol-atom basis and are listed in Table 1. The number of atoms used in normalizing the heat of reaction is the total number of atoms in the fuel and AP adjusted stoichiometrically. These normalized heats of reaction are comparable, even for fuels with large disparity in heats of formation, such as graphite, naphthalene and DHT. So, from an enthalpic perspective, it appears unnecessary to resort to exotic compounds with large positive heats of formation for enhancing the energy content of fuel/oxidizer matrices.

Yet, these calculations were based on the assumption that a burning reaction reaches equilibrium efficiently (i.e., reacting to completion to produce water and carbon dioxide), which is hardly the case. Pyrotechnicians are perhaps familiar with the use of naphthalene as a fuel, if it could be called that. A mixture of naphthalene and potassium chlorate burns with dense carbonaceous smoke, which precludes any notion that such a reaction effectively reaches equilibrium condition. Burning sugars, or sugar-like fuels such as starches or cellulose, are not any better. Paradoxically, potassium benzoate trihydrate, which has a low heat of formation on a mol-atom basis, does burn comparatively cleanly with an oxidizer; how-

ever, it still produces much smoke. Most of this smoke is attributed to the formation of potassium compounds rather than soot-like combustion products. The high-nitrogen fuels, BTaw, BT, DHT and their derivatives, together with the appropriate amount of oxidizer *burn with little or no soot production*. This is attributed to the high nitrogen makeup of these formulations that allows them to burn with great efficiency and to reach equilibrium condition rapidly.

Because these formulations burn cleanly, only small amounts of metal colorants are needed to color the flame. This double-bonus of sootless flames and low metal contents has made these formulations desirable in low-smoke pyrotechnic applications.

Sensitivity

The sensitivity of these high-nitrogen fuels, their salts and mixtures with AP were measured by impact analysis using a Type 12 machine. More details on the procedure can be obtained from a handbook compiled by Dobratz.^[4] An impact analysis is reported as a drop height (H_{50}), which is the height where a 2.5 kg weight—when dropped onto a 40 mg sample on sandpaper—has a 50% possibility of initiation. The maximum height that can be reached with the impact machine is 320 cm. For comparison, pentaerythrite tetranitrate (PETN) has a drop height of approximately 13 to 16 cm.^[4] The drop heights of the pure high-nitrogen fuels and their metal salts are listed in Table 2. Most of these fuels and salts are fairly insensitive ($H_{50} > 320$ cm), which makes them desir-

Table 2. Impact Sensitivities of High-Nitrogen Fuels and their Salts. Names and Formulas Are Given in the Synthesis Section.

Sample	H ₅₀ (cm)
DHT	65
BT	15
DA-BT	>320
DHA-BT	94
DHz-BT	>320
HA-BT	34
Hz-BT	112
DHT-BT2w	264
BTAw	>320
BTA (anhydrous)	26
DA-BTAw	>320
DHz-BTAw	>320
A-BTA	>320
Hz-BTA	>320
Sr-BT4w	>320
Ba-BT4w	>320
Cu-BT2w	23
Sr-BTA4w	>320
Ba-BTA	>320
Cu-BTA2w	269

able for storing and shipping. Pure AP oxidant, too, has a drop height greater than 320 cm. However, impact sensitivity does increase when these same fuels are mixed with AP. The H₅₀ values of a 34/66 weight ratio of dihydroxylammonium 5,5'-bis-1H-tetrazole (DHA-BT) and AP, a 50/50 ratio of BTAw/AP, and a

50/50 ratio of DHT/AP are 23, 27 and 33 cm respectively. Furthermore, the impact sensitivities of fuel and AP mixtures have been found to decrease with increasing atmospheric humidity. This is typical behavior of heterogeneous mixtures of fuel and inorganic oxidant, such as AP. Table 3 shows how similar DHT/AP formulations increase in impact sensitivity when the relative humidity (RH) is dropped from ca. 60 to 25% RH. Thus mixtures that are rather insensitive in a humid environment can become more sensitive with drier weather.

Stability

Because many of these materials are hydrated and amine salts, it was deemed worthwhile to perform thermogravimetric analysis (TGA) to determine at which temperatures loss of water, loss of amine and onset of decomposition are incurred.^[7] To simulate the effect of oven-drying, the TGA was performed at an extremely slow rate (0.1 °C/min). An example of a raw TGA spectrum is shown in Figure 3, which is a plot of a BTAw sample's weight versus temperature. Because numerous analyses had been performed and raw TGA spectra are unwieldy, the data were reworked and presented in a more utilizable format (see Figure 4). The shaded blocks in Figure 4 represent regions of different mass loss rates between 25 and 225 °C. These mass losses are due to decomposition and evaporation of organic amine and hydrated water. BTAw, for example, loses

Table 3. Impact Results of Various DHT-AP Formulations Demonstrate That Impact Sensitivity Is Highly Dependent on the Relative Humidity of the Atmosphere in Which the Analysis Is Performed. This Phenomenon Is Typical of Binary Compositions That Contain Fuel and Ammonium Perchlorate.

Composition (wt. %)				H ₅₀ (cm)	RH (%)
DHT	AP	Metal	Salt		
50.0	50.0	—	—	33	62
47.5	47.5	5.0	CuS	27	60
30.5	69.5	—	—	14	26
49.5	49.5	1.0	Li ₂ CO ₃	19	27
46.5	46.5	7.0	H ₃ BO ₃	22	20
47.5	47.5	5.0	SrCO ₃	19	28

hydrated water at a nominal rate (between 0.001 and 0.01%/min^[8]) in a temperature region from 74 to 94 °C. The rate increases above 0.01%/min at 94 °C, but later falls below 0.01%/min at 116 °C when the hydrated water has been depleted. Diammonium bis-(1(2)H-tetrazol-5-yl)-amine monohydrate (DA-BTAw), a substance having a more complex TGA profile than BTAw, loses water at ca. 55 °C, the first ammonia molecule at ca. 112 °C, the second ammonia molecule at ca. 165 °C, and finally begins decomposing at ca. 180 °C.

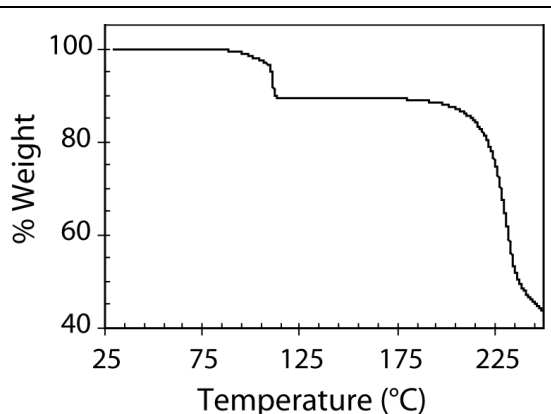


Figure 3. TGA analysis of BTAw at a rate of 0.1 °C/min. The loss of weight is recorded as a function of temperature. Hydrated water is first lost from 74 to 116 °C; decomposition begins at ca. 175 °C.

It must be noted that impact and friction sensitivities of a formulation can be greatly enhanced by the loss of hydrated water. For example, the drop height of BTAw is greater than 320 cm, but decreases to 26 cm when dried to its anhydrous form, BTA. Therefore, great care must be taken with mixtures con-

taining BTA, especially when mixed with an oxidizer. Fortunately it is fairly difficult to dry BTAw to BTA (ca. 112 °C for several hours) and BTA readily hydrates back to BTAw in air at 50% relative humidity. Drying is most useful with formulations containing the tetrahydrated strontium and barium salts of BT and BTA. Such mixtures have improved ignitability when some of the hydrated water from these salts is removed.

A simple test procedure was developed to determine at what humidity levels anhydrous salts convert back to their hydrated form. Four hygrometers were used for these controlled exposure tests. A saturated solution of potassium acetate at the bottom of a sealed chamber generates a 20% RH environment at room temperature. Likewise, saturated solutions of magnesium nitrate, sodium acetate and dibasic sodium phosphate (Na_2HPO_4) produce 52, 76 and 96% RH environments, respectively.^[9] Tared anhydrous samples were placed in the four hygrometers and their weights were measured a number of times over the course of several weeks. Samples that rehydrated weighed more, while those samples that remained anhydrous kept their original weight. The data are noted in the Synthesis section.

Ion exchanges between salts can be problematic for some of these formulations. Hydrazine and hydroxylammonium salts of BT or BTA can metathetically exchange with AP in a solution environment (such as water) to form stable ammonium derivatives of BT or BTA and the highly unstable *hydrazinium and hydroxylammonium perchlorates*. Therefore the risk of forming explosive salts precludes the use of hydrazine and hydroxylammonium salts for practical applications.

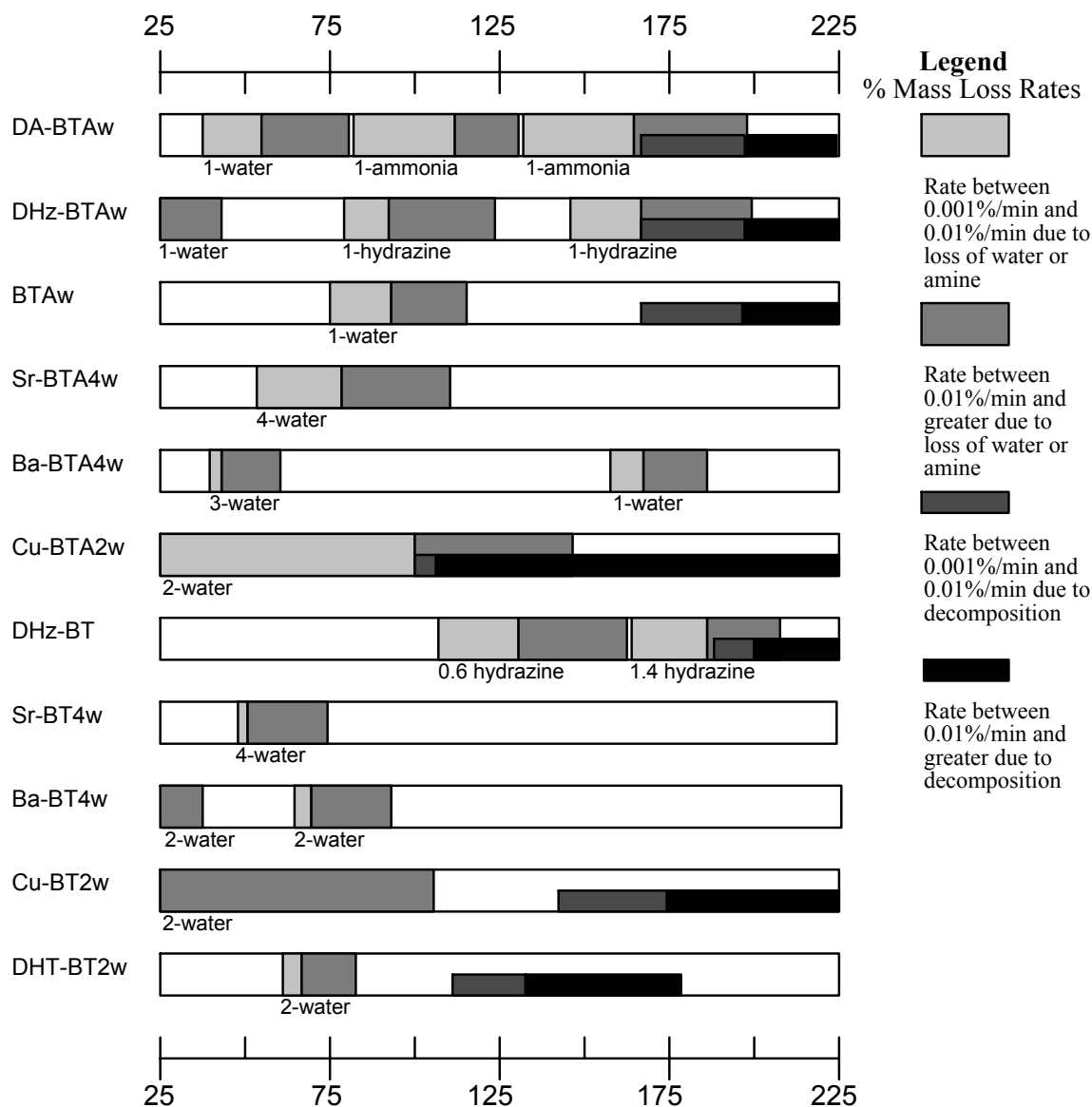


Figure 4. The thermal gravimetric analysis (TGA) data of various fuels and metal salts that undergo reversible decomposition (i.e., loss of hydrated water or organic amine) were reworked for clarity. Shaded blocks represent regions of different mass loss rates between 25 and 225°C. These analyses were performed at a slow rate (0.1 °C/min) to simulate the effect of oven-drying.

Synthesis

The synthetic procedures described below should only be attempted by those experienced with energetic material synthesis, equipped with proper laboratory facilities, and capable of properly disposing of the hazardous chemical waste. The materials used are toxic and flammable, most notably sodium azide, sodium cyanide and hydrazine. In addition, explosive metal

azides are easily formed from the metathetical exchange between sodium azide and metal salts. Some of these azides, such as silver, copper and lead azides, are extremely friction and heat sensitive. Hydrazine and its derivatives should be regarded as potential carcinogens and treated with care. All reagents were purchased from commercial sources except where noted. Elemental analyses were performed using a Perkin Elmer Series II CHNS/O Analyzer, Model 2400. Poor agreement between theoretical and meas-

ured results is a characteristic problem in the elemental analysis of high-nitrogen compounds. However all compounds were purified to the point that agreement of at least two elements was within 0.4%. All nuclear magnetic resonance (NMR) spectra were obtained on a JEOL GSX-270 spectrometer. Chemical shifts (δ) are reported relative to internal tetramethylsilane = 0 for ^{13}C NMR spectra.

The preparation of DHT was first reported in 1963,^[5] however, a more simplified procedure has been developed.^[3,6] The reported literature of BT, BTaw, their salts and hydrates is scanty and mostly located in obscure patents and government reports. The predominant interest in these compounds, as detailed by the uncovered literature, is their use as automobile air-bag gas generants and rocket propellant additives.

The syntheses of the numerous salts of BTaw and BT are similar, so a general method of synthesis is described here. The exact quantities and reagents are better detailed for each compound below that uses this general method. BTaw or BT, and one or two equivalents of organic amine or metal hydroxide are reacted in a sufficient amount of deionized water necessary for recrystallization. The resulting slurry mixture is stirred and heated to boiling, and—if necessary—filtered hot to remove insoluble impurities. The clear solution is cooled by an ice bath to approximately 10 °C with vigorous stirring to initiate precipitation. The salt is collected by filtration and air-dried.

5,5'-Bis-1*H*-tetrazole (BT)

The preparation of BT involves two steps, whereby manganese 5,5'-bis-1*H*-tetrazolate (Mn-BT) is generated as an intermediate followed by its conversion to the free acid when treated with a buffered solution of carbonic acid. The following preparation is a summarized adaptation of a method outlined by R. A. Henry.^[10]

To a 5-L flask, containing 2.4 L of water, 260 g sodium azide (4.00 mol) and 200 g sodium cyanide (4.08 mol) were added. While being stirred and cooled by an ice bath, 220 g of manganese dioxide (2.53 mol) were added.

Afterwards, a solution—comprised of 400 g concentrated sulfuric acid (4.08 mol), 320 g glacial acetic acid (5.33 mol) and 8 g copper(II) sulfate pentahydrate (26 mmol), previously dissolved in 1.0 L water—was added at a rate so that the reaction temperature was between 20 and 30 °C. After the addition, the mixture was brought to 90 °C over a one hour period and maintained between 90 and 95 °C for 3 hours. The reaction was cooled and the crude product, possibly containing some copper salts, was filtered and air-dried to yield 390 g of Mn-BT (102%).

To a slurry—composed of 200 g of Mn-BT (1.05 mol) and 1.6 L water—was added gradually 120 g of sodium carbonate (1.13 mol) over a 10 minute period. The mixture was boiled for 1.5 hours, filtered and the solids washed with 200 mL of boiling water. The filtrates were combined and neutralized with concentrated hydrochloric acid until CO₂ evolution stopped. An excess amount of concentrated HCl (140 mL) was added to ensure the precipitation of the di-acid, and not the less soluble acid-sodium salt. At this point any soluble copper salts were precipitated by either titrating with a 5% sodium sulfide solution^[11] or bubbling hydrogen sulfide gas. Thereafter the solution was reduced to 700 mL by boiling, cooled to 0 °C, and filtered to remove the crude product. Yields ranged from 97 to 107 g (65 to 75%). ^{13}C NMR (DMSO-*d*₆): δ 147.7.

The drop height of BT is 15 cm, which suggests that this material is too sensitive for use as a pyrotechnic fuel alone. The salts of BT, however, are much less sensitive and are readily applicable for low-smoke applications. It is strongly advised that when BT is freshly prepared and still contains moisture, that it be converted to the salt rather than air-dried and stored.

Diammonium 5,5'-Bis-1*H*-tetrazolate (DA-BT)

Using the general synthesis method, 10 g of BT (72 mmol) and 20 mL concentrated ammonium hydroxide were reacted in 300 mL water. DA-BT is one of the most stable high-nitrogen fuels; the onset of decomposition is ca. 280 °C. This salt is commercially available in bulk from

a US distributor at a cost of approximately US\$66 per kilogram.^[12]

Analysis for C₂H₈N₁₀:

Calculated: C, 13.95; H, 4.68; N, 81.36.

Found: C, 14.02; H, 4.94; N, 82.21.

Dihydrazinium 5,5'-Bis-1H-tetrazolate (DHZ-BT)

Using the general synthesis method, 15 g BT (0.11 mole) and 11 g hydrazine monohydrate (0.22 mole) were reacted in 100 mL of water. ¹³C NMR (DMSO-d₆): δ 154.4.

Analysis for C₂H₁₀N₁₂:

Calculated: C, 11.88; H, 4.99; N, 83.13.

Found: C, 11.93; H, 5.02; N, 83.27.

The filtrate of the above reaction, which contains a significant amount of soluble DHZ-BT, was treated with 30 mL of concentrated ammonium hydroxide to precipitate DA-BT. The recovered DA-BT can be recrystallized or converted to another salt. DHZ-BT loses approximately 0.6 hydrazine at ca. 130 °C, and loses the remaining hydrazine at ca. 195 °C. Star samples composed of this fuel melted and decomposed before catching fire. For this reason, DHZ-BT is perhaps one of the poorest performing fuels. However, stars formulated with copper salts burned with relative ease, which is attributed to the catalytic effect of copper salts on hydrazine. DHZ-BT might find use as an additive to adjust the ignitability or burn characteristics of pyrotechnic formulations.

Hydrazinium 5,5'-Bis-1H-tetrazolate (Hz-BT)

Using the general synthesis method, BT (8.0 g, 58 mmol) and hydrazine monohydrate (2.9 g, 58 mmol) were reacted in 50 mL of water. TGA shows that this monoamine salt is thermally stable to 175°C. ¹³C NMR (DMSO-d₆): δ 149.3.

Analysis for C₂H₆N₁₀:

Calculated: C, 14.12; H, 3.55; N, 82.33.

Found: C, 14.33; H, 3.67; N, 83.28.

Dihydroxylammonium 5,5'-Bis-1H-tetrazolate (DHA-BT)

Using the general synthesis method, BT (30 g, 0.22 mol) and 27 mL of 50% hydroxylamine solution (0.44 mol) were reacted in 1 L of water. The onset of decomposition is ca. 200 °C.

Analysis for C₂H₈N₁₀O₂:

Calculated: C, 11.77; H, 3.95; N, 68.61.

Found: C, 11.83; H, 4.21; N, 68.54.

Hydroxylammonium 5,5'-Bis-1H-tetrazolate (HA-BT)

Using the general synthesis method, BT (22.5 g, 0.16 mol) and 10 mL of 50% hydroxylamine solution (0.16 mol) were reacted in 90 mL of water. The onset of decomposition is ca. 196 °C.

Analysis for C₂H₅N₉O:

Calculated: C, 14.04; H, 2.94; N, 73.67.

Found: C, 14.00; H, 2.92; N, 73.86.

Barium 5,5'-Bis-1H-tetrazolate Tetrahydrate (Ba-BT4w)

Using the general synthesis method, BT (3.20 g, 23.2 mmol) and barium hydroxide octahydrate (7.40 g, 23.5 mmol) were neutralized in 200 mL water. Ba-BT4w loses its four hydrated water molecules in two stages. Two water molecules are readily lost when the barium salt is heated to ca. 40 °C, and the remaining two waters are lost when heated to ca. 90 °C. Anhydrous Ba-BT shows no indication of decomposition when heated above 300 °C. Because Ba-BT4w is partially efflorescent at room temperature, the hydrate was dried at 150 °C for several hours prior to elemental analysis. Anhydrous Ba-BT rapidly recovers one water at 20% RH over a period of three days. In the same time, the dry salt recovers two water molecules at 52 and 76% RH. At 96% RH, two waters are rapidly hydrated, and the remaining two waters are slowly recovered over a period of three weeks.

Analysis for C₂N₈Ba·4H₂O:

Calculated: C, 8.79; H, 0; N, 40.99.

Found: C, 8.79; H, 0.19; N, 40.80.

Strontium 5,5'-Bis-1*H*-tetrazolate Tetrahydrate (Sr-BT4w)

Using the general synthesis method, BT (1.37 g, 9.9 mmol) and strontium hydroxide octahydrate (2.66 g, 10 mmol) were neutralized in 50 mL water. Four molecules of hydrated water are lost when Sr-BT4w is heated to ca. 75 °C. Similar to the barium salt, this material appears to be thermally stable above 300 °C. Anhydrous Sr-BT recovers approximately one half water over three weeks at 20% RH. At 52% RH and above, the dry salt recovers approximately three water molecules within three days, while the fourth water is hydrated slowly over a period of four weeks.

Analysis for $C_2N_8Sr \cdot 4H_2O$:

Calculated: C, 8.12; H, 2.73; N, 37.89.

Found: C, 8.07; H, 2.60; N, 38.13.

Copper(II) 5,5'-Bis-1*H*-tetrazolate Dihydrate (Cu-BT2w)

To a warmed solution composed of BT (1.38 g, 10 mmol) and 50 mL water was added a solution of copper(II) sulfate pentahydrate (2.5 g, 10 mmol) and 20 mL water. The bright blue solid was filtered and air-dried. Cu-BT2w loses one molecule of water readily below 80 °C, and loses its second water from 80 to 110 °C. The copper salt is fairly stable having an onset of decomposition from ca. 140 to 145 °C.

Analysis for $C_2N_8Cu \cdot 2H_2O$:

Calculated: C, 10.19; H, 1.71; N, 47.55.

Found: C, 10.12; H, 1.86; N, 46.04.

3,6-Dihydrazino-*s*-tetrazinium 5,5'-Bis-1*H*-tetrazolate Dihydrate (DHT-BT2w)

To 13.8 g of BT (0.10 mol) in 200 mL of water was added 14.2 g DHT. The slurry was stirred for 48 hours, whereupon the original red color of DHT changed to a bright orange. The product was collected by filtration and air-dried. The two hydrated waters are rapidly lost at ca. 75 °C. Anhydrous DHT-BT remains non-hydrated at 76% RH, but recovers the two water molecules at 96% RH over a period of several weeks.

Analysis for $C_4H_8N_{16} \cdot 2H_2O$:

Calculated: C, 15.19; H, 3.82; N, 70.87.

Found: C, 15.28; H, 3.84; N, 71.59.

Bis-(1(2)*H*-tetrazol-5-yl)-amine Monohydrate (BTaw)

The syntheses of BTaw and its hydrated, acid sodium salt were first described by Norris and Henry.^[13] In one method cyanoguanyl azide is treated with azide in the presence of a trialkylammonium salt as an acid catalyst; in the second, sodium dicyanoamide is reacted with azide and trialkylammonium salt catalyst. These preparations have the drawback of utilizing a commercially expensive catalyst that converts to an odorous free-based trialkylamine as a by-product. Highsmith et al. have improved the synthetic method in their detailed US patent; for convenience, an extracted excerpt (Example 27) of the highest yielding method is included as note 14. It should be noted that the patent authors have not characterized nor inferred the synthesized amine as the monohydrate. The effect of drying the product in vacuo at 60 °C for three days, as specified by Example 27, is *insufficient* for converting the monohydrate to the anhydrous form. This might have been an oversight since their reported method of characterizing the amine was by ¹³C NMR only, an analytical technique that cannot detect hydrated water. Using the patented synthesis method, the authors estimate the bulk cost of BTaw to be between US\$50 and \$100 per kilogram. ¹³C NMR (DMSO-*d*₆): δ 153.4.

The purification of BTaw, which was easily done by recrystallization from water, was critical for proper burning and flame coloration of our pyrotechnic formulations. To 4 L of boiling water were added 85g of crude BTaw. The solution was filtered hot and cooled slowly with stirring. The material was collected by filtration and air-dried. As shown in Figures 3 and 4, hydrated water is lost very slowly at ca. 80 °C but increases in rate when heated to ca. 110 °C. Anhydrous BTA remains non-hydrated at 20% RH and becomes 70% hydrated after one week at 52% RH. The onset of decomposition of BTA is approximately 170 °C. The impact sensitivity of pure BTaw is greater than 320 cm but drops to 26 cm when converted to

the anhydrous form, BTA. Thus for reasons of safety it is not desirable to dry BTAW to the anhydrous form for use as a pyrotechnic fuel. In addition, given that a 50/50 wt. % mixture of BTAW and AP has an impact sensitivity of 27 cm, it is very likely that such a mixture—if dried to remove the hydrated water—would exhibit much greater sensitivity. Our typical BTAW pyrotechnic formulations consisted of 50/50 wt. % fuel to AP, to which some metal salt colorant was added. More details on these and other formulations are in the Flame Color section.

Diammonium Bis-(1(2)*H*-tetrazol-5-yl)-amine Monohydrate (DA-BTAW)

Using the general synthesis method, BTAW (5.8 g, 34 mmol) and concentrated ammonium hydroxide solution (5.7 g, 0.10 mol) were neutralized in 30 mL water. ^{13}C NMR (DMSO- d_6): δ 158.9.

Analysis for $\text{C}_2\text{H}_9\text{N}_{11}\cdot\text{H}_2\text{O}$:

Calculated: C, 11.71; H, 5.40; N, 75.09.

Found: C, 11.99; H, 5.54; N, 75.26.

DA-BTAW is one the most soluble high-nitrogen salts, which makes its use as a pyrotechnic fuel impractical. Synthesis and purification of this material usually resulted in poor yield due to attrition, and again, there was more loss of the fuel through leaching when DA-BTAW formulations were wetted with water and processed into stars.

Ammonium Bis-(1(2)*H*-tetrazol-5-yl)-amine (A-BTA)

Using the general synthesis method, BTAW (17.1 g, 0.10 mol) and concentrated ammonium hydroxide (5.8 g, 0.10 mol) were neutralized in 500 mL of water. This mono-ammonium salt has a very low bulk density, having the appearance of cotton. This ammonium derivative of BTA is much less soluble in water than DA-BTAW. ^{13}C NMR (DMSO- d_6): δ 156.2.

Analysis for $\text{C}_2\text{H}_6\text{N}_{10}$:

Calculated: C, 14.12; H, 3.55; N, 82.33.

Found: C, 14.27; H, 3.61; N, 82.58.

Dihydrazinium Bis-(1(2)*H*-tetrazol-5-yl)-amine Monohydrate (DHZ-BTAW)

Using the general synthesis method, BTAW (17.1 g, 0.10 mol) and hydrazine monohydrate (10.5 g, 0.21 mol) were neutralized in 175 mL water. DHZ-BTAW is efflorescent at room temperature depending on the level of humidity and length of exposure to dry air. The anhydrous form of this salt recovers one water molecule at 20% RH over several days.

Analysis for $\text{C}_2\text{H}_{11}\text{N}_{13}\cdot\text{H}_2\text{O}$:

Calculated: C, 10.21; H, 5.57; N, 77.41.

Found: C, 10.19; H, 5.88; N, 76.61.

Hydrazinium Bis-(1(2)*H*-tetrazol-5-yl)-amine (Hz-BTA)

Using the general synthesis method, BTAW (8.0 g, 47 mmol) and hydrazine monohydrate (2.4 g, 47 mmol) were reacted in 125 mL water.

Analysis for $\text{C}_2\text{H}_7\text{N}_{11}$:

Calculated: C, 12.97; H, 3.81; N, 83.22.

Found: C, 13.16; H, 3.96; N, 83.52.

Strontium Bis-(1(2)*H*-tetrazol-5-yl)-amine Tetrahydrate (Sr-BTA4w)

Using the general synthesis method, BTAW (6.3 g, 37 mmol) and strontium hydroxide octahydrate (10 g, 38 mmol) were neutralized in 400 mL water. The anhydrous form of Sr-BTA recovers about two water molecules after one month at 20% RH. Over the same period, all four waters are recovered at 52% RH.

Analysis for $\text{C}_2\text{HN}_9\text{Sr}\cdot 4\text{H}_2\text{O}$:

Calculated: C, 7.73; H, 2.92; N, 40.56.

Found: C, 7.77; H, 2.75; N, 40.85.

Barium Bis-(1(2)*H*-tetrazol-5-yl)-amine Tetrahydrate (Ba-BTA4w)

Using the general synthesis method, BTAW (2.6 g, 15 mmol) and barium hydroxide octahydrate (5.0 g, 16 mmol) were neutralized in 300 mL water. The tetrahydrated salt readily loses three waters at ca. 60 °C, but the removal of its fourth (last) water requires prolonged heating at ca. 175 °C. The monohydrate of Ba-BTA does not recover any water at 20% RH,

but hydrates the remaining three molecules of water at 52% RH over a period of one month.

Analysis for $C_2HN_9Ba \cdot 4H_2O$:

Calculated: C, 6.66; H, 2.52; N, 34.97.

Found: C, 6.72; H, 2.28; N, 35.30.

Copper(II) Bis-(1(2)*H*-tetrazol-5-yl)-amine Dihydrate (Cu-BTA2w)

To a boiling solution of BTaw (1.0 g, 5.9 mmol, in 50 mL water) was added a solution of copper(II) sulfate pentahydrate (1.5 g, 6.0 mmol in 20 mL water). The green precipitate was filtered and air-dried.

Analysis for $C_2HN_9Cu \cdot 2H_2O$:

Calculated: C, 9.58; H, 2.01; N, 50.29.

Found: C, 9.65; H, 1.96; N, 49.84.

3,6-Dihydrazino-*s*-tetrazine (DHT)

The various synthetic methods of DHT have been discussed in previous publications.^[3,5,6] DHT formulations containing copper salts have been found to be unsuitable for long term storage, especially in humid environments. Stars composed of such formulations swelled into dark porous masses approximately twice their original size when stored for several months. In addition, the burn rate of DHT is increased by the addition of copper salts. For these reasons, the authors have relied on BTaw and BT as the choice fuel-base for all formulations containing copper colorant. Iron(III) oxide was found to profoundly increase the burn-rate of DHT, and the authors strongly advise not to use it in DHT-based formulations.

Flame Color

Colored flames are obtained by the introduction of metallic salts into a fuel/oxidizer matrix. The excitation of gaseous metal monochlorides is the chief source of the emission spectra for copper, strontium and barium flames.^[15] In many traditional pyrotechnic formulations, chlorine sources such as PVC or Parlon[®] are used to enhance the formation of the monochlorides. In order to achieve the cleanest burn with the least amount of smoke, these high-nitrogen formulations have AP as

both oxidizer and chlorine donor. It is possible to substitute some of the AP with AN without serious loss in color-performance, but for sake of simplicity, singly recrystallized AP^[16] was used exclusively.

The flame colors of various star compositions were measured using an Ocean Optics S2000 Series Fiber Optic Spectrophotometer coupled to a SAD500 interface. The diffraction grating was type 2 (200–850 nm) and the entrance slit was 25 microns wide. The instrument wavelength response was calibrated with an LS-1 tungsten halogen light source obtained from Ocean Optics. Although Ocean Optics gives the color temperature of the light source as 3100 K, Meyerriecks^[17] believes the true filament temperature to be closer to 3030 to 3035 K. The authors chose 3035 K as the filament temperature and calculated the appropriate emittance data as a function of wavelength using Planck's formula.

With these emittance values and the spectral data of the tungsten halogen lamp, wavelength dependent correction coefficients were calculated and incorporated into a spreadsheet. The spreadsheet was used to tabulate spectral data, correct instrument response, integrate and calculate a color coordinate using C.I.E. 1931 tristimulus coefficients. This was done by multiplying the emittance with each of the three tristimulus coefficients (in 5 nm increments) to give three subsequent curves. These curves were numerically integrated to give three areas, represented as **X**, **Y**, and **Z**. The *x* and *y* color coordinates were obtained by normalizing the areas.

$$x = X / (X+Y+Z) \text{ and } y = Y / (X+Y+Z)$$

Fortner and Meyer^[18] provide a comprehensive discussion about the C.I.E. color system and its history. This method is a reasonable attempt to characterize visually observed color in a 2-D coordinate system.

Some of these formulations were burned as a powdered mix while other times they were burned as stars. Stars were made by wetting the formulation with deionized water, pressing them into shape and air-drying. No discernible spectral difference could be found between powder and star samples. The samples were

Table 4. Color Coordinate Values (C.I.E. 1931) of Various DHT Formulations.

Composition (wt. %)				Color	x	y
DHT	AP	Metal	Salt			
47.5	47.5	5.0	Sr-BT4w	Red	0.697	0.291
47.5	47.5	5.0	Cu-BTA2w	Blue	0.206	0.144
46.5	46.5	7.0	BaF ₂	Green	0.226	0.648
47.0	47.0	6.0	Boric Acid	Green	0.357	0.489
48.3	48.3	3.4	CaCO ₃	Red-Orange	0.650	0.347
49.5	49.5	1.0	Li ₂ CO ₃	Pumpkin	0.534	0.398

burned on a porcelain plate, and the position of the fiber optic lens relative to the burning sample was adjusted to obtain the greatest response by the spectrophotometer. A number of burns were recorded, and those that gave reasonably similar values were averaged. Reproducibility was generally good with an estimated variability of ± 0.01 in the color coordinates.

Tables 4, 5 and 6 list various high-nitrogen pyrotechnic formulations together with their measured coordinate color values. In addition to the above color data, three pyrotechnic formulations describing the primary colors—red, blue and green—were prepared from traditional ingredients and analyzed spectrophotometrically. Their formulations and respective color coordinates are given in Table 7. These formulations were selected from a large collection of traditional formulations and tested for best color purity. In spite of this, and because of the enormous quantity of published pyrotechnic formulations, the authors do not suggest that these have the best color purity of all formulations. Nevertheless, they are useful for comparing traditional and high-nitrogen flame colors.

To illustrate the enhanced color purity of the high-nitrogen flame, Figure 5 is a graph of the color coordinates taken from Tables 4 through 7 of the 1931 C.I.E. Chromaticity Diagram. The triangle in the center of the diagram is constructed from the three color coordinates obtained from Table 7. This triangular area represents the approximate region of possible colors when different ratios of the primary colors, green (barium), blue (copper) and red (strontium) are mixed in a traditional-style formulation and burned. In theory, these colors are limited to the ingredients listed in Table 7. All of the high-nitrogen color coordinates representing formulations containing 5 to 7 wt. % of barium, copper or strontium colorants fall outside of the triangle. (The few points within the triangle are formulations that do not contain barium, copper or strontium.) This demonstrates that color purity of pyrotechnic flames can be improved by the use of high-nitrogen fuels.

Table 5. Color Coordinate Values (C.I.E. 1931) of the Various BT-Based Formulations.

Composition (wt. %)						
DHT-BT2w	AP	Metal	Salt	Color	x	y
47.5	47.5	5.0	Sr-BTA4w	Red	0.702	0.290
47.5	47.5	5.0	Cu-BTA2w	Blue	0.187	0.123
46.5	46.5	7.0	Ba-BT4w	Green	0.212	0.675
DHA-BT						
DHA-BT	AP	Metal	Salt(s)	Color	x	y
47.5	47.5	5.0	Sr-BT4w	Red	0.707	0.291
47.5	47.5	5.0	Cu-BTA2w	Blue	0.189	0.136
46.5	46.5	7.0	BaF ₂	Green	0.230	0.650
43.5	52.0	2.7	Cu-BTA2w	Purple	0.352	0.179
		+1.8	Sr-BT4w			
43.5	52.0	1.8	Cu-BTA2w	Red-Purple	0.446	0.214
		+2.7	Sr-BT4w			
43.0	52.0	2.1	Cu-BTA2w	Pink	0.524	0.289
		+2.9	CaCO ₃			
42.3	50.7	0.2	Cu-BTA2w	Blue-Green	0.209	0.588
		+6.8	Ba-BT4w			
HA-BT						
HA-BT	AP	Metal	Salt	Color	x	y
47.5	47.5	5.0	Sr-BT4w	Red	0.703	0.291
47.5	47.5	5.0	Cu-BTA2w	Blue	0.193	0.129
46.5	46.5	7.0	Ba-BT4w	Green	0.204	0.684
DHZ-BT						
DHz-BT	AP	Metal	Salt	Color	x	y
42.5	52.5	5.0	Sr-BTA4w	Red	0.673	0.303
42.5	52.5	5.0	Cu-BTA2w	Blue	0.221	0.165
42.0	51.0	7.0	Ba-BTA4w	Green	0.265	0.636
Hz-BT						
Hz-BT	AP	Metal	Salt(s)	Color	x	y
40.0	55.0	5.0	Sr-BTA4w	Red	0.700	0.290
40.0	55.0	5.0	Cu-BTA2w	Blue	0.197	0.131
39.0	54.0	7.0	Ba-BT4w	Green	0.186	0.714
41.2	51.4	0.3	Cu-BTA2w	Blue-Green	0.219	0.587
		+7.1	Ba-BT4w			
DA-BT						
DA-BT	AP	Metal	Salt	Color	x	y
42.5	52.5	5.0	Sr-BTA4w	Red	0.696	0.291
42.5	52.5	5.0	Cu-BTA2w	Blue	0.182	0.116
51.0	42.0	7.0	Ba-BTA4w	Green	0.227	0.674

The greatest improvement in color purity is that of barium green. Traditional color flames have color coordinate values that center about $x = 0.4$ and $y = 0.5$, which make it nearly impossible to generate blue-green flames with mixtures of barium and copper salts. Such traditional compositions generate white light, or pale blue-green at best. High-nitrogen green flames, on the other hand, are considerably more pure and have color values shifted away from the central portion of the chromaticity diagram (white light region). For this reason, formulations containing mixtures of copper and barium give aesthetically pleasing shades of blue-green. High-nitrogen formulations with boric acid col-

orant do not give a deep green color that can be obtained with barium salts, but the much less toxic nature of boric acid makes it suitable for indoor applications. The color purity of DHT/ boric acid composition is nearly the same as the best traditional barium formulation. Coloring high-nitrogen flames with very low concentrations (ca. 1%) of lithium salts create interesting shades of pumpkin-orange, whereas calcium carbonate gives an intense red-orange color. Formulations with copper and calcium salts generate a wide variety of intense pink, purplish pink and purple flames. Strontium and copper salts give bright and pure shades of purple and red-purple flames.

Table 6. Color Coordinate Values (C.I.E. 1931) of the Various BTA-Based Formulations.

Composition (wt. %)						
BTAw	AP	Metal	Salt(s)	Color	x	y
47.5	47.5	5.0	Sr-BT4w	Red*	0.700	0.289
47.5	47.5	5.0	Cu-BTA2w	Blue*	0.177	0.108
47.5	47.5	5.0	Ba-BT4w	Green*	0.196	0.700
46.5	46.5	6.7	Ba-BT4w	Blue-Green	0.185	0.471
		+0.3	Cu-BTA2w			
47.5	47.5	3.1	Sr-BTA4w	Purple	0.368	0.197
		+2.1	Cu-BTA2w			
DHZ-BTAw						
DHz-BTAw	AP	Metal	Salt	Color	x	y
38.0	57.0	5.0	Sr-BT4w	Red	0.685	0.302
38.0	57.0	5.0	Cu-BTA2w	Blue	0.199	0.127
37.0	56.0	7.0	Ba-BT4w	Green	0.348	0.573
Hz-BTA						
Hz-BTA	AP	Metal	Salt	Color	x	y
40.0	55.0	5.0	Sr-BT4w	Red	0.693	0.298
40.0	55.0	5.0	Cu-BTA2w	Blue	0.200	0.126
39.0	54.0	7.0	Ba-BT4w	Green	0.337	0.581
DA-BTA						
DA-BTA	AP	Metal	Salt	Color	x	y
38.0	57.0	5.0	Sr-BT4w	Red	0.695	0.294
38.0	57.0	5.0	Cu-BTA2w	Blue	0.188	0.121
37.0	56.0	7.0	Ba-BT4w	Green	0.311	0.613
A-BTA						
A-BTA	AP	Metal	Salt	Color	x	y
40.0	55.0	5.0	Sr-BT4w	Red	0.700	0.294
40.0	55.0	5.0	Cu-BTA2w	Blue	0.185	0.121
39.0	54.0	7.0	Ba-BT4w	Green	0.204	0.685

*The spectrum of this formulation is shown in Figure 6.

Table 7. Color Coordinate Values (C.I.E. 1931) of the Red, Blue and Green Formulations Using Traditional Ingredients. These Formulations Were Found To Burn with Best Color Purity.

Composition (wt. %)	Color	x	y
60% Strontium nitrate	Red	0.653	0.315
20% Magnalium alloy			
10% Polyvinyl chloride			
10% Red gum			
61% Potassium perchlorate	Blue	0.218	0.185
17% Cupric oxide			
10% Polyvinyl chloride			
6% Hexamine			
3% Red gum			
3% Dextrin			
56% Barium nitrate	Green	0.366	0.522
18% Polyvinyl chloride			
10% Magnalium alloy			
6% Potassium perchlorate			
5% Red gum			
5% Hexamine			

In Figure 6, the spectra of the three traditional formulations representing the primary colors (Table 7) are shown together with selected spectra of high-nitrogen flames. The most apparent difference is that traditional blue and green spectra have poorer baselines. The extra light output over most of the visible spectral region is akin to “washing out” the blue or green light with white light. Because strontium monochloride emits light efficiently, the baselines of both traditional and high-nitrogen red spectra are comparatively better. In the traditional red spectrum, however, there is a broad peak of significant intensity at ca. 606 nm (red-orange). This emission, which is attributed to SrOH, slightly degrades the red color purity. Additional sources of color degradation come from sodium (589 nm) and potassium impurities, which are ubiquitous in traditional ingredients. Fortunately this is less of a problem with high-nitrogen formulations due to their inherent purity.

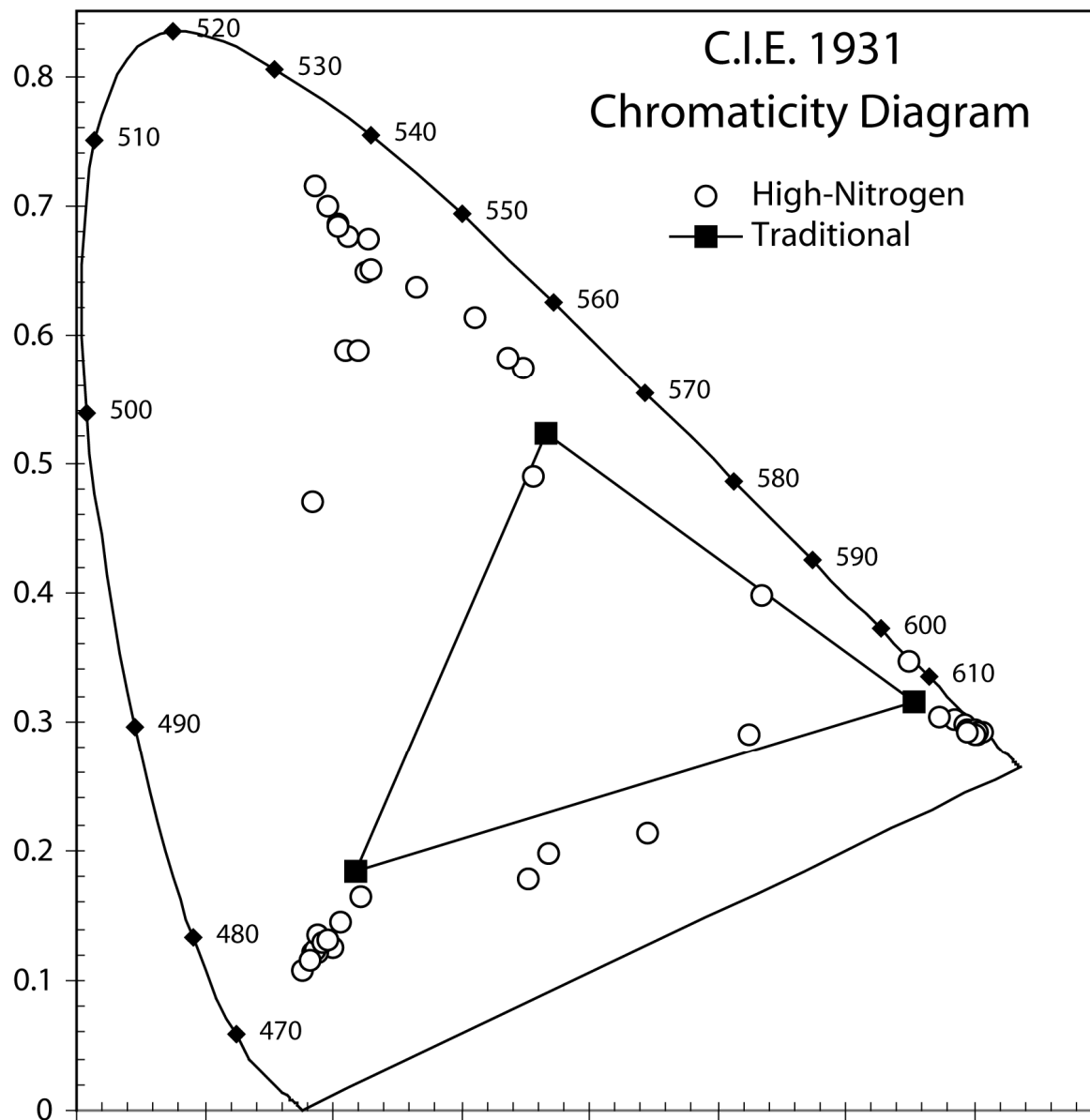


Figure 5. Color coordinates taken from Tables 4 through 7 are shown on a C.I.E. 1931 Chromaticity Diagram. The central triangular region approximately represents the possible colors that can be obtained using traditional fuels and barium, copper and strontium metal colorants (see Table 7).

Red, Blue and Green Spectra

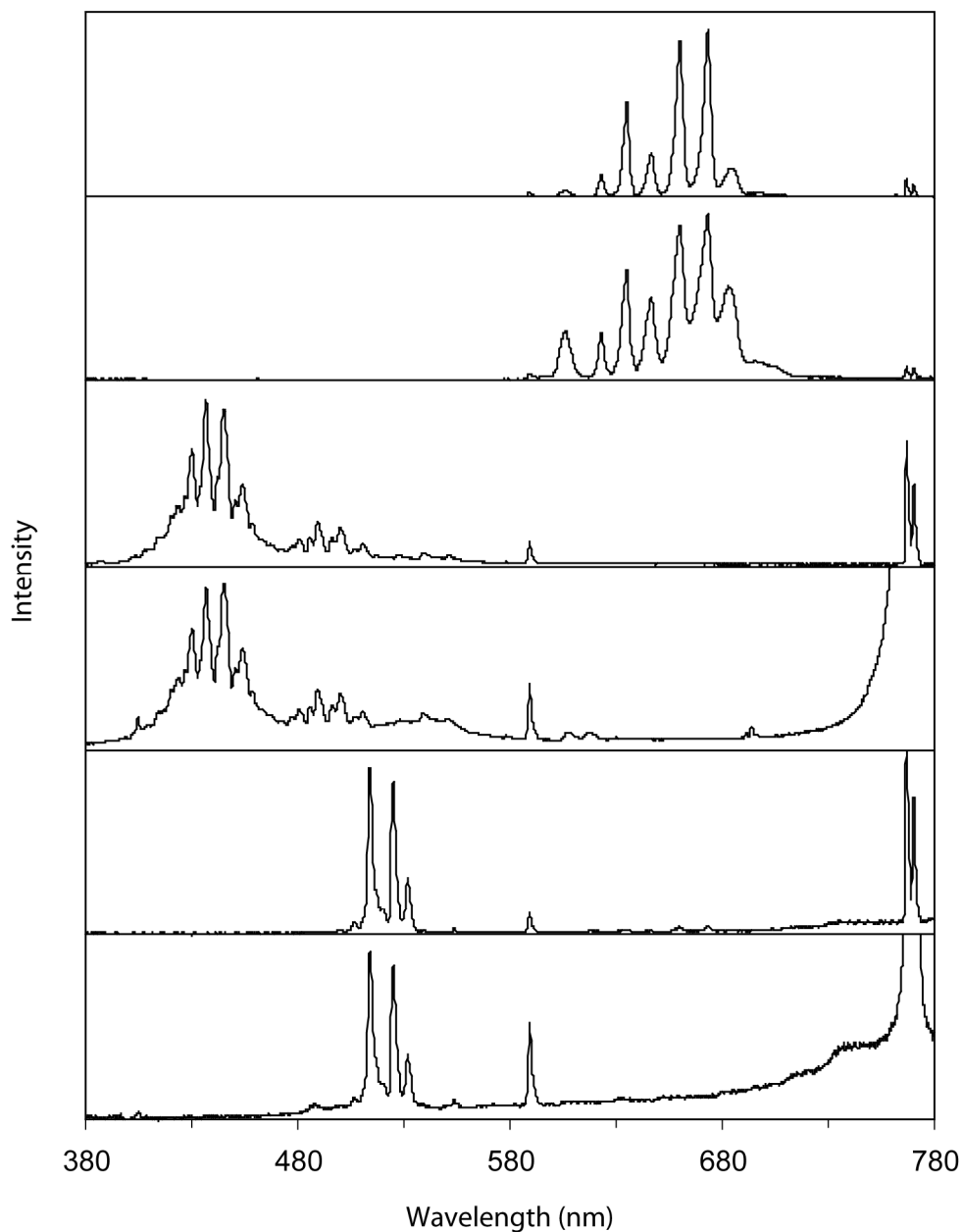


Figure 6. Cleaner baselines and reduced ancillary emissions from impurities are the typical differences between the spectra of traditional (see Table 7) and high-nitrogen flames. The spectra are from top down: high-nitrogen strontium red; traditional strontium red; high-nitrogen copper blue; traditional copper blue; high-nitrogen barium green and traditional barium green. The formulations of the high-nitrogen spectra are the first three in Table 6. The peak at 589 nm is due to sodium impurity. The traditional blue and green formulations generated strong potassium emissions (ca. 760 nm) that were clipped by the spectrophotometer. The calculated color coordinate values for these spectra were not corrected because the tristimulus values are approximately zero in this clipped region.

Table 8. Three Primary Color Series Were Formulated and Photometrically Analyzed To Demonstrate the Effect of Metal Salt Concentration on Flame Color Purity. The Formulations Are in Wt. % and the Color Coordinates Are Based on the C.I.E. 1931 System.

Red				
DHT	AP	Sr-BT4w	x	y
47.5	47.5	5.0	0.697	0.291
48.0	48.0	4.0	0.699	0.292
48.5	48.5	3.0	0.687	0.295
49.0	49.0	2.0	0.685	0.290
49.5	49.5	1.0	0.649	0.318
49.75	49.75	0.5	0.597	0.356
Blue				
BTAw	AP	Cu-BT2w	x	y
46.25	46.25	7.5	0.179	0.115
47.5	47.5	5.0	0.177	0.108
48.5	48.5	3.0	0.182	0.113
49.1	49.1	1.8	0.193	0.128
49.5	49.5	1.0	0.215	0.157
Green				
BTAw	AP	Ba-BT4w	x	y
25.0	50.0	25.0	0.204	0.693
32.5	50.0	17.5	0.171	0.731
37.5	50.0	12.5	0.182	0.705
45.0	50.0	5.0	0.196	0.700
47.5	50.0	2.5	0.228	0.662

The effect of varying the concentration of metal salt on flame color purity was measured for red, blue and green high-nitrogen flames. The experimental color coordinates for the three color series are found in Table 8. Figure 7 gives detailed placement of these coordinates on the C.I.E. 1931 Chromaticity Diagram. For red colored flames, the transition where the color rapidly deteriorates with decreasing amount of Sr-BT4w is approximately 2 wt. %. Although formulations within the 2 to 5 wt. % metal colorant range have similar color values (i.e., the same color purity), a 5 wt. % strontium formulation has a more intense color than that of the 2 wt. % formulation. For the blue series, formulations composed of 3 to 7.5 wt. % Cu-BT2w gave similar color values, and only with 1.8 wt. % copper salt did the color degrade only slightly. Statically burned copper-based blue stars had unaesthetic orange flame tips. However, the orange flame-tips disappear when the burning

stars are propelled through the air or burned in a nitrogen atmosphere. It is believed that the blue-emitting species, CuCl, is converted by atmospheric oxygen to CuO (orange-emitting) in the outer envelope of the flame. Burning a star in nitrogen atmosphere precludes the formation of CuO, and it may be that when a burning star is moving through the air, the flame envelope is too cool for CuO emission. Flame-tip chemistry is briefly discussed in a pyrotechnic treatise.^[19] The green series—five formulations of varying Ba-BT4w concentrations—shows that a fairly concentrated amount of barium salt (ca. 17.5 wt. %) is needed for the best possible color purity. However, a formulation composed of 25 wt. % Ba-BT4w has a color purity no better than that obtained from 5 wt. % Ba-BT4w. This degradation in color purity with formulations greater than 17.5 wt. % is attributed to the incandescence of solid barium products.

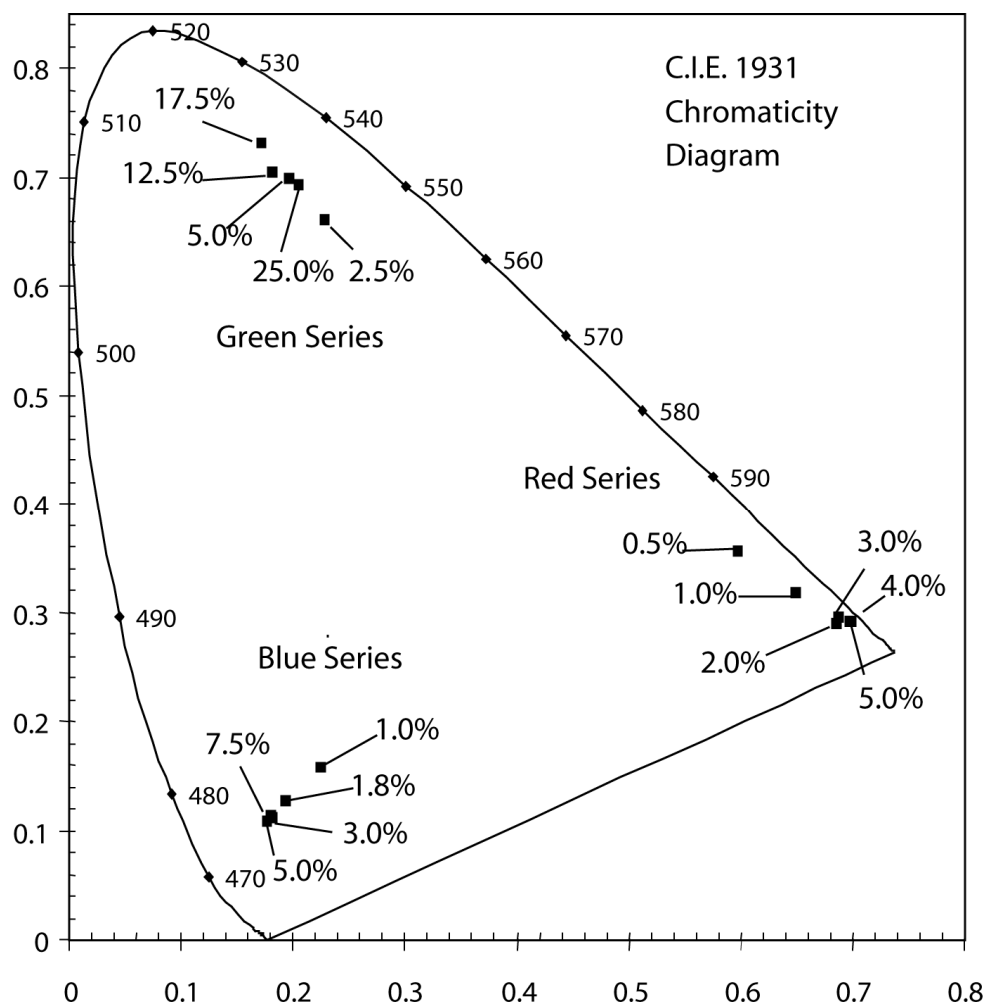


Figure 7. The same high-nitrogen color series taken from Table 8 are represented on a C.I.E. 1931 Chromaticity Diagram. These results demonstrate that color purity can still be maintained with unprecedented low levels of metal salts.

Conclusion

A number of high-nitrogen fuels and salts were synthesized and investigated for their utility in low-smoke applications. It was found that mixtures of high-nitrogen fuels and oxidant ammonium perchlorate require only 1 to 7 wt. % metal colorants to achieve exceptionally pure flame colors. This level of metal content is considerably less than that found in traditional pyrotechnic formulations. The spectral data of a large variety of burning high-nitrogen formulations were gathered and converted into useful C.I.E. 1931 color coordinates. These results are reported together with those of several tradi-

tional pyrotechnic formulations. In addition, impact sensitivity testing was performed to provide baseline hazards of these high-nitrogen pyrotechnic ingredients, and thermogravimetric analysis was conducted to provide stability data.

Notes and References

- 1) Patent Pending.
- 2) Also known as Hz₂Tz.
- 3) D. E. Chavez and M. A. Hiskey, *Journal of Pyrotechnics*, No. 7, 1998, p 11.

- 4) B. M. Dobratz, *LANL Explosives Handbook. Properties of Chemical Explosives and Explosives Simulants*, National Technical Information Service, UCRL-52997, 1981.
- 5) H. J. Marcus and A. Remanick, *J. Org. Chem.*, Vol. 28, 1963, p 2372; US Patent 3,244,702, April 5, 1966.
- 6) D. E. Chavez and M. A. Hiskey, *J. Heterocyclic Chem.*, Vol. 35, 1998, p 1329.
- 7) TGA analyses were performed using a High Resolution Modulated TGA 2950 manufactured by TA Instruments.
- 8) The unit, %/min, or mass percent per minute, is used in this paper to describe mass loss rate.
- 9) N. A. Lange, *Lange's Handbook of Chemistry*, 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p 1432.
- 10) Adapted from a synthesis method described by R. A. Henry, Code 38505, Chemistry Division, Naval Weapons Center, China Lake, CA 93555 USA.
- 11) A large excess of sodium sulfide should be avoided since under acidic conditions colloidal sulfur can be formed and contaminate the product.
- 12) Summit Pharmaceuticals Corp., 400 Kelby Street, Fort Lee, NJ 07024 USA. Phone: (201) 585-9004, Fax: (201) 585-9653.
- 13) W. P. Norris and R. A. Henry, *J. Org. Chem.*, Vol. 29, 1964, p 650.
- 14) T. K. Highsmith, R. M. Hajik, R. B. Wardle, G. K. Lund and R. J. Blau, Methods for Synthesizing and Processing bis-(1(2(H)-tetrazol-5-yl)-amine, US Patent 5,468,866, Nov. 21, 1995; "Example 27. In a 22 liter flask equipped with a mechanical stirrer, nitrogen inlets, reflux condensers, and thermometer was placed 1848 g of boric acid and 840 g of sodium dicyanoamide in 4.6 liters of distilled water. To this solution was added 1296 g of sodium azide in 4.0 liters of distilled water. The reaction mixture was then refluxed 48 hours at which time a sample was taken, evaporated in a stream of nitrogen, and analyzed by ¹³C NMR. The hot solution was then pumped into a 5°C solution of 2.4 liters of water and 2.4 liters of concentrated HCl. The acidification was not allowed to exceed 15°C by the addition of ice as necessary to the acid solution. This was done in order to obtain small, amorphous particles. The precipitated BTA was collected by filtration. The solid was then washed by suspension in distilled water, stirring vigorously and subsequently refiltered. This process was repeated until the washings obtained had a pH of 3. The filtercake was then dried in vacuo at 60°C for several days. The product was obtained (1222 g) as a white buff solid which was pure by ¹³C NMR."
- 15) A. A. Shidlovskiy, *Principles of Pyrotechnics*, Mashinostroyeniye Press, Moscow, 1964, pp 182–186; T. Shimizu, *Fireworks. The Art, Science and Technique*, Pyrotechnica Publications, Austin, TX, 1981, pp 57–61; J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, New York, 1985, pp 150–163.
- 16) Singly recrystallized AP was made by dissolving 45 g commercial AP in 100 g boiling water, filtering hot, and cooling to 5°C to initiate precipitation. The crystalline solid was filtered and dried.
- 17) W. G. Meyerriecks, private communication, December, 1998.
- 18) B. Fortner and T. E. Meyer, *Number by Colors: A Guide to Using Color to Understand Technical Data*, TELOS, The Electronic Library of Science, Santa Clara, CA, 1997.
- 19) K. L. and B. J. Kosanke, *Lecture Notes for the Chemistry of Pyrotechnics*, Journal of Pyrotechnics, Inc., 1996, p VII-40. Also *Notes for Pyrotechnic Chemistry*, Journal of Pyrotechnics, Inc., 1997.

Fragmenting Steel Firework Mortar Tubes

S. G. Myatt* and M. R. Edwards**

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

**Department of Materials and Medical Sciences, Cranfield University,
RMCS Shrivenham, Swindon, SN6 8LA, United Kingdom

ABSTRACT

Firework maroon shells were exploded inside mild steel spiral wound mortar tubes with various mitigation systems in place. It was found that the number of fragments was substantially reduced when the tube was prevented from expanding freely by sandbags or by burial of the tube in sand. For mitigation systems that allowed free expansion of the tube, the number of fragments was similar to that produced when no mitigation was employed. Mitigation systems should extend to the top of the tube to prevent fragments from hitting spectators or operators at displays.

Keywords: firework, mortar tube, safety, fragment, mitigation, steel, sandbag

Introduction

When steel tubes are used to launch firework shells a major hazard occurs when the lifting charge of the shell fails to ignite and the bursting charge explodes when the shell is still in the mortar tube. This can cause the mortar tube to fragment resulting in the production of energetic projectiles. Such accidents have resulted in fatalities in Japan^[1] and the United States^[2] and severe injuries to operators and spectators.^[1,3-5] An accident of this type occurred at the Glasgow Garden Festival in 1988, as a result of which a firework display operator had to have his leg amputated. Six spectators were also injured.^[1] Following this, the UK Health and Safety Executive initiated research into mortar fragment hazards.

Previous work in the literature has shown that the premature explosion of maroon shells

in 0.8 mm wall thickness mild steel tubes can cause fragments with masses of up to 200 g to be produced^[6] and that they can be projected up to 120 metres.^[7] In addition, other work^[8] has shown that mortar fragments with masses of up to 100 g are capable of travelling at 512 m/s. Fragments of this type have sufficient energy to cause severe penetrative injuries while larger, slower moving fragments could also cause injuries by blunt trauma.^[9] Clearly, it would be unacceptable if such fragments hit spectators at a display. Therefore, methods are needed to ensure that the fragments are prevented from reaching spectators or operators. Methods in current use include the implementation of large safety distances, remote firing, burying the mortar tubes in the ground, containing them within sand- or earth-filled barrels, or surrounding them with sandbags. A survey of current UK fireworks practice that covered mitigation methods^[10] indicated a fairly extensive use of partially buried mortar tubes, especially for the larger calibres, but only rarely was the exposed portion of the mortar tube protected.

The aim of the present work is to compare the effectiveness of two 'contact' mitigation methods (sandbags and burial in sand-filled barrels), and a system using tyres, which allows free expansion of the mortar tube, as a means of mitigating the effects of fragments created by the explosion of shells in spiral wound steel mortar tubes. Tyres are a recognised form of screening to reduce projectile hazards in the demolition industry.^[11,12]

Experimental

Mass and linear distance measurements made during this work can be traced to National Standards.

The shell and mortar tube combinations that had been shown to produce the largest number of fragments in previous work were used.^[13] Most trials used 75 and 152 mm calibre spiral wound tubes with maroon shells fired in them. A few firings were carried out in 160 mm tubes with effect multibreak shells. In all cases the lifting charge was removed, the shell inverted, and suspended in the mortar tube at the desired height. The spiral wound tubes were made from a 0.07% carbon steel, according to British Standard 1449, with mild steel base plates welded to the tubes using a Metal Inert Gas (MIG) technique. Lengths and wall thicknesses of mortar tubes are given in Table 1.

Table 1. Mortars Used in Fragmentation Trials.

Calibre (mm)	Wall Thickness (mm)	Length of Mortar Tube (mm)
75	1.65	600
152	2.00	1000
160	2.00	1000

The mitigation systems used were as follows:

Tyres: Used car tyres, intended to fit 13 inch (330 mm) diameter rims, were stacked on top of each other and tied together. Mortar tubes of 75 or 152 mm calibre were placed, free standing, centrally inside the stack. Tests in which the 75 mm shell was suspended half way up the mortar tube had tyres extending to the top of the tube or to the top of the shell. For shells fired half way up 152 mm tubes, the tyres extended to the top of the tube.

Barrels: Details of the barrels used are given in Table 2. Mortars were positioned on the major axis and sand was then placed in the barrels in layers 30 cm deep and tamped after each layer was added. The process was repeated until the sand was 20 mm from the top of the barrel for the 75 mm mortar tubes and flush with the top of the barrel for the 152/160 mm tubes. Trials were also carried out with mortar tubes placed in empty 220–225 litre barrels and 70 litre bins (Table 2). Sufficient sand (<10 cm) was put in the base of the barrel to allow the mortar tubes to remain upright. The distance from the outside of the tube to the inside of the barrel wall was 230 mm for 225 litre barrels with 75 mm tubes, 190 mm for 225 litre barrels with 152/160 mm tubes, and 150 mm for 70 litre bins with 75 mm tubes.

Table 2. Barrels used in Mitigation Trials.

Description of Barrel	Material	Height (mm)	Diameter (mm)	Volume (litres)	Wall Thickness (mm)
Extrusion blow moulded drum with compression moulded L-shaped rings top and bottom	HDPE	928.00	572.00	220.00	2.3
Extrusion blow moulded drum with two lifting/rolling hoops. Open top	HDPE	900.00	560.00	225.00	8.0
Electrically welded side seam, two pressed out rolling hoops.	Mild steel	965.00	585.00	225.00	1.0
Extrusion blow moulded plastic bin. Open top	HDPE	635.00	370.00	70.00	5.1

Sandbags: Woven polypropylene bags (lay-flat dimensions of 770 mm length × 335 mm width) were filled with sand and packed around the mortar tube. The bags were either stacked to a height level with the top of the tube or to a height level with the top of the shell, which was suspended half way up the tube. The distance from the outside of the mortar tube to the outside edge of the sandbag mitigation system was 240 mm, which was comparable with trials using 225 litre barrels.

Some of the sandbag and barrel mitigation experiments were carried out twice, once using dry sand and once using damp sand. The damp sand had a moisture content in the range 8.5–12.2% (w/w), the comparable range for dry sand was 0.4–2.6% (w/w). Moisture contents were determined gravimetrically.

Tests were carried out in the middle of a 4 m square Blast Cell which had wood-lined walls to trap high velocity fragments. To determine the effectiveness of the mitigation systems, fragments were classified as either penetrating into the wood lining of the Blast Cell, lying on the floor of the Blast Cell or being trapped in the

mitigation system.

Results

Results for the 75 mm mortar tubes with various methods of mitigating the fragments are shown in Table 3 [at the end of the article] and Figure 1. These indicate that:

1. The number of fragments was greatly reduced by mitigation systems in intimate contact with the mortars, such as sandbags or sand-filled barrels, while the reduction in number of fragments was much less in the case of systems which had an air gap between the mortar tube and the mitigation systems, such as tyres or empty barrels.
2. The effectiveness of the mitigation system in retaining fragments was increased when it covered the full length of the tube, rather than extending only to the top of the shell.
3. The most hazardous situation occurred when a shell was exploded at the top of the mortar tube because more fragments escaped from the mitigation system with sufficient energy to penetrate into the wood lining of the Blast Cell.

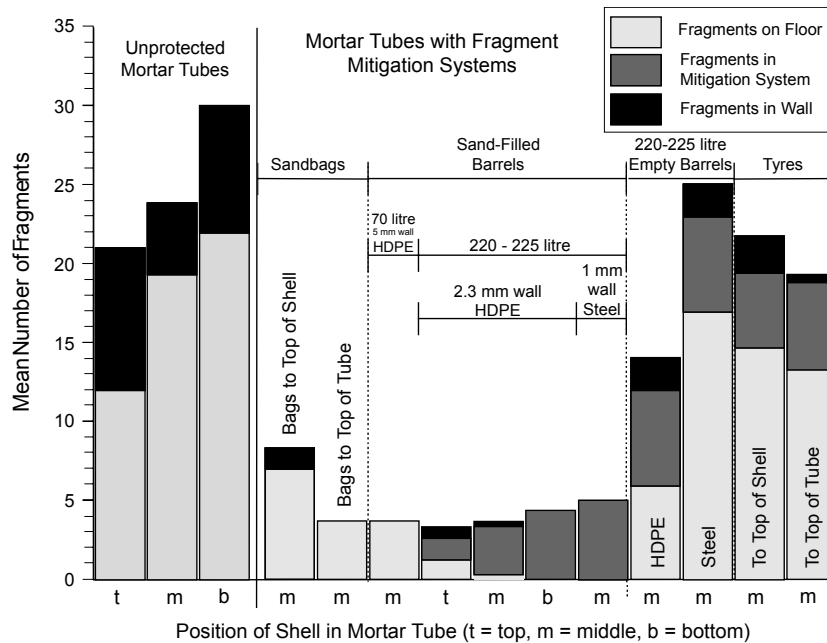


Figure 1. Distribution of fragments generated from 75 mm calibre spiral wound steel mortar tubes when maroon shells are exploded in them with various mitigation systems in place.

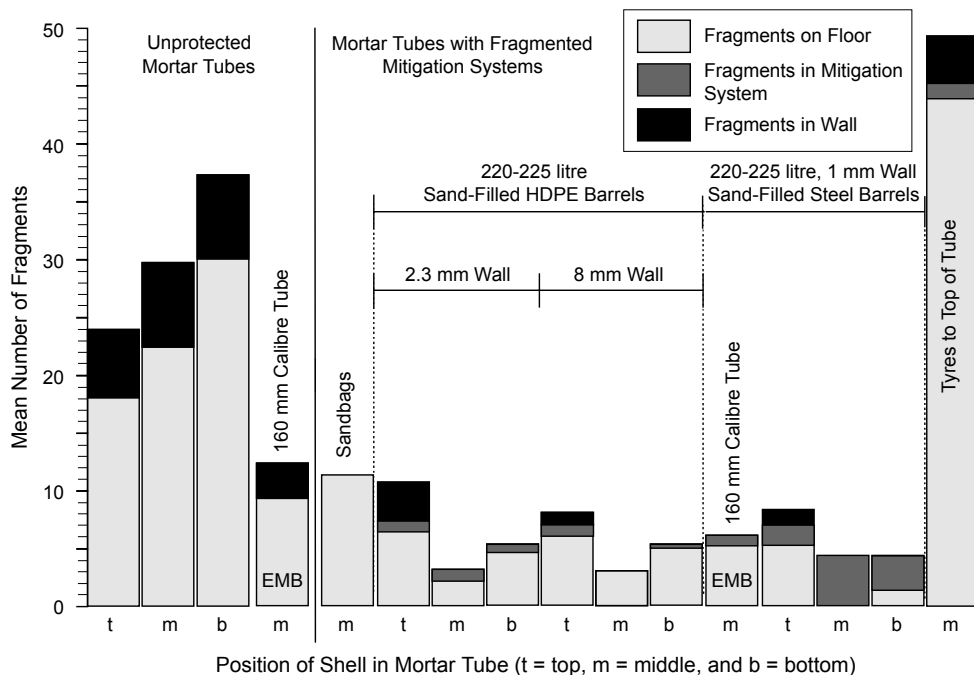


Figure 2. Distribution of fragments generated from 156/160 mm calibre spiral wound steel mortar tubes when maroon and effect multibreak shells (EMB) are exploded in them with various mitigation systems in place.

Similar results were found for maroon shells fired in 152 mm mortar tubes (Table 4 [at end of article] and Figure 2).

The effect of moisture content on the effectiveness of sand mitigation systems was unclear.^[13] 75 mm tube trials showed an increase in the mean number of fragments generated when dry sand was used (4.7 fragments compared to 3.7 fragments for damp sand), while the 152 mm tube tests showed the reverse trend (11.3 fragments for damp sand compared to 6.7 fragments for dry sand). Since these data are inconclusive, and most sand used in the UK for this purpose would be damp, only the results from ‘damp sand’ trials have been included in this paper.

Tests with the 70 litre bin, using a maroon shell in a 75 mm mortar tube, showed that the mean number of fragments was reduced to 3.7, but that the plastic bin was totally destroyed. Inspection of the internal surfaces of the bin showed no witness marks. This indicated that the fragments from the mortar tube had not penetrated the 150 mm of sand between the tube and

the bin wall, before the bin was destroyed by the pressure from the explosion.

Discussion

Previous work^[13] has shown that when maroon shells are exploded in unmitigated 75 and 152 mm calibre mortar tubes, many small fragments of masses less than 50 g, and a few large fragments of masses greater than 400 g, are produced. Often the larger fragments originate from the baseplate or the main tube remote from the igniting shell. Similar tests using effect multibreak shells in 160 mm calibre spiral tubes produced substantially fewer fragments which were distributed approximately equally between these two mass groups.

Any fragment mitigation system must be able to cope with two distinct types of fragment:

1. fast-moving fragments (up to 512 m/s),^[8] usually with masses less than 100 g,
2. slower fragments (up to 44 m/s),^[8] often with masses greater than 400 g.

The former will present a hazard to both operators and spectators, while the latter are only likely to be hazardous to operators working within the safety zone between the fireworks and the spectators. To reduce hazards, a mitigation system can either catch the fragments formed by the pressure of the bursting charge, or it can both modify the fragmentation process and catch the fragments formed. Of the systems studied, empty barrels and tyres are systems that merely catch fragments, while sandbags, sand- or earth-filled barrels or, by implication, burial in the ground, are systems that modify the fragmentation behaviour, since they all reduce the number of fragments considerably (Figures 1 and 2).

If the fragmentation of an unmitigated tube is considered, the tube will expand in diameter as the internal pressure rises. When the tensile strength of the tube material is exceeded, which will occur at many points on the tube surface more or less simultaneously, the tube will fragment. For an unmitigated tube there will be little resistance to this expansion from the presence of the air outside the tube, whereas for a tube buried in sand there will be resistance to tube expansion from the mass of the sand in contact with the expanding tube. Thus there will be a smaller tensile strain in the tube, and fragmentation will start from fewer origins, creating a smaller number of fragments. Therefore, mitigation systems based on empty barrels or tyres will allow the tube to expand freely, and so the number of fragments produced with these mitigation systems will be similar to those produced in the absence of any mitigation system (Figures 1 and 2). If a tube is buried to anything less than its top, there is the possibility of the charge bursting in the unburied part of the mortar tube, which will produce a large number of fragments that will be free to fly unhindered by sand or soil. Repeat firings from mortar tubes that have been buried in the ground can cause a 'pile driving' effect, which causes the tube to be driven further into the ground with each firing.^[14] In such cases, mitigation of the mortar by burying its full length in the ground would allow soil to fall into the tube as subsequent firings took place. The extent of 'pile-driving' could be reduced by increasing the area over which the recoil force acts (e.g., by placing

wooden boards under the base of the mortar tube, or by using a wide collar at the tube neck which rests on the soil surface). This could be designed to be removable for transport purposes. Where 'pile-driving' is thought to be a problem, a hybrid mitigation system of partial burial and sandbagging of the portion of the mortar that protruded above the ground may be appropriate providing that the sandbags are placed in contact with the mortar tube to act as a barrier to tube expansion. The number of fragments is then likely to be reduced in a similar way to that achieved by full burial (Tables 3 and 4).

Mitigation systems should ideally be reusable. Since sandbags and 70 litre bins of sand were destroyed in the tests, this suggests that such mitigation systems will not be as suitable as either burying the full length of the mortar tube or using a large barrel. However, sandbags do have the advantage that they can be prepared before the day of the display and placed easily around the mortar tube. Also, Figures 1 and 2 indicate that although the sandbags were destroyed during the tests, no fragments were retrieved from the Blast Cell wall. This indicates that they have an effectiveness at reducing fragment travel comparable to that of sand filled barrels.

Conclusions

1. Steel mortar tubes should be surrounded by a mitigation system that covers the full length of the tube. One exception would be when spectators and operators firing the display are positioned beyond the foreseeable fragment travel range.
2. Mitigation systems such as sand-filled barrels and sandbags reduce the number of fragments as well as catching the fragments that are produced. These systems are therefore to be preferred to systems such as tyres or empty barrels, where there is no effect on the number of fragments generated.

Acknowledgements

The authors would like to thank Dr. R. K. Wharton, Head of Explosives Section, Health and Safety Laboratory, for guidance during the course of the work, and Mr. B. G. P. Freeder, Mr. S. A. Formby, Mr. I. M. Howard and Mr. E. Mellor, all of the Health and Safety Laboratory, for experimental assistance. They also thank the Health and Safety Executive for financial support of the project and Dr. A. W. Train of the Explosives Inspectorate of the Health and Safety Executive for his advice.

References

- 1) R. K. Wharton, "Areas for Future Research Identified by Recent Accidents in the Pyrotechnics Industry", *Proc. 16th International Pyrotechnic Seminar*, Jönköping, Sweden, 1991, pp 514–530.
- 2) Anonymous, "Shooter Fatality in Florida", *Fireworks Business*, No. 126, 1994, p 3.
- 3) D. Harmon, "Exploding Insight", *American Fireworks News*, No. 133, 1992, p 2.
- 4) Anonymous, "PGI Convention Chairman Injured in Display Incident", *Fireworks Business*, No. 126, 1994, p 3.
- 5) B. Saltzman, "Expect the Unexpected", *American Fireworks News*, No. 161, 1995, pp 1–2.
- 6) E. Contestabile, R. A. Augsten, R. R. Vandebeek, T. R. Craig, D. Wilson and E. Nagy, Accompanying debris distribution graphs from "Evaluation of Fireworks Mortars", *Canadian Explosives Research Laboratory, Mining Research Laboratories CANMET*, Energy, Mines and Resources, Canada, Report MRL91-051(TR), 1991.
- 7) E. Contestabile, R. A. Augsten and T. R. Craig, "Evaluation of Firework Mortars", *Proc. 1st Intl. Symp. on Fireworks, Montreal, Canada*, 1992, pp 46–78.
- 8) S. G. Myatt, "Determination of the Velocity of Fragments Produced from Exploding Firework Maroon Shells", *J. Pyrotechnics*, No. 8, 1998, pp 43–51.
- 9) M. R. Edwards, S.G. Myatt and S. Ellis, "The Hazards Posed by Fragments from Ruptured Steel Mortar Tubes", *J. Pyrotechnics*, No. 9, 1999.
- 10) S. G. Myatt and R. K. Wharton, "A Survey of Factors Relating to the Use of Mortars at Firework Displays in the UK", *Pyrotechnica*, Vol. XVI, 1995, pp 50–56.
- 11) Manufacturer's literature W. C. D. Jowenko, Explosieve Demolitie, Markt 15, 4331 L J Middelburg, The Netherlands.
- 12) Manufacturer's literature The American Blasting Mat Co., 737 E 23rd Street, Norfolk, VA 23504, USA.
- 13) S. G. Myatt, "An Experimental Study of the Fragmentation of Steel Firework Mortar Tubes, and Methods of Reducing the Hazard", *MPhil Thesis*, Cranfield University, 1996/7.
- 14) K. L. Kosanke, Private communication Kosanke/Wharton.

Table 3. Fragment Data from 75-mm Calibre Steel Mortar Tubes When Shells Have Been Exploded in Them While Using Different Mitigation Systems.

Position of Shell in Mitigation System	Type of Mitigation System Used	Mean Number of Fragments			Mean Mass of Fragments (g)	Mean Percentage Mass of Fragments		
		Total	In Wall	On Floor		In Mitigation	In Wall	On Floor
75 mm maroon shell at top	Unmitigated	21.00	9.00	12.00	2471.00	6.60	93.40	n/a
	220–225 litre. 2.3 mm wall thickness HDPE barrel	3.30	0.70	1.00	2356.00	1.00	3.60	95.40
75 mm maroon shell at middle	Unmitigated	23.80	4.50	19.30	2458.00	5.80	94.20	n/a
	Empty 220–225 litre. 1.0 mm wall thickness steel barrel	25.00	2.00	17.00	2350.00	1.00	48.90	50.10
	Empty 220–225 litre. 2.3 mm wall thickness HDPE barrel	14.00	2.00	6.00	2352.00	1.30	6.80	91.90
	Tyres to top of shell	21.70	2.30	14.70	2290.00	1.50	70.40	28.10
	Tyres to top of tube	19.30	0.50	13.30	2277.00	0.60	51.40	48.00
	Sandbags to top of shell	8.30	1.30	7.00	2311.00	1.70	98.30	n/a
75 mm maroon shell at bottom	Sandbags to top of tube	3.70	0.00	3.70	2359.00	0.00	100.00	n/a
	220–225 litre. 2.3 mm wall thickness HDPE barrel	3.70	0.30	0.30	2375.00	0.30	14.50	85.20
	220–225 litre. 1.0 mm wall thickness steel barrel	5.00	0.00	0.00	2270.00	0.00	0.00	100.00
	70 litre. 5.1 mm wall thickness HDPE bin	3.70	0.00	3.70	2379.00	0.00	100.00	0.00
75 mm maroon shell at bottom	Unmitigated	30.00	8.00	22.00	2450.00	8.20	91.80	n/a
	220–225 litre. 2.3 mm wall thickness HDPE barrel	4.30	0.00	0.00	2375.00	0.00	0.00	100.00
n/a = not applicable. For unmitigated firings no fragments can be retained in the mitigation system, while for sandbagging the mitigation system is destroyed leaving fragments on the floor or in the walls								

Table 4: Fragment Data from 152/160 mm Calibre Steel Mortar Tubes When Shells Have Been Exploded in Them While Using Different Mitigation Systems.

Position of Shell in Mitigation System	Type of Mitigation System Used	Mean Number of Fragments			Mean Mass of Fragments (g)	Mean Percentage Mass of Fragments		
		In Wall		On Floor		In Wall	On Floor	In Mitigation
		Total	In Wall	On Floor		In Wall	On Floor	In Mitigation
152 mm maroon shell at top	Unmitigated	24.00	6.00	18.00	9490.00	5.20	94.80	n/a
	220-225 litre 2.3 mm wall thickness HDPE barrel	10.70	3.30	6.30	10028.00	5.60	13.70	80.70
	220-225 litre 8.0 mm wall thickness HDPE barrel	8.00	1.00	6.00	10171.00	1.20	17.60	81.20
	220-225 litre 1.0 mm wall thickness steel barrel	8.30	1.30	5.30	10070.00	1.40	14.10	84.50
152 mm maroon shell at middle	Unmitigated	29.70	7.30	22.30	9357.00	3.30	96.70	n/a
	Tyres to top of tube	49.30	4.00	44.00	9927.00	0.70	51.70	47.60
	Sandbags to top of tube	11.30	0.00	11.30	9669.00	0.00	100.00	n/a
	220-225 litre 2.3 mm wall thickness HDPE barrel	3.70	0.00	2.70	9700.00	0.00	74.30	25.70
152 mm maroon shell at bottom	220-225 litre 8.0 mm wall thickness HDPE barrel	3.00	0.00	3.00	9768.00	0.00	100.00	0.00
	220-225 litre 1.0 mm wall thickness steel barrel	4.30	0.00	0.00	9916.00	0.00	0.00	100.00
	Unmitigated	37.30	7.30	30.00	9285.00	8.20	91.80	n/a
	220-225 litre 2.3 mm wall thickness HDPE barrel	5.30	0.00	4.70	9664.00	0.00	97.00	3.00
160 mm multibreak shell in middle	220-225 litre 8.0 mm wall thickness HDPE barrel	5.30	0.00	5.00	9871.00	0.00	74.10	25.90
	220-225 litre 1.0 mm wall thickness steel barrel	4.70	0.00	1.70	9492.00	0.00	33.80	66.20
	Unmitigated	12.30	3.00	9.30	10841.00	5.40	94.60	n/a
	220-225 litre 1.0 mm wall thickness steel barrel	6.00	0.00	5.00	10956.00	0.00	57.80	42.20
n/a = not applicable. For unmitigated firings no fragments can be retained in the mitigation system, while for sandbagging the mitigation system is destroyed leaving fragments on the floor or in the walls								

Combustion of Ti/C Pyrolants

Michinori Takizuka,* Toshio Onda,* Takuo Kuwahara,** and Naminosuke Kubota***

* Propellants, Explosives & Pyrotechnics Division, Hosoya Kako Co., Ltd.,
Sugao 1847, Akiruno, Tokyo 197-0801, Japan

** Research & Development Center, Aerospace Division, Nissan Motor Co., Ltd.
Fujiki 900, Tomioka 370-2398, Japan

*** Mitsubishi Electric Corporation, Kamimachiya 325, Kamakura 247-0065, Japan

ABSTRACT

The thermochemical characteristics of pyrolants composed of titanium (Ti) and carbon (C) were studied in order to develop high energy release materials used for igniters and fireworks. Since the Ti and C reaction occurs only at temperatures above 1200 K, polytetrafluoroethylene (PTFE) was mixed with the Ti/C pyrolants as an oxidizer. Various types of experiments were performed to gain information on the role of each ingredient. The results, measured by differential thermal analysis and thermal gravimetry, indicated that PTFE melts at about 605 K and reacts exothermically at about 830 K with Ti. The burning rate of the pyrolants increases as the mixing ratio of Ti and C approaches the stoichiometric ratio, (i.e., the burning rate increases as the adiabatic flame temperature increases within the range of the samples tested). Since the reaction starts from the surface of the Ti particles, the burning rate increases as the total surface area of the Ti particles increases.

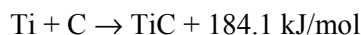
Keywords: pyrolant, titanium, carbon, polytetrafluoroethylene, PTFE

Introduction

Energetic materials composed of metal particles and oxidizing materials, the so-called pyrolants, are used for igniters and fireworks. Typical pyrolants are made with titanium (Ti), zirconium (Zr), magnesium (Mg), or aluminum (Al) as fuel components and crystalline oxidizers such as potassium perchlorate (KClO₄), po-

tassium nitrate (KNO₃), or ammonium perchlorate (NH₄ClO₄).

Polytetrafluoroethylene (PTFE) consisting of -C₂F₄- is a typical polymeric oxidizer for metal fuels. PTFE decomposes thermally and produces F₂, which acts as an oxidizer. The mixture of Mg and PTFE is a typical pyrolant.^[1-4] It is known that Ti reacts with carbon to form titanium carbide, TiC, as



accompanied with high heat release.^[5,6] Based on a theoretical computation, the adiabatic flame temperature is 3460 K for the stoichiometric ratio of Ti and C. However, this reaction occurs only at temperatures well above 1200 K. Accordingly, to initiate the reaction requires that a high heat flux be given to the pyrolants.

Since the reaction between Ti and PTFE occurs with relatively low ignition energy, the addition of PTFE aids the ignition of the mixture of Ti and C particles. The heat produced by the reaction between Ti and PTFE is provided to the remaining Ti, which then reacts with C in the high temperature region.

Experimental Methods

Formulation of Ti/C Pyrolants

Four types of pyrolant samples were made to determine the effect of the mass fraction of Ti, $\xi(\text{Ti})$, on the burning rates of this class of pyrolants. The mass fraction of PTFE, $\xi(\text{PTFE})$, mixed within the Ti/C pyrolant samples was $\xi(0.091)$, which included a small amount of Viton: C₅H_{3.5}F_{6.5} (VT). The VT was used as a binder for the Ti, C, and PTFE particles. The

size of Ti, C, and PTFE particles were 20, 0.5, and 5 μm in diameter, respectively. Each pyrolant sample was prepared as a pressed pellet. The Ti and C particles with PTFE particles were placed in a cylindrical-shaped container made of steel and pressed with a hydraulically operated piston. The piston pressure was about 200 MPa in order to make the density of the pyrolant pellets more than 0.95 theoretical density. The size of each pellet was 10 mm in diameter and 10 mm in length. The chemical compositions of the pyrolant samples tested are listed in Table 1.

Table 1. Chemical Compositions of the Ti/C Pyrolants Tested in this Study.

$\xi(\text{Ti})$	Chemical Composition (mass %)		
	Ti	C	PTFE/T
$\xi(0.8)$	72.7	18.2	9.1
$\xi(0.6)$	54.5	36.4	9.1
$\xi(0.4)$	36.4	54.5	9.1
$\xi(0.2)$	18.2	72.7	9.1

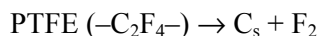
Thermal Decomposition and Burning Rate Measurements

The thermal decomposition process of the Ti/C pyrolants was measured using thermal gravimetry (TG) and differential thermal analysis (DTA). Both experiments were operated with various heating rates (0.083 K/s to 0.25 K/s) in argon atmosphere at 0.1 MPa. The mass of the sample used for each test was approximately 2.0 mg and was kept in a cell made of non-reactive quartz.

The burning rate of the Ti/C pyrolants was measured with a chimney-type burner that was pressurized with nitrogen gas. Each pressed pellet was set on a holder in the burner and was ignited from the top. The ignition was accomplished by using an electrically heated nichrome wire. The regressing surface was recorded with a high-speed video camera through a transparent quartz window that was mounted on the side of the burner. The burning rate was obtained from the recorded video tape.

Results and Discussion

Figure 1 shows the result of the TG and DTA experiments (heating rate of 0.25 K/s) of the Ti/C pyrolant $\xi(0.8)$ sample done in an argon atmosphere. An exothermic reaction initiated at 805 K and terminated at 850 K. The peak exothermic temperature was observed at 837 K. The mass loss started at the same temperature as the onset of the exothermic reaction (805 K). The mass loss terminated at about 10% at 850 K when the observed exothermic reaction terminated. No thermal changes or mass loss changes were observed above 850 K within the range of the temperature tested. The results indicate that the observed mass loss is due to the thermal decomposition of PTFE as



This thermal decomposition probably includes some oxidation reaction of F_2 and Ti, which is considered by the observed exothermic reaction.^[1]

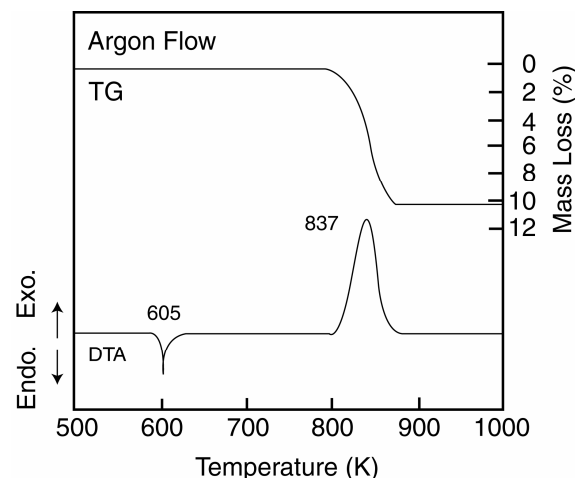


Figure 1. Thermal decomposition of Ti/C pyrolant $\xi(0.8)$ with PTFE in an argon atmosphere (heating rate of 0.25 K/s).

Figure 2 shows an Arrhenius plot, the relationship between the reciprocal temperature of the exothermic peak temperature versus heating rate, of the DTA experiments. The results indicate that the peak temperature increased linearly as the heating rate increased in the log (recipro-

cal temperature) versus log (heating rate) plot. The activation energy of the observed exothermic reaction and the mass loss reaction was determined to be 210 kJ/mol for all samples tested, $\xi(0.2)$ to $\xi(0.8)$, in this study.

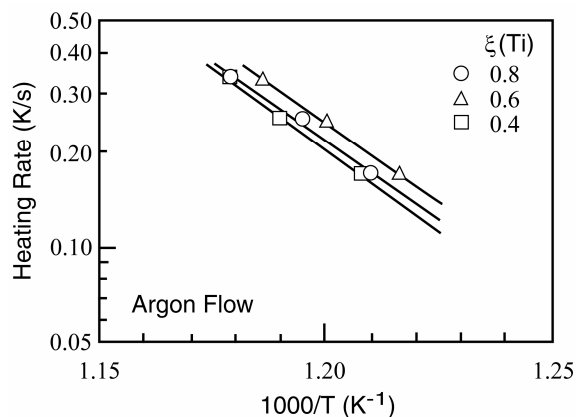


Figure 2. Arrhenius plot of DTA exothermic peak temperature.

The burning rate increased linearly in the log (pressure) versus log (burning rate) plots for the pyrolants of both $\xi(0.6)$ and $\xi(0.8)$ as shown in Figure 3. The pressure exponent of burning rate n defined in $r = a \cdot p^n$ was determined to be relatively independent of $\xi(\text{Ti})$, $n = 0.45$ for $\xi(0.6)$ and $n = 0.40$ for $\xi(0.8)$. Though the burning rate increased as $\xi(\text{Ti})$ increased at pressure of 0.1 MPa, the burning rate of the pyrolant $\xi(0.4)$ was very low, and no self-sustaining combustion occurred when the pyrolant $\xi(0.2)$ was ignited. The self-sustaining combustion limit was determined to be about $\xi(\sim 0.3)$ at pressures below 1.0 MPa.

The burning rate was also dependent on the particle size of Ti mixed within the pyrolants. As shown in Figure 4, the burning rate of the pyrolant composed of Ti particles of 20 μm in diameter was higher than that for particles of 50 μm in diameter at 0.1 MPa in the $\xi(\text{Ti})$ range tested. This increased burning-rate effect appeared as $\xi(\text{Ti})$ increases. It is evident that the reaction of Ti occurs at the surface of each Ti particle. Thus, the reaction of Ti and C is considered to be dependent on the total surface area of Ti particles, $\zeta(\text{Ti})$, mixed within the pyrolant. Figure 5 shows the results of the relationship

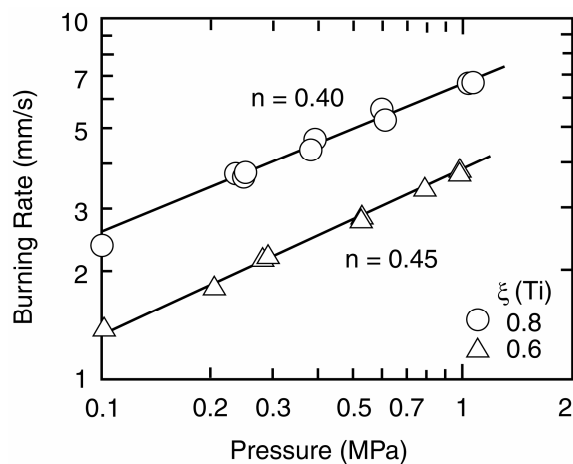


Figure 3. Burning rate characteristics of Ti/C pyrolants as a function of pressure and $\xi(\text{Ti})$.

between the burning rate and $\zeta(\text{Ti})$ at 0.1 MPa. The burning rate increased as $\zeta(\text{Ti})$ increased when the same sized Ti particles were used. In addition, the burning rate appeared to be high when large sized Ti particles were used at the same $\zeta(\text{Ti})$.

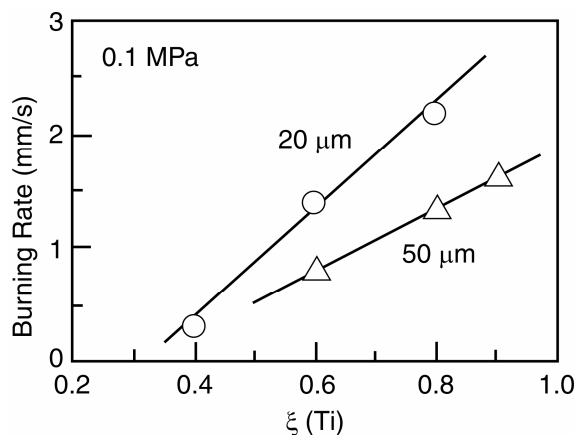


Figure 4. Burning rate characteristics of Ti/C pyrolants as a function of $\xi(\text{Ti})$ and the particle size of Ti.

The combustion process of the pyrolants was observed by using a high-speed video camera. Though whitish-yellow flames were seen on and above the burning pellet $\xi(0.8)$, the light emission from the combustion product decreased as $\zeta(\text{Ti})$ decreased. Porous, agglomerated materi-

als were formed continuously above the burning pellets. TiC was found in the materials using an X-ray micro-analyzer. However, a quantitative analysis has not been done yet.

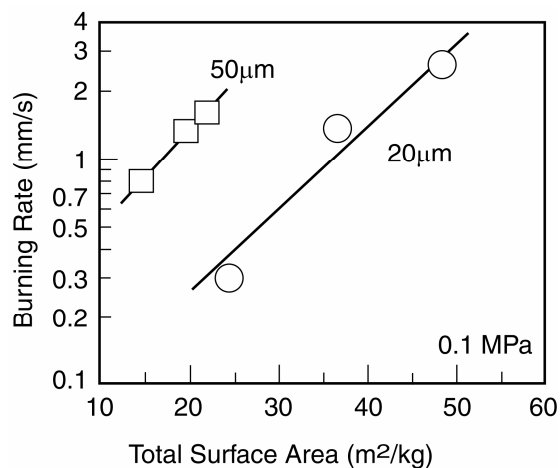


Figure 5. Burning rate characteristics of Ti/C pyrolants as a function of $\zeta(\text{Ti})$ and the particle size of Ti.

Conclusions

Stable and continuous burning of the pyrolants composed of Ti and C was obtained by the addition of a small amount of PTFE. The thermal analysis using TG and DTA indicated that the reaction between Ti and C with PTFE started an exothermic reaction at 805 K in an argon atmosphere. This is considered to occur due to the decomposition reaction of PTFE.

The burning rate measurements and the observation of the combustion process indicate that the burning rate of Ti/C pyrolants increases linearly in log (pressure) versus log (burning rate) for the mass fractions of Ti, $\xi(0.8)$ to $\xi(0.6)$

tested in this study. The pressure exponent of the burning rate was determined to be from 0.40 to 0.45 in the pressure range from 0.1 MPa to 1.0 MPa. The burning rate is dependent on the total surface area of the Ti particles mixed within the pyrolants. Though the detailed combustion mechanism of Ti/C pyrolants has not been identified, the results indicate that the addition of PTFE plays a significant role in the observed stable burning of Ti/C pyrolants.

References

- 1) N. Kubota and C. Serizawa, "Combustion of Magnesium/Polytetrafluoroethylene", *J. Propulsion and Power*, Vol. 3, No. 4, 1987, pp 303–307.
- 2) T. Kuwahara, S. Matsuo, and N. Shinozaki, "Combustion and Sensitivity Characteristics of Mg/TF Pyrolants", *Propellants, Explosives, Pyrotechnics*, Vol. 22, 1997, pp 198–202.
- 3) N. Kubota and C. Serizawa, "Combustion Process of Mg/TF Pyrotechnics", *Propellants, Explosives, Pyrotechnics*, Vol. 12, 1987, pp 145–148.
- 4) T. Kuwahara and T. Ochiai, "Burning Rate of Mg/TF Pyrolants", *Proceedings of the 18th International Pyrotechnics Seminar*, 1992, pp 539–549.
- 5) T. Kuwahara and M. Takizuka, "Combustion and Sensitivity Characteristics of Metal/TF Pyrolants (Mg/Ti/Zr/TF Pyrolants)", *Kayaku Gakkaishi*, Vol. 59, No. 1, 1998, pp 18–24.
- 6) M. Takizuka, T. Onda, T. Kuwahara, and N. Kubota, "Thermal Decomposition Characteristics of Ti/C/TF Pyrolants", AIAA Paper 98-3826, 1998.

Effect of Differing Charcoal Types Upon Handmade Lift Powder

Charles Wilson

223 Hillside Road, Evergreen, CO 80439, USA

ABSTRACT

Experimental production of charcoal via the retort method is discussed. Charcoals were made from various substances; of special interest were woods belonging to the Salicaceae (willow) family. Lift powders were made using these charcoals and their performance compared using a device for testing powders under conditions similar to those used for propelling fireworks aerial shells. The author found that handmade powders often outperformed commercially available powders in this application.

Keywords: Black Powder, charcoal type, performance testing

Introduction

Charcoal is the largest single variable in the performance of Black Powder. The author undertook the testing of different charcoals as a result of "pyrogolf"^[1] testing that was done during the Pyrotechnics Guild International (PGI) convention in Stephens Point, Wisconsin during 1995. Very similar research and testing has been done by others, particularly by Roger O'Neill^[2] and Stan Williams.^[3]

Charcoal Production Method

The retort method for destructive distillation was used to produce the various charcoals tested. The retort was fabricated from a medium sized steel pet food can, which can survive several distillations at red heat. Tabs were cut at three equidistant locations on its end and folded down to secure the end cover.

The can was prepared for distillation by packing it tightly with carbonaceous material. This minimized the volume of oxygen initially in the retort without impeding outflow of gases. When wood was used to produce charcoal, the bark was first removed. It was then sawed to a length about one inch less than the height of the retort and made into ½-inch thick sticks.

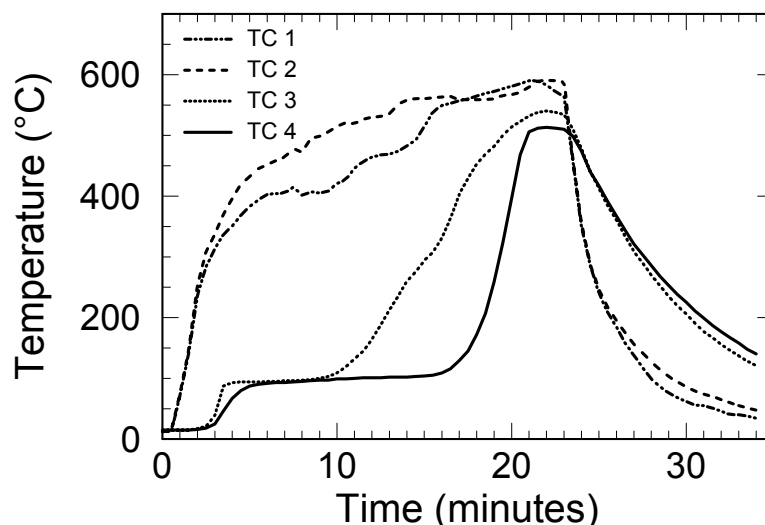
A large outdoor charcoal barbecue with a separate smoke compartment was used as a readily available heat source.

A moderately large fire was constructed using commercial charcoal briquettes, about 1 gallon by volume. Once they were completely red hot, the can was placed in a circle of briquettes, which were then piled up against the sides of the can. An extra briquette placed on top of the can also helped to distribute heat more evenly. The can was placed with its vented end down; its cover secured with the tabs. After a few minutes, the exhaust from the vent would ignite. This extra heat raised the retort temperature and completed the carbonization of the contents without oxygen.

Any leaks in the side of the can ruined the experiment because oxygen inside the can either consumed the contents, leaving little charcoal, or decreased the yield while increasing ash content of the charcoal.

If the retort was kept at red heat, the contents were turned into a high quality charcoal in about 35 minutes. When gasses from the retort stopped flaming, the can was removed from the heat by lifting it straight up and placing it on bricks with the vented end again facing down.

The resulting charcoal sticks were cool within an hour. At that point, the can was opened. Exposure to air can be unfortunate if the charcoal is pyrophoric enough to re-ignite at this point. The author has seen this happen on one



- TC1 – Thermocouple placed on metal surface of the can
- TC2 – Thermocouple placed just inside can
- TC3 – Thermocouple placed between center and edge of can
- TC4 – Thermocouple placed inside a stick of wood in the center of the can

Figure 1. Temperature profiles from retort during distillation.

occasion. For this reason, a small batch is safer than a large one.

Figure 1 shows the temperatures during a test run as measured by thermocouples placed in four locations. Peak temperature in center of can was 540 °C, and peak temperature in the wood sample tested was 513 °C. No sign of any exotherm was observed in these data, although many commercial charcoal producers see one beginning at about 275 °C.^[5] There is considerable evidence that temperature of pyrolysis affects the reactivity of the charcoal. In the author's experience, the appearance of the finished charcoal sticks is a good indication of the reactivity and performance of a given charcoal in lift powder. Good charcoal should have a smooth surface with few, if any, cracks or fissures.

This method relied upon the small size of both the retort and the carbonaceous material being pyrolyzed to control temperature. Batch to batch differences were obtained when the retort was not fully loaded. In addition, the cross sectional area and thermal insulating properties of a given material affected the quality of the charcoal. This was clearly seen in test results.

Starting Materials

Many species of wood were tested. Table 1 lists the common names and classification of trees considered for wood samples. In addition to various woods, Kentucky bluegrass clippings, cotton balls and cotton fabric were also used to make charcoal. The materials used to produce commercial charcoals are unknown.

Aspen grows abundantly in the Rocky Mountain region and is usually readily available as firewood. Maple used was the variety known as Silver Maple, widely grown as a shade tree in many parts of the US. Some species of trees used in this test grow in similar locations at elevations of up to 7500 feet. Narrow Leaf Cottonwood, Rocky Mountain Willow, and Thinleaf Alder can often be found growing within a few feet of each other.

Narrow Leaf Cottonwood (NLC) and Aspen are both members of the Willow family, in the Poplar group. In particular, NLC bears a strong resemblance to Black Willow, which explains the initial interest in its use. Other Poplar species may also be interesting but have not yet

Table 1. Classification of Trees Considered for Wood Samples.

Common Name	Family	Classification
Ailanthus (Tree of Heaven)	Ailanthus (Quassia)	<i>Ailanthus altissima</i>
Alder, Red	Birch	<i>Alnus rubra</i>
Alder, Thinleaf	Birch	<i>Alnus tenuifolia</i> Nutt.
Apple (Oregon Crabapple)	Rose	<i>Malus fusca</i>
Aspen	Willow	<i>Populus tremuloides</i> Michx.
Buckthorn, Alder	Buckthorn	<i>Rhamnus frangula</i> L. ^[4]
Buckthorn, Carolina	Buckthorn	<i>Rhamnus caroliniana</i>
Cherry (Chokecherry)	Rose	<i>Prunus virginiana</i>
Cottonwood, Narrow Leaf	Willow	<i>Populus angustifolia</i> James
Grape (unknown variety)	Grape	<i>Vitis</i>
Maple, Silver	Maple	<i>Acer saccharinum</i>
Serviceberry	Rose	<i>Amelanchier</i> Medic. sp.
Teak	Vervain	<i>Tectonia grandis</i>
Willow, Black	Willow	<i>Salix nigra</i>
Willow, Rocky Mountain	Willow	<i>Salix monticola</i> Bebb

been tried. Willow has historically been credited with producing the highest performance charcoal for Black Powder. Unfortunately, none of the current literature distinguishes among the various species of Willow that have been found effective. Two different species of Willow were tested for this article.

For comparison purposes, test data includes a powder made from charcoal supplied by Guy Lichtenwalter. This charcoal was made from an unidentified species of Willow (although thought to be Black Willow) from the Sierra foothills of California. This charcoal was produced using a larger retort method, which has been described elsewhere.^[6] A sample of Black Willow-based powder made by Jack Fielder was also tested. A sample of Aspen based powder and a second made from Skylighter^[7] “air float charcoal” was contributed by Steve Hubing.

It has been suggested that Maple^[8] is the source of charcoal currently used by Goex^[9] to make their Black Powder. Unfortunately, the species of Maple is unknown. One would suspect that wide variation in performance could be obtained between hard (i.e., Sugar and Black Maple) and softer species such as Silver Maple. This author and others have concluded that softer woods should produce the fastest charcoal for Black Powder lift.^[10]

Of particular interest was the Alder Buckthorn charcoal, much praised in nineteenth century Britain for its high gas and lower solids output. The British refer to this tree as a Dogwood.^[11] The author is indebted to Paul Judd for a sample of wood from the native American species of *Rhamnus*, Carolina Buckthorn, which was found growing in Oklahoma. He also contributed a sample of powder made from Carolina Buckthorn.

The French are known to have used Alder (*Alnus Glutinosa*) charcoal in Black Powder. Two varieties of Alder found in the US were used for this paper.

An interesting aspect of the various charcoals is the appearance of the powdered forms. Silver Maple turns into a very black substance, which in turn produces a very dark Black Powder. The cotton balls used in these trials were obtained at the grocery store. Yield from these was extremely low, and produced a whitish-gray charcoal. Cotton fabric was obtained from discarded T-shirts.

Don Kark provided Teak wood samples. The author is indebted to Rich Weaver for providing a sample of Ailanthus wood and for acting as a sounding board. Ailanthus was targeted as a likely candidate for lift quality charcoal because of the characteristics of fast growth and relatively low density. It is believed that Ailanthus

may never have been tried as a charcoal source for Black Powder in the US, since it has only recently been introduced here as an ornamental. It may be a good source of charcoal as the tree is now considered a weed.

Production of Lift Powder

Over the years, much debate has centered on the methods used to make high quality Black Powder. Lichtenwalter has consistently demonstrated that simple ball milling procedures can produce good powders, and the author used a similar approach for this work.

The author feels that the so-called CIA method is simply more trouble than it is worth. For those not familiar with this method, a good description may be found in McDowell's work.^[12]

Better ball mill designs^[13] and implementations than those used by the author will expedite powder manufacture.

To be made into lift powder, the charcoal sticks are first placed in a heavy-duty polyethylene bag. The bag is rapped with a light mallet until the sticks have been reduced to smaller chunks and dust. These were placed in a hobbyist rock tumbler along with a handful of 0.54-inch lead rifle balls. The tumbler jar used for these tests had a volume of less than one liter.

The tumbler was operated out of doors, well away from any structures. Twelve hours of milling may have been more than was necessary; however, it meshed with other daily activities. After twelve hours, the mill contents were separated with a sieve and the charcoal powder "air float" was put in a suitable container.

The next step was to produce an intermediate charcoal plus sulfur fuel powder using a weight ratio of three to two. A 160 gram batch thus contained 96 grams of charcoal and 64 grams of sulfur. The mill jar and media were cleaned before starting this phase. The charcoal and sulfur were also milled for twelve hours.

The last milling step combined the mixed fuel powder with granular potassium nitrate oxidizer. A weight ratio of one to three will produce a resulting powder with the Waltham Abbey 15/3/2 (75/15/10) proportions. The mill jar and media were again cleaned before this step. The mill was operated outdoors for twelve hours, preferably during a snowstorm, under heavy walled HDPE buckets stacked together.

Much of the debate over Black Powder manufacture centers on the next step. It is well documented that lift powder grain size (and density?) will determine its suitability for a particular size and weight of shell. The power of the lift is affected by the method used to produce the grains of powder. This experimenter has found that reasonably durable powders produced with a simple hand operated arbor press and a high quality comet pump offer the best combination of durability and performance.

The milled powder was combined with a small amount of distilled water in a steel bowl in the same manner as a pyrotechnic star composition would be prepared to make pumped stars. When the dampened powder had just reached the stage of clumping together, it was pumped into pellets with a one-inch star pump under an arbor press. The pellets were allowed to dry for a week before they were "corned".

For testing purposes, two of the powders were grained by dampening the mill dust and forcing it through a sieve. The dried rough powder was then sieved through a 12-mesh screen; the portion remaining on a 20-mesh screen was used. These powders were made from Aspen and Maple charcoal and are denoted by the letter "S" in Table 2.

The pressed powders were grained by hammering the dry powder pellets between heavy polyethylene sheets. The "corned" powder that passed a 4.5-mesh sieve and remained on a 12-mesh screen was tested as 2FA powder, and the passing powder that remained on a 20-mesh screen was tested as 4FA powder. Other mesh sizes were not used.

Table 2. Powder Tests (5 gram Samples).

Charcoal Type	Ave. Velocity (ft/s)	Ave. Peak Pres. (psi)	Bulk Density (g/cc)
Goex 4F	250	130	1.00
Commercial Air Float	14	7	0.54
Cotton Balls	36	19	0.71
Grape	180	80	0.72
Cotton Fabric	180	91	0.75
Apple	210	110	0.68
Teak	220	130	0.71
Cherry	230	120	0.68
Serviceberry	260	180	0.75
Rocky Mountain Willow	300	290	0.74
Alder Buckthorn	320	340	0.75
Silver Maple H	330	390	0.68
Aspen H	360	460	0.68
Silver Maple S	360	560	0.61
Carolina Buckthorn ⁽¹⁾	380	550	0.69
Aspen S	380	600	0.56
Carolina Buckthorn ⁽²⁾	383	547	—
Red Alder ⁽¹⁾	410	640	0.68
Red Alder ⁽²⁾	410	640	0.68
Pacific Willow	420*	730	0.75
NLC	430	660	0.71
Goex 2F	200	84	0.86
NLC 2F	220	170	0.74

* Based on less than three successful tests.

All tests used 5.0 grams of powder and were run at approximately 80 °F.

The apparatus was cleaned after every set of 10 tests, and the order of powder types was varied.

Everything is reported to 2 significant figures.

Bulk densities were determined by settling in a tube 1.0 cm in diameter. Thus there was an edge effect making large grains appear less dense.

⁽¹⁾⁽²⁾ Red Alder was run in both the first and second series of tests. Carolina Buckthorn was produced in two different batches from two charcoal runs, and tested in the first and third series of tests. Note the close agreement in the findings.

S and **H** versions of powder refer to Soft and Hard grain.

Note: Moisture determinations were run on all powder samples in the second series of tests (4 hr. at 75 °C). In no case was there more than a 0.4% weight loss.

Table 3. Results of Powder Tests (3.5 gram Samples).

Charcoal Type	Ave. Velocity (ft/s)	Ave. Peak Pressure (psi)
Skylighter Air Float(Hubing)	70	—
Carolina Buckthorn (Judd)	226	117
Aspen (Hubing)	237	—
Thinleaf Alder	270	240
Ailanthus	328	396
Alder Buckthorn (Fielder)	445	762
Black Willow (Fielder)	473	819

Note that the best powders in Table 3 outperform those in Table 2. If the Aspen performance is used as a baseline, the values for speed in Table 3 should be multiplied by 1.6 to obtain the expected speed if 5 grams had been used.

Results

Powder performance was determined using a test apparatus designed to simulate the approximate conditions in the firing of aerial shells.^[14] Results are shown in Tables 2 and 3. The interpretation is rather straightforward, and only a few comments are needed. The best performance was obtained first from the Willow charcoal obtained from Guy Lichtenwalter and the Black Willow based powder from Jack Fielder. The author's NLC based powder was a significant performer as well. Note that Goex brand Black Powder gives results that are lower than most of the handmade samples. The Fielder Buckthorn-based powder and the author's Ailanthus-based powder also performed respectably.

Future Research

The production of the best charcoal from Carolina Buckthorn and Alder Buckthorn is still being studied. It is possible that these Buckthorn varieties require more careful drying before pyrolysis than other types of wood. The high performance of Ailanthus also merits more research to elucidate the relationship between the physical and chemical properties of the wood with the charcoal produced from it.

There have been numerous pyrogolf competitions over the past few years, and it is quite

likely that the best charcoal from any one wood species has yet to be made. One PGI pyrogolf participant very nearly won the first event with a Maple based lift powder. Another participant made a very good powder from Red Cedar.

The author plans to obtain scanning electron micrographs of several of the charcoals discussed here. A heuristic method of determining the degree of graphite structure in the charcoal will then be applied. In a related study, the volatile components of a particular charcoal could potentially be removed with solvents. Then the charcoal would be compared to itself, with and without these volatile components. Oglesby^[16] indicates that powder made from so-called "stripped" charcoal is just as fast as or faster than the original.

The effects of the various pressing methods also need to be studied. It is clear that, in general, the lower the density of the grains, the faster the powder.

Another aspect of a given charcoal is the percentage used to produce the powder. All of the experimental lift powders discussed in this work and by O'Neill^[17] use the 15/3/2 Waltham Abbey proportions, but a given charcoal may produce better results in a 6/1/1, 25/5/4 or even 5/1/1 mixture. This has not been studied.

Finally, a significant aspect of commercial Black Powder should be examined. Namely, Goex brand powder burns significantly cleaner than the handmade lift powders discussed here.

For most pyrotechnic applications this is of no great importance, but for lift powders it could mean more successive firings from a given mortar without the need for cleaning. The measurement of a relatively clean burning property with respect to ball mill type, chemical purity and other physical factors should be examined.

References

- 1) Guy Lichtenwalter, "Pyro Golf", *Pyrotechnics Guild International Bulletin*, No. 96, 1995, p 31.
- 2) Roger O'Neill, "A Systematic Study of the Performance of Charcoals in Pyrotechnic Compositions", *Pyrotechnica XVII*, 1997, p 10.
- 3) Stan Williams, "The Wonder of Charcoal", *Pyrotechnics Guild International Bulletin*, No. 98, 1996, p 31. Note also that Stan supplies video tapes on non-commercial Black Powder production.
- 4) In Britain, may still be referred to as *Frangula alnus* Miller.
- 5) B. L. Browning, Ed., *The Chemistry of Wood*, Wiley Interscience Publishers, New York, 1963, p 275.
- 6) Guy Lichtenwalter, "Cheap Black Powder and Other Inexpensive KNO₃/Charcoal Compositions", *American Fireworks News*, No. 176, 1996, p 7.
- 7) Skylighter, Inc., PO Box 480, Round Hill, VA 22141, USA.
- 8) Stan Williams, PML communication, 1995.
- 9) Goex, Inc., PO Box 659, Doyline, LA 71023, USA.
- 10) Lloyd Scott Oglesby, *Glitter, Chemistry and Techniques*, American Fireworks News, Dingmans Ferry, PA, 2nd ed., 1989, p 14.
- 11) Ronald Lancaster, *Fireworks, Principles and Practice*, 2nd ed., Chemical Publishing Company, New York, 1992, p 48.
- 12) Ted McDowell, "Black Powder Doesn't Need Machinery", *American Fireworks News*, No. 186, 1997, p 4.
- 13) Lloyd Sponenburgh, Part 1: "Ball Milling — Some Science of a Black Art"; Parts 2–4: "Construction of an Inexpensive, Efficient Ball Mill" *American Fireworks News*, Nos. 171–174, 1995 & 1996.
- 14) K. L. and B. J. Kosanke, "An Instrument for the Evaluation of Black Powder as a Propellant for Aerial Shells", *Proceedings of the 3rd International Symposium on Fireworks*, 1996.
- 15) O'Neill, *op. Cit.*, p 22.
- 16) Oglesby, *op. Cit.*, p 15.
- 17) O'Neill, *op. Cit.*, p 12.

Continued from page 16

Errata

Issue 9, Summer 1999 – corrected words are listed in **bold** type to help the reader locate them.

Page 60, column 2, last paragraph contains 3 errors. The paragraph should read:

"The melting points of yttrium, erbium, **thulium** and lutetium are similar to that of titanium."

"If the monoxide emission colors were sufficiently intense to be visible above white light from hot oxide particles, **yttrium** would be expected to produce **red** sparks, and the other three metals, green."

Communications

Brief technical articles, comments on prior articles and book reviews

Peak In-Mortar Aerial Shell Accelerations

K. L. and B. J. Kosanke
PyroLabs, Inc., 1775 Blair Road,
Whitewater, CO 81527, USA

ABSTRACT

Internal mortar pressures were measured for a range of somewhat typical fireworks aerial shell firing conditions. These data were used to determine the peak shell accelerations produced during firing. Under the conditions investigated, peak aerial shell acceleration ranged from approximately 4 to 16 km/s² (400 to 1600 times the acceleration due to gravity) and appeared to be mostly independent of nominal shell size.

As a check on the acceleration results, the same mortar pressure data were used to calculate aerial shell muzzle velocities. These were found to be in close agreement with measured velocities.

Keywords: fireworks, aerial shell, acceleration, muzzle velocity, mortar pressure, pressure impulse

Introduction

For safety reasons, a fireworks display operator needs to know that aerial shells leave the mortar at high speed. Further, it is important to know approximately how far the aerial shells can travel. However, it is not important for the operator to know the rate of acceleration of aerial shells within mortars as they are fired. Similarly, except to know that the acceleration is great and the resulting inertial forces on the shells are large, the shell manufacturer does not need detailed knowledge of the magnitude of aerial shell

acceleration. Nonetheless, it is sometimes a topic of discussion, and knowledge of these accelerations would satisfy the curiosity of a number of individuals. This short article is intended to help satisfy that curiosity.

Several years ago data was collected, albeit for another purpose, that can be used to calculate the acceleration of aerial shells while being fired from mortars. These data are internal mortar pressures as a function of time for various shell parameters (e.g., size and shape, lift type and mass, and shell mass). At the same time, the muzzle velocity of the shells was measured and can be used as a check on the calculated shell accelerations. Some examples of the basic data and the results produced are presented in this article.

Background

If the forces acting on a body are known, it is a simple matter to calculate the acceleration produced. Pressure has the units of force per area; for example, newtons per square meter (also termed pascals and abbreviated Pa). Accordingly, the force (F) acting on an aerial shell with a known cross-sectional area (A) perpendicular to the pressure gradient, when experiencing a pressure difference (P) between one side and the other, is^[1]

$$F = P \cdot A \quad (1)$$

Then simply by rearranging Newton's second law of motion, and knowing the mass (m) of the aerial shell, the acceleration (a) it experiences can be calculated as

$$a = F/m \quad \text{or by substitution} \quad (2)$$

$$a = P \cdot A/m \quad (3)$$

Figure 1 is an example of the pressure measured inside a mortar as a shell is being fired. Because the pressure is not constant during the firing, neither is the acceleration of the shell. Nonetheless, equation 3 accurately predicts the acceleration at every instant, providing the mortar pressure at the same instant is used. Thus,

the shell's acceleration reaches a maximum when the mortar pressure peaks, and this peak acceleration can be calculated using equation 3.

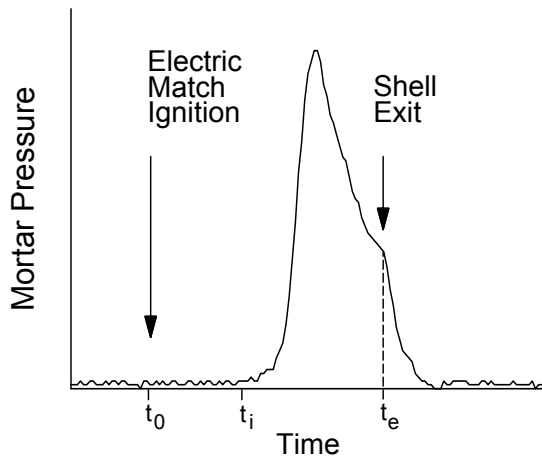


Figure 1. Typical internal mortar pressure during the firing of an aerial shell.

In the same tests where mortar pressures were measured, aerial shell muzzle velocities were also measured. This provided an opportunity to indirectly confirm the accuracy of the peak acceleration determinations by using the mortar pressure data also to predict the measured muzzle velocities.

In general, for any body, its change in veloc-

ity (v) in response to a time dependent acceleration can be represented by

$$v_f - v_i = \int_{t_i}^{t_f} a(t) dt \quad (4)$$

where the subscripts i and f are for initial and final values. For an aerial shell initially at rest (stationary), substituting for acceleration using equation 3, and integrating over the time of exposure to the pressure in the mortar equation 4 becomes

$$v_m = A/m \int_{t_i}^{t_e} P(t) dt \quad (5)$$

where v_f is now muzzle velocity (v_m) and t_f is now the time of exiting (t_e), see Figure 1.

The integral in equation 5 is usually referred to as pressure impulse (I_p). In these tests, values for the pressure impulse were determined and used to calculate the aerial shell muzzle velocities from equation 6.

$$v_m = A/m \cdot I_p \quad (6)$$

Experimental

For uniformity, all of the test shells for this project were assembled using molded plastic shell casings. Nominal shell size ranged from 3 to 8 inches. Most shells were spherical in shape, but some 3- and 4-inch shells were cylindrical.

Table 1. General Test Shell and Mortar Information.

Nominal Shell Size (inches)	Mortar Diameter (mm)	Mortar Length (m)	Shell Shape	Shell Diameter (mm)	Shell Mass (g)
3	79	0.51	Spher.	66	135
			Cylin.	67	180
4	103	0.61	Spher.	95	350
			Cylin.	92	500
5	129	0.76	Spher.	119	620
6	154	0.76	Spher.	144	1140
8	203	0.91	Spher.	193	2700

To convert millimeters to inches, divide by 25.4.

To convert meters to inches, multiply by 39.4.

To convert grams to pounds, divide by 454.

Table 2. Test Shell Firing Results.

Nominal Shell Size (inches)	Shell Shape	Lift Mass (g)	Peak Pressure (kPa)	Pressure Impulse (kPa·s)	Measured Velocity (m/s)	Calculated Velocity (m/s)	Peak Acceleration (km/s ²)
3	Spher.	28	430	4.5	80	85	8
	Cylin.	28	500	5.0	90	95	10
4	Spher.	28	210	3.2	65	65	4
		46	660	5.9	125	125	14
	Cylin.	50	880	7.9	110	105	12
			1200	8.0	110	105	16
			970	7.9	100	105	13
			770	7.5	100	100	10
5	Spher.	50	610	5.9	100	105	11
6	Spher.	85	680	7.4	110	110	10
8	Spher.	155	830	11.2	120	125	9

To convert grams to ounces, divide by 28.3.

To convert kilopascals to pounds per square inch, divide by 6.89.

To convert meters per second to feet per second, multiply by 3.28.

In an attempt to have the spherical shells perform in a similar manner to typical oriental shells, the lift powder used was a fairly homogeneous blend of powder harvested from a collection of shells manufactured in China. The lift powder for the cylindrical shells was 2F fireworks Black Powder manufactured by Goex.^[2] The air temperature at the time of firing ranged from 21 to 27 °C (70 to 80 °F). The tests were conducted at about 1400 m (4600 ft) above sea level, resulting in air pressure of approximately 850 mbar. Additional mortar and shell test information is provided in Table 1.

All mortars were steel with piezoelectric pressure gauges installed in the mortar plug. In this way the internal mortar pressures were measured as the shells were fired.^[3] The mortars were also fitted with a series of trip wire sensors to detect the passage of the shell after exiting the mortar. Signals from the trip wires controlled a series of time counters to produce the data used to calculate velocities of the shells as they exited the mortar.^[4]

The test results are reported in Table 2. In each case, the peak mortar pressure reported was the highest value from the digital pressure data. Pressure impulse is the sum of the pressure data, starting from the first sign of pressure rise (t_i) and ending at the point of shell exit (t_e) (such

as identified in Figure 1). The measured velocity of the exiting shell was determined by noting the time taken for the shell to travel a known distance after exiting the mortar. The calculated shell velocity was determined by substituting the measured pressure impulse and the known cross-sectional area and mass for the aerial shell into equation 6. The peak shell acceleration was determined from equation 3, using the measured peak mortar pressure.

To be consistent with the general reliability of the data, in Table 2 peak pressures were reported to the nearest 10 kPa, pressure impulses were reported to the nearest 0.1 kPa·s, measured and calculated muzzle velocities were reported to the nearest 5 m/s, and peak accelerations were reported to the nearest 1 km/s².

Discussion

The aerial shells had been assembled such that their mass, the type and amount of lift powder, and the mortar specifications were fairly representative of typical aerial shells. However, caution is warranted in applying the results of these tests in situations where any of the conditions are different.

An examination of the results for the series of 4-inch cylindrical shells provides an indication of the general reliability of these data. Note that while the peak pressures (and peak accelerations) for these firings varied considerably, the pressure impulses (and thus muzzle velocities) were in relatively close agreement. The authors have seen this same type of large variability in peak mortar pressure, yet reasonably consistent overall performance, in numerous other confined-combustion measurements. The reason for this effect is not clear but is suspected to be the result of small dynamic differences in the ignition and initial flame spread within the pyrotechnic charge (an interesting subject, but beyond the scope of this article.)

There was relatively close agreement between measured and calculated shell muzzle velocities, not only for the 4-inch cylindrical shells, but all others as well. Further, the muzzle velocities were reasonably close to 100 m/s (330 ft/s), regardless of shell size. This is consistent with the results reported by Shimizu,^[5] Contestabile,^[6,7] and in unpublished results of the authors. Thus there is a reasonably high degree of confidence in the reported results.

The maximum shell accelerations typically ranged from 8 to 12 km/s² and appear to be mostly independent of nominal shell size. In part, the 4 km/s² value reported in Table 2 was a result of using a smaller than normal amount of shell lift powder. However, it may also be a reflection of the widely varying peak pressures thought to result from the differences in ignition and flame spread mentioned above. Similarly, the 14 and 16 km/s² values may again be the result of these same differences.

These peak acceleration results can be put into perspective, recalling that the acceleration due to gravity is 9.8 m/s². Accordingly, at their maximum acceleration, these somewhat typical aerial shells were experiencing approximately 400 to 1600 times the acceleration due to gravity. Obviously, this produces powerful forces on the contents of the shell (so-called set-back forces) and indirectly on the shell's casing as well. For example, in the relatively new "Lampare" style aerial salutes (maroons), there is generally a container of liquid fuel, combined in some fashion with a charge of flash powder. Consider a

liquid fuel with a density of 0.85 g/cc that is placed in a container with a height of 150 mm (about 6 inches). If that shell is propelled such that it receives the peak acceleration seen in the tests reported above, the liquid pressure at the bottom of the container would range from 0.5 to 2.0 MPa (70 to 290 psi). Thus it is clear why some fuel containers fail catastrophically during shell firing and why the fuel containers typically are strongly encased.

Acknowledgements

The authors wish to thank Scot Anderson, Wes Smith and Larry Weinman for their review of an earlier version of this article.

Notes and References

- 1) This is a simplification in that things such as drag forces produced by the combustion gases rushing past the exterior of the shell are not considered. However, this is not expected to introduce a significant error in the results being reported.
- 2) Goex, Inc., PO Box 659, Doyline, LA 71023, USA.
- 3) The pressure gauges were PCB Piezotronics 101A04, connected to PCB Piezotronics 480D06 amplifying power supplies. The data were recorded using Fluke Scopemeters model 95 or 97, then transferred to a computer for processing.
- 4) K. L. and B. J. Kosanke, "Measurement of Aerial Shell Velocity", *American Fireworks News*, No. 157, 1994. This article was also reprinted in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 3 (1993 to 1994)*.
- 5) T. Shimizu, *Fireworks, From a Physical Standpoint*, Reprinted by Pyrotechnica Publications, 1985, p 183.
- 6) E. Contestabile, "A Study of the Firing Characteristics of High Altitude Display Firework Shells", CANMET, MRL 88-020 (OPJ), 1988.

7) E. Contestabile, T. R. Craig, R. A. Augsten and R. R. Vandebek, "Evaluation of Large Diameter Fireworks Shells and Mortars", CANMET, MRL 90-41 (OP), 1990.



Comment on:

"Review of 'Pollution Caused by Fireworks' by D. Gnauth White" by Monona Rossol, Issue 7, p 74.

In reference to the letter published in Issue 7, "Another Fog Study" by Monona Rossol, the data Ms. Rossol presented does not support her conclusion. The data indicates that something is happening during the performance to reduce the musicians' lung function, but the data does not show that "clearly special effects are harming the musicians". The summary of Dr. Moline's report does not say what is doing this, it only notes the effect. The special effects could be doing this, or it could be something else.

I would also like to take this opportunity to inform Journal readers of the existence of the ESTA Technical Standards Program (TSP). ESTA is the Entertainment Services and Technology Association, and the TSP is an ANSI accredited program consisting of the Technical Standards Committee and various Working Groups. A Fog and Smoke Working Group is currently drafting a standard for theatrical fog.

The TSP Fog and Smoke Working Group includes manufacturers, dealers, and users of fog and smoke effects. Anybody with an interest in fog and smoke is eligible to join the group; you do not have to be a member of ESTA.

For more information about ESTA's Technical Standards Program, go to their web site at '<http://www.esta.org/>', or contact the Technical Standards Manager at ESTA, 875 Fifth Ave., Suite 2302, New York, NY 10001, phone 212-244-1505, fax 212-244-1502, e-mail: standards@esta.org.

Nathan Kahn
Theatre Effects
642 Frederick St.
Hagerstown, MD 21740 USA
phone: 301-791-7646
fax: 301-791-7719
e-mail: nathan@theatreff.com

[Ed. Due to an e-mail problem, this letter—originally written on July 13, 1998—was only recently received by the *Journal of Pyrotechnics*.]

Reply from Monona Rossol:

It is unrealistic of Mr. Kahn to assert that the "special effects could be doing this, or it could be something else." There is no other rational explanation of the reduction of lung function seen in all the musicians plus documentation that seven people developed asthma requiring daily medication in an orchestra of 25 people in only three years of exposure. These kinds of problems have only been reported in shows that use special effects. And having spoken with many of these musicians, they assure me that the symptoms clearly start when the smoke enters the pit.

It is also important for readers to know more about ESTA than Mr. Kahn tells you. The voting members of ESTA are primarily special effects manufacturers and distributors and their paid consultants.

Unlike the other standard setting organizations to which I belong, ESTA requires voting members to attend meetings. The ESTA meetings are held all over the country and members must be able to afford to fly to meetings, stay in hotels and take two or three days off work several times a year. This policy effectively eliminates participation from members who do not have a large financial interest in continuing to make, sell, and or use special effects.

I am a voting member of many committees of the American Society of Testing and Materials, and two committees of the National Fire Protection Association. Attendance at meetings

of ASTM and NFPA is not required and members can keep up by reading the minutes and voting on proposals by mail. In fact, ASTM often pays the airfare for non-industry members in order to assure a balance of interests at committee meetings.

Whenever industry representatives refer to “standards”, we should ask who sets those standards.

Monona Rossol



Review of *Fireworks Principles and Practice*

Ronald Lancaster

3rd ed., Chemical Publishing, New York, 1998
ISBN 0-8206-0354-6

Barry Sturman

6 Corowa Court, Mount Waverley
Victoria 3149 Australia

It is unlikely that many readers of these pages have not yet bought a copy of the third edition of the Reverend Ronald Lancaster’s *Fireworks Principles and Practice* (Chemical Publishing, New York, 1998). Those who have ignored this edition, because they already own first or second editions, should think again. If you enjoyed the previous editions, you will find still more to enjoy in this latest one.

Comparison of the Tables of Contents of the Three Editions.

First edition (1972)	Second edition (1992)	Third edition (1998)
The History of Fireworks ^[a]	The History of Fireworks ^[a]	The History of Fireworks ^[a]
Firework Materials	Firework Materials	Firework Displays ^[b]
		Gunpowder
		Firework Materials
General Pyrotechnic Principles	General Pyrotechnic Principles	General Pyrotechnic Principles
		Chemistry of Firework Composition ^[c]
		Legislation ^[d]
Mixing and Charging	Mixing and Charging	Mixing and Charging
Containers	Containers	Containers
Stars	Stars	Stars
Coloured Fires, Bengals, Lances, Portfires, Torches	Coloured Fires, Bengals, Lances, Portfires, Torches	Coloured Fires, Bengals, Lances, Portfires
Roman Candles, Comets, Mines	Roman Candles, Comets, Mines	Roman Candles, Comets, Mines
Noisemakers	Noisemakers	Noisemakers
Rockets ^[e]	Rockets	Rockets
Drivers, Saxons, Tourbillions	Drivers, Saxons, Tourbillions	Drivers, Saxons, Tourbillions

Comparison of the Tables of Contents of the Three Editions. (Continued)

First edition (1972)	Second edition (1992)	Third edition (1998)
Shells	Shells	Shells
Gerbs, Fountains, Rains, Squibs, Cones	Gerbs, Fountains, Rains, Squibs, Cones	Gerbs, Fountains, Rains, Squibs, Cones
Pinwheels and Crackers	Pinwheels and Crackers	Pinwheels and Crackers
Indoor Fireworks	Indoor Fireworks	Indoor Fireworks
Fuses, Quickmatch	Fuses, Quickmatch	Fuses, Quickmatch
Smoke	Smoke	Smoke
Exhibition Fireworks	Exhibition Fireworks	Exhibition Fireworks
The Manufacturing Processes for Fireworks Composition ^[c]	The Manufacturing Processes for Fireworks Composition ^[c]	The Manufacturing Processes for Fireworks Compositions. Japanese Fireworks ^[c]
		Glossary
		References
		Index
19 Chapters with 274 Pages	19 Chapters with 318 Pages	24 Chapters with 448 Pages

[a] Written by Roy E.A. Butler; [b] Written by J. Mark Lancaster; [c] Written by Takeo Shimizu; [d] Written by Thomas A.K. Smith; [e] Written by Ronald G. Hall.

When the first edition appeared in 1972, it was the first new book in English to deal with the technical details of firework making since the publication of the revised and enlarged second edition of George Washington Weingart's *Pyrotechnics* in 1947. The reprinting of Weingart's book in 1968 provided the stimulus for Lancaster's first book. Previously, Lancaster had contributed a chapter on fireworks to Dr. Herbert Ellern's *Military and Civilian Pyrotechnics*. At the time the first edition of *Fireworks Principles and Practice* was published, Lancaster was chaplain of Kimbolton School and a firework consultant to Pains-Wessex Ltd. He is now the Managing Director of Kimbolton Fireworks Ltd., by far the largest of the very few remaining firework manufacturing operations in Britain. Lancaster is a Fellow of the Royal Society of Chemistry and has been made a Member of the Most Excellent Order of the British Empire in recognition of his achievements. It is only to be expected that the writings of such a distinguished fireworker would be eagerly sought by anyone interested in pyrotechny.

The first two editions are so similar in size and appearance that it is difficult to tell them apart on the bookshelf. The third edition is a larger book, and, unlike the previous editions, is

provided with a dust jacket. A very appealing feature is a large range of black and white photographs, including many from the archives of Brock's Fireworks. The reproduction of these photographs does not always do them justice. It is disappointing to find poorly reproduced pictures in an expensive reference book, especially when cheap magazines and advertising brochures routinely contain pictures reproduced to a far higher standard. The book is also illustrated with many line drawings. The standard of these drawings varies considerably; some are first rate, while a few are oversimplified to the point of being of little or no value. The few bad ones, which have survived all three editions, are out of place in an otherwise excellent book.

The first edition of this book introduced many to the work of Dr. Takeo Shimizu, the great Japanese pyrotechnist. Dr. Shimizu has contributed a whole new chapter to the third edition. This chapter, entitled "The Chemistry of Firework Composition", is not a general treatment of that subject but a selection of concise, informative comments on specific effects, including firefly, micro-stars, glitter and strobe.

The three other new chapters include a comprehensive discussion of gunpowder by Lancas-

ter, and one by Dr. Thomas Smith on legislation for the control of fireworks. This latter subject is obviously of vital interest to anyone contemplating an involvement with fireworks. A prospective pyrotechnist might well conclude that the effort and cost of compliance with the ever-increasing legislative controls would far outweigh any pleasure or profit that might have come from working with fireworks. It is better to find this out at the start, and abandon one's pyrotechnic ambitions, than to discover it later. Such is the pace of regulation that any summary will soon be out of date. The subject certainly cannot be ignored and deserves its place in the book.

Lancaster's son Mark has contributed a most interesting chapter on firework displays, with discussion of the different display styles typical of Spain, Mexico, Malta and Japan. A useful glossary of over three hundred terms related to fireworks has also been included in this edition.

The first chapter in the book, R.E.A. Butler's *The History of Fireworks*, has been extensively revised and provides a fascinating, detailed treatment of the subject. A tremendous amount of research must have been carried out in the preparation of this chapter. As would be expected, there is much information on the British firework industry. That story is rather depressing. In the first half of this century British firms were world leaders in fireworks. In more recent years the once renowned companies have evidently fallen victim to businessmen bent on rationalization. After a series of mergers, acquisitions and takeovers, the old firms have variously abandoned fireworks in favor of military pyrotechnics and signals, given up manufacture of fireworks to become importers and display operators, or in some instances have disappeared completely. One can only wonder just how much knowledge and accumulated experience in all aspects of firework making has been lost. We are fortunate that Ronald Lancaster has provided a permanent record of some of the insights he has gained in over 35 years in the industry.

As evident from the Table of Contents, Lancaster's own chapters cover a great deal of material. In general, these chapters document how things were (and are) done in the British firework industry and are not a compendium of

specific, detailed instructions on how to build fireworks. Readers seeking such information will find it in publications such as *Pyrotechnica*, the *Bulletin of the Pyrotechnics Guild International*, and the wide range of material offered by American Fireworks News. They would be well advised first to read Lancaster for essential background information. Lancaster presents a large number of formulae; he also outlines the procedures and techniques involved in making fireworks. He emphasizes that there are all sorts of subtle factors that can make the difference between success and failure, particularly when one needs to produce consistently well-performing products on a commercial scale.

If one had to make any criticism of the content of the book, it would be that some of the chemicals discussed, while of historical interest, really ought not to be used in modern practice. Examples include the arsenic sulfides (realgar and orpiment) and copper acetoarsenite (Paris green). In these days of concern about health and safety, the toxicity of the products of combustion of arsenic compounds should rule out their use in pyrotechny. In his chapter on firework materials, Lancaster writes (p 96): "Arsenic is safe to handle, of course, provided that precautions are taken to keep it out of the nose and mouth. ...it should be remembered that soluble barium, for example, is equally toxic." That is not quite right. While soluble barium is undoubtedly toxic, no proven long-term effects are known.^[1] Ingestion of arsenic is known to be associated with serious long-term effects including certain types of cancer.^[2] To equate the toxicity of arsenic and soluble barium is to underestimate that of arsenic and to overstate that of barium. It would be most unfortunate if zealous regulators were to use Lancaster's remarks to justify prohibition of barium salts in fireworks. Pyrotechny can well do without arsenic but would be much the worse if deprived of barium.

Since the publication of the first edition of this book, there has been discussion of the dangers of mixing aluminium, nitrates and chlorates. There is concern that the metal might react with the nitrate and form ammonia, which might then react with the chlorate to form the spontaneously explosive ammonium chlorate.^[3] An example of such a mixture, a green/silver pillbox star, ap-

peared on page 92 of the first edition. It is surprising to find the same composition appearing again, without comment, in this edition (p 213).

These criticisms aside, this book is the latest and best version of a classic work by one of the leading figures in the firework industry. It should be read, and re-read, by anyone who is involved with that industry or who has more than a passing interest in fireworks. Readers of this Journal will want to own a copy, especially if they already have an earlier edition.

References

- 1) W. Zschiesche, K. H. Schaller, "Biological indicators for the assessment of human exposure to industrial chemicals. Soluble barium compounds". Comm. Eur. Communities, [Rep.] EUR 1994, (EUR 14815) pp 1,3,5-21; *Chem. Abstr.* **121**:294472J.
- 2) N. Irving Sax and Richard J. Lewis, Sr., *Dangerous Properties of Industrial Materials*, 7th ed., Van Nostrand Reinhold, New York, 1989.
- 3) See, for example, *The Best of AFN*, American Fireworks News, Dingmans Ferry, PA, 1985, pp 45-47.



Review of *Explosives Engineering*

Paul W. Cooper

Wiley-VCH, Inc., 1996
ISBN 0-471-18636-8 — 450 pages

L. Weinman

9051 Sugartree Trail
Huntsville, AL 35802, USA

This book is intended as a non-trivial text for those interested in the technology and science that lies behind explosive events and devices.

While the book starts with introductions to some very basic chemical concepts, this reviewer is of the opinion that the book's intended audience is not the rank amateur, but the working professional, who may not have a background in this area, but is technically competent in some engineering or scientific field. This is bolstered by a (proper) reliance on the use of mathematical descriptions of concepts and events. While the math involved is not overly advanced, it does require some college level courses to be fully comprehended.

The text comprises six sections containing a total of thirty chapters, and is approximately 450 pages in length. At odds with the book's title is that only the last section actually deals with engineering applications. The bulk of the book is devoted to the chemistry and physics of detonation, explosives, explosive effects, and explosive devices. Not obvious from the title is the overwhelmingly military/governmental orientation of the uses and devices presented. However, this is not entirely unexpected, especially if one considers that the bulk of the basic work done in this field is at the behest of the military—and that Mr. Cooper spent most of his career employed in that area. Furthermore, private companies and organizations are generally reluctant to disseminate what they may consider to be proprietary.

The first section, *Chemistry of Explosives*, introduces the nomenclature and reactions that are needed to understand the basics of explosives.

The second section, *Energetics of Explosives*, introduces thermodynamics and goes on to cover the thermophysics, thermochemistry, and reactions that lead to the estimation of the detonation properties.

The third section, *Shock Waves*, continues from the previous section by describing the phenomena of the shock wave and covers the equations and current theory describing the shock wave and its interactions.

The fourth section, *Detonation*, speaks to the effects within the explosive itself. This joins together much of the previous material presented.

The fifth section, *Initiation and Initiators*, covers the theory of initiation (which is not limited to detonation) and the theory that governs the function of some types of initiating devices.

The last section, *Engineering Applications*, starts with a section on scaling. This is important in many design areas as the required development testing of full scale items may not be financially or "politically" feasible. Also covered is information on fragments, blast effects, jetting, and explosive welding.

It must be stressed that this book is primarily devoted to the area of "high", or detonating, explosives and has minimal, but not zero, information dealing with general pyrotechnics, and fireworks in particular. However, this reviewer would recommend that the pyrotechnic, and especially the fireworks, community read and understand the information presented in the excellent section on initiators and particularly the section on hot-wire initiators.

In contrast to an earlier book by Mr. Cooper, also published by Wiley-VCH, this book is reasonably free of typographic and other errors.

The reviewer would recommend this book to anyone who wanted to increase their knowledge and understanding of the field of explosives and their effects.



Review of **Selected Pyrotechnic Publications of Dr. Takeo Shimizu, Part 3: Studies on Fireworks Colored-Flame Compositions**

Dr. Takeo Shimizu

Journal of Pyrotechnics, 1998

ISBN 1-889526-11-8

Barry Sturman

6 Corowa Court, Mount Waverley,
Victoria 3149 Australia

This latest volume in the Pyrotechnic Literature Series presents a series of papers on work done by Dr. Shimizu in 1958 at the Hosoya Fireworks Company. Originally published in the *Journal of the Industrial Explosives Society, Japan*, the papers have been translated into English for this publication. Dr. Shimizu himself translated all but one of them. Even though this work is about 40 years old, it is by far the most complete and authoritative on the subject. This extensive volume (120 pages) will be of great interest for anyone wanting to acquire a scientific understanding of colored pyrotechnic flames. Those of a more practical inclination will find many formulas for colored flame compositions, nearly always with extensive detail on the effects of varying the proportions of the ingredients.

The work begins with a theoretical discussion of the line-reversal method of measuring the temperature of a flame. Unfortunately a typographical error in the initial explanation of the method will be confusing to those new to the subject. No doubt this will be corrected in future printings. The diagram on page 2, which illustrates this section, is correct.

In the following chapter, Dr. Shimizu presents the results of applying the line-reversal

method to the measurement of the flame temperatures of burning firework compositions. The conclusions of this work have been published briefly elsewhere;^[1a] this paper gives all the detail that is so characteristic of Dr. Shimizu's work.

Dr. Shimizu next discusses the spectra of colored pyrotechnic flames. The first paper in this section focuses on the spectral features observed in the flames of compositions without added color-producing agents. These background spectra contribute to the color of the flame, usually to its detriment. Dr. Shimizu identifies the intense yellow emission from sodium (present in impurities) and continuous "black body" spectra from incandescent particles as the main background features that detract from the color of pyrotechnic flames. The spectral backgrounds of the various flames are discussed in detail and approaches to reducing the backgrounds are explained.

The next paper treats red, yellow and green firework flames. Spectra of flames from compositions containing salts of strontium, sodium, barium and calcium are presented and discussed. At the time this work was being done academic spectroscopists were studying colored flames with the aim of identifying the molecules responsible for the characteristic spectral features. In an author's note, Dr. Shimizu relates the findings of one such study^[2] to his own observations and his earlier conclusions. The spectral bands he originally attributed to gaseous strontium monoxide (SrO) turned out to come instead from strontium monohydroxide (SrOH) and strontium monochloride (SrCl). Dr. Shimizu correctly identified the main species responsible for the green color of barium flames as barium monochloride (BaCl). He correctly points out that gaseous barium monoxide (BaO) produces emission bands over most of the visible spectrum, coloring the flame white.^[3a] Gaseous barium monohydroxide (BaOH, not mentioned by Dr. Shimizu) has green emission bands that overlap those of BaCl and extend further towards the blue end of the spectrum.^[4] Presumably, their presence would not detract from the color of a green flame. In practice, the production of a clear green flame entails maximizing the emission of BaCl and minimizing that of BaO. Dr. Shimizu notes that pyrotechnic flames colored with calcium compounds can range from nearly red to

yellowish. The color depends on the relative intensities of the red and orange bands from calcium monochloride (CaCl) and the green and orange bands that Dr. Shimizu attributes to calcium monoxide (CaO) but which spectroscopists have shown to come from calcium monohydroxide (CaOH).^[3b,5]

Flames colored with sodium salts derive their yellow color from the pair of sodium atomic emission lines at 589.0 and 589.6 nanometers. The color is strongly influenced by the presence of a background of continuous radiation. In high temperature flames this can be so intense that the flame is a yellowish-white color. In cooler flames containing potassium salts, the flame appears reddish yellow; with ammonium perchlorate, "the flame looks pure yellow".

Dr. Shimizu devotes an entire chapter to blue firework flames. He begins with a description of what happens when a copper wire is introduced into the flame of a gasoline burner, with and without the introduction of hydrogen chloride or chlorine gas. Three colors are seen: blue, light green and red-orange. The last, writes Dr. Shimizu, "always appears at the tip of the flame. Therefore it may be caused by CuO due to the oxygen in the air". The correctness of this suggestion is supported by the spectroscopy literature, which lists a series of bands from CuO in the orange-red region of the spectrum.^[3c] Dr. Shimizu writes, "It is well known that blue flames come from CuCl band spectra. However where does the light green come from? Perhaps the emitter has a different structure from that of the blue." Once again Dr. Shimizu's suggestion is confirmed by the spectroscopists, who attribute the green emission to CuOH.^[6] The problem of creating a satisfactory blue flame is essentially that of maximizing the intensity of the CuCl spectrum in the flame. Dr. Shimizu demonstrates how this can be done with compositions using ammonium perchlorate and potassium perchlorate, and he explains the great superiority of the former. The effect of various chlorine donors is also discussed, and the difficulty of achieving a satisfactory blue flame with high-temperature compositions based on magnesium is explained.

A short chapter discusses the flame spectra of high-temperature compositions that contain

aluminium instead of magnesium. The behavior of the two metals is very different, with aluminium tending to form sparks. Dr. Shimizu suggests that the difference is associated with the higher melting point of aluminium. The context indicates that *boiling* point is intended (“the vaporization of aluminium in the flame is not complete”). The melting points of the two metals are similar (660.4 °C for Al, 648.8 °C for Mg) but their boiling points are very different (2467 °C for Al, 1107 °C for Mg).^[7] In the text the melting points are given as 1800 °C for Al and 1100 °C for Mg. These are incorrect, and the value quoted for Al would also be incorrect for the boiling point. Dr. Shimizu comments on the beauty of the sparks produced from some of the mixtures he tested. He notes that the best color effects were produced with lower percentages of aluminium in the composition, but “the effects are much less than when magnesium is used in the compositions”. The conclusion is “it is difficult to obtain good colored flames when using aluminium as the fuel”.

The final paper discusses compositions for practical use. This chapter alone would be worth the price of the book. The results of the previous chapters are summarized, and examples of effective compositions are presented. An enormous amount of work must have gone into making and testing all these compositions. In nearly every case triangle diagrams show the range of components that can produce effective results. An exception is the final composition given, that “burns with a beautiful blue when the diameter is more than 20 mm”. This composition is most unusual, consisting of barium nitrate, magnesium, hexachloroethane and copper powder. A similar mix of the first three ingredients is reported to make a “very good” *green* flame.^[8] It is interesting that a rather small variation, with the addition of only 5 additional percent of copper powder, can make “a superior blue”.

The publication includes a biography of Dr. Shimizu, compiled by Craig Villeneuve. This, consisting largely of an autobiography that Dr. Shimizu provided to Mr. Villeneuve in response to a request for information about his life and influences, provides a nice balance to the technical material presented in the rest of the volume.

A few apparent errors were noticed. Some have already been mentioned; it is also worth noting that on page 57, column 2, paragraph 5, line 2, “strontium sulfate” appears where it seems that “strontium nitrate” was intended. Strontium sulfate is almost insoluble in water and could not be used in the preparation of strontium carbonate as described. Strontium nitrate would be perfectly satisfactory. Several of the Figures in Chapter 7 show “C₆Cl₆” (i.e., hexachlorobenzene) while the text refers to hexachloroethane (C₂Cl₆) and never to hexachlorobenzene. Presumably the Figures should show “C₂Cl₆”.

Table 10, page 29, lists color agents tested with ammonium perchlorate. The list includes strontium chlorate and barium chlorate; these could well be misprints. It would be dangerous to mix chlorates with ammonium perchlorate.^[1b] In the continuation of table 10 on page 30, barium chloride is listed, not barium chlorate, but sodium chlorate appears where sodium chloride was listed on page 20. It is very likely that “chloride” was intended, not “chlorate”, throughout Table 10.

This publication is an important contribution to the literature of pyrotechny. It is highly recommended to all those interested in the scientific and technical aspects of colored pyrotechnic flames.

References

- 1) T. Shimizu, *Fireworks, The Art, Science and Technique*, Maruzen Co. Ltd., Tokyo, 1981; [a] pp 54–56; [b] p 96.
- 2) M. Charton and A. G. Gaydon, “Band Spectra Emitted by Strontium and Barium in Arcs and Flames”, *Proceedings of the Physical Society A*, Vol. 69, 1956, p 520.
- 3) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 3rd ed., Chapman & Hall, London, 1963; [a] p 82; [b] p 136; and [c] p 157.
- 4) C. G. James and T. M. Sugden, “New Identification of the Flame Spectra of the Alkaline-Earth Metals”, *Nature*, Vol. 175, 1955, pp 333–334.
- 5) J. van der Hurk, Th. Hollander and C. Th. J. Alkemade, “Identification of the Emit-

ters of Some Visible Alkaline-Earth Bands in Flames”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 13, 1973, pp 273–288.

- 6) E. M. Bulewicz and T. M. Sugden, “Determinations of the Dissociation Constants and Heats of Formation of Molecules by Flame Photometry. Part 3 – Stability of Gaseous Cuprous Hydroxide”, *Transactions of the Faraday Society*, Vol. 52, 1956, pp 1481–1488.
- 7) R.C. Weast, Ed. , *CRC Handbook of Chemistry and Physics*, 63rd ed., CRC Press, Boca Raton, FL, 1982–83.
- 8) *Experiments in Developing Green Flare Formulas*, U.S. Naval Ammunition Depot, Crane, Indiana. Publication AD 632 683, National Technical Information Service, Springfield, VA, 1959, p 5, formula no. 30.



Review of **Hearing Protection** **A Guide for Those Who** **Manufacture, Test, or** **Use Explosives**

Confederation of British Industry
Explosives Industry Group, 1998
ISBN 0-85201-548-8

John Bergman

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

This publication addresses a much wider range of hearing protection issues than explosive noise *per se*. Despite its being structured specifically around British standards and regulations, its applicability to noise sources of all kinds should make it useful to safety personnel and industrial hygienists in any manufacturing environment.

The guide opens with a comprehensive checklist for assessing noise problems, possible methods for reducing noise and noise exposure, choosing the most appropriate protective devices, managing the use of hearing protection by employees, and keeping records. The essentials that must be considered in any hearing protection program are concisely addressed in this convenient and easily understood tool.

As mentioned previously, some sections of the publication deal with regulations that apply only in the United Kingdom. Persons in other parts of the world must therefore view these sections in the context of their own country's laws and standards, and make appropriate allowances. Still, taken as generalities, there are many universally applicable concepts available in these pages.

Other sections deal with the training of competent persons to oversee hearing protection programs, the assessment and selection of equipment, the care and maintenance of protective equipment, training of employees, and the sur-

veillance of employee health (audiometry). While all of these are useful, the section on the assessment and selection of equipment will probably be of primary technical interest to most readers. Various types of noise exposure and methods for their quantification are discussed, as are commonly used measuring instruments. The characteristics, strengths, and weaknesses of available hearing protection devices are provided in a detailed table, and equipment selection methods based on noise type, frequency, and intensity are presented. The latter are keyed to very helpful worked examples with all calculations, found in the appendices (called "annexes" in this publication).

The appendices contain, in addition to the worked calculations, an extensive list of related books and publications, British legislation and British Standards, resource addresses, and a glossary of terms. The publication is 53 pages in length, including references, appendices, and glossary.



Review of *The Chemistry of Explosives*

Jacqueline Akhavan
RCS Paperbacks, 1998
ISBN 0-85404-563-5

K. L. Kosanke

1775 Blair Road, Whitewater, CO 81527, USA

This 173-page, paper-bound book was published by the Royal Society of Chemistry (RCS) and authored by Jacqueline Akhavan of Cranfield University, Royal Military College of Science, United Kingdom. The text potentially helps fill a gap in the literature of explosives by providing more information on the chemistry of manufacturing and functioning of explosives. Unfortunately, it still is much more a text about explosives than it is about the chemistry of explosives. Even more unfortunately, it is not a particularly good book. Its approach is fairly superficial and it contains a disturbing number of errors.

Writing a text book is an incredibly ambitious undertaking, especially for an individual author. Not only is there the need to assemble a tremendous amount of information, but also that information needs to be essentially 100% correct. Even being 99% correct is really not good enough. Probably what was needed, in the case of this text, was one or two additional authors (or paid editors) to help identify and eliminate the more consequential errors that found their way into the text. If these errors are corrected in the second edition of this work, it would be a fairly good general reference text, and if it is expanded to include more actual chemistry, it would potentially be quite a good text.

Chapter 1, Introduction to Explosives is a brief and fairly interesting historically based discussion of explosives.

Chapter 2, Classification of Explosive Materials identifies the classes of explosive materials and goes on to present a moderate amount of

technical information about a collection of primary and secondary high explosives.

Chapter 3, Combustion, Deflagration and Detonation is a summary of some basic information about these processes, with the greatest attention paid to detonation.

Chapter 4, Ignition, Initiation and Thermal Decomposition is a brief introductory discussion of these subjects.

Chapter 5, Thermochemistry of Explosives is a fairly thorough discussion of the subject as applied to secondary high explosives, especially considering the length of the text. Here there is a greater emphasis on chemistry than most texts on explosives.

Chapter 6, Equilibria and Kinetics of Explosive Reactions contains some information rarely seen in texts on explosives, but only addresses secondary high explosives.

Chapter 7, Manufacture of Explosives is an interesting presentation of general information on the manufacture of various high explosives.

Chapter 8, Introduction to Propellants and Pyrotechnics is an extremely brief introduction to broad and complex subjects.

Some of the more noteworthy strengths of this text are its Table of Contents and Subject Index, both of which are extensive and definitely facilitate using the text for reference. Also it provides more information about the chemistry than most other texts on explosives.

As stated above, the greatest weaknesses of this text are that it only contains a little more chemistry than other texts on explosives, and that it contains a troublesome number of errors as well. A few examples of these errors are:

Page 23 lists "potassium chlorate" as a primary explosive, when it definitely is not.

Page 46 gives atmospheric pressure as 9.869 N·mm⁻² and uses this number in a calculation, when this pressure is about 100 times too great.

Page 56 states that deflagrating explosives are "not affected by strength of container", when there is little if anything else that affects their performance more than the degree of confinement.

Page 59 incorrectly identifies the thermal runaway (or critical) temperature as the ignition temperature for a pyrotechnic.

Page 65 states "Almost all explosive trains contain a primary explosive as the first component." One of the most common explosive trains is the detonator (blasting cap), which begins with a pyrotechnic igniting and/or delay charge before the primary high explosive component.

Page 68 states "The amount of chemical energy H generated by the decomposition of an explosive will give information on the sensitivity of the explosive ... a high value of H will result in a more sensitive explosive." This seems to be a confusion of enthalpy (heat) of reaction and activation energy. It is also wrong and is contradicted by Table 5.12 in this text, which documents primary (sensitive) explosives as generally being poorer energy producers than secondary (relatively insensitive) explosives.

Page 76 states "The heats of formation for a reaction containing explosive chemicals can be described as the total heat evolved when a given quantity of a substance is completely oxidized in an excess amount of oxygen, resulting in the formation of carbon dioxide, water and sulfur dioxide." At best this is a bad mix of definitions for heat (enthalpy) of combustion and heat (enthalpy) of reaction; and it definitely is not correct.

Page 95 equates force (F) to (nRT) and (PV), when the terms from the ideal gas equation have the units of work (force times distance).

Page 154, when discussing heat-generating devices, states "Heat generating pyrotechnic compositions contain zinc, zirconium or barium chromate, and manganese.", when at best this is overly simplistic and appears to be a failed attempt to borrow from Ellern's *Military and Civilian Pyrotechnics*.

For additional comments regarding the chapter on pyrotechnics, see the following review by Barry Sturman. It is hoped that there will someday be a corrected and expanded second edition of this book, and that it will then become the excellent text it could be.



Review of *The Chemistry of Explosives*

Jacqueline Akhavan
RCS Paperbacks, 1998
ISBN 0-85404-563-5

Barry Sturman

6 Corowa Court, Mount Waverley, Victoria 3149
Australia

The prestigious Royal Society of Chemistry (RSC) is the professional organization of Britain's chemists. It also publishes many books and journals on chemistry and related subjects, including RSC Paperbacks. According to the Society, "RSC Paperbacks are a series of inexpensive texts suitable for teachers and students and give a clear, readable introduction to selected topics in chemistry. They should also appeal to the general chemist."^[1a] A book from this source on the chemistry of explosives is expected to be a very useful addition to the literature, especially when the author is a Senior Lecturer at Cranfield University, Royal Military College of Science, UK.

To form an opinion about a new textbook that deals with subjects with which one is somewhat unfamiliar, one naturally turns to those sections about which one does have prior knowledge. In this instance, it was appropriate to look at the sections on the history of explosives and on pyrotechnics. It did not take long to get the impression that all was not well.

On the very first page it is stated that "in 220 BC an accident was reported involving black powder...".^[1b] This statement surely needs a supporting reference, but there is none. In the second paragraph the old legend of "a German monk called Berthold Schwartz" is repeated as if it were fact, complete with a date (1320).^[1b] Almost 40 years ago, Professor J. R. Partington wrote of Berthold Schwartz: "Black Berthold is a purely legendary figure like Robin Hood (or perhaps better, Friar Tuck); he was invented solely for the purpose of providing a German

origin for gunpowder and cannon".^[2] Dr. Akhavan does not cite Partington, but she does cite "The Chemistry of Powder and Explosives" by Professor T. L. Davis.^[3] Davis, who wrote in the early 1940s, refers to Berthold Schwarz and it is clear that the issue of whether Schwarz was a historical figure (as distinct from a legendary one) was controversial even then.^[3a]

The section on pyrotechnics includes a table of pyrotechnic smoke compositions.^[1c] Column 1 of that table, labeled "Pyrotechnic composition", includes "silicon tetrachloride and ammonia vapour", an example of a *non-pyrotechnic* smoke producing system. The list also includes "phosphorous (sic) pentoxide and phosphoric acid". These materials, far from being an example of a "pyrotechnic composition", are the *products of combustion* of white phosphorus burning in air. Incidentally, it is most surprising to see the word "phosphorus" spelled incorrectly in a publication of the Royal Society of Chemistry.

The section on light generating compositions contains the statement "In order to emit light in the visible region the temperature of the reaction must be greater than 3000 K".^[1c] This is obviously wrong. A candle flame emits visible light, and its temperature is nowhere near 3000 K. Dr. Shimizu lists the burning temperatures of several fuel and oxidant combinations useful for coloured flames; they range from 2025 to 2455 °C (2298 to 2728 K).^[4]

The section on coloured light also contains a fundamental error. Dr. Akhavan identifies the chemical species responsible for the emission of red, green and blue light from compositions containing compounds of strontium, barium and copper, respectively, as the ionized metal monochloride molecules SrCl^+ , BaCl^+ and CuCl^+ .^[1d] This contradicts the pyrotechnic literature, which clearly identifies the principal emitting species as the neutral monochloride molecules. See, for example references 4a, 5, and 6.

In the section on noise-generating pyrotechnics, Dr. Akhavan states "A louder bang can be achieved by using a pyrotechnic flash powder which generates more gas than black powder and therefore produces a louder bang".^[1e] Is it true that flash powder "generates more gas than black powder"? Flash powder can be a simple mixture of potassium perchlorate and powdered

aluminium.^[7] The gas responsible for the explosive effect of such a flash powder is presumably potassium chloride and aluminium oxide that have been vaporized by the heat of the reaction. Simple chemical calculations show that a flash powder consisting of a stoichiometric mixture of aluminium and potassium perchlorate would produce 0.004751 moles of potassium chloride and 0.006334 moles of aluminium oxide per gram of powder. If all the products were vaporized, they would produce 0.011085 moles of gas per gram of powder. If the vaporized products were dissociated to some extent at the temperature of the reaction, then the number of moles of gas would be correspondingly greater. As for black powder, Davis^[3b] cites the results of Noble and Abel, who found that 1 gram of black powder produced 271.3 cc of permanent gas measured at 0 °C and 760 mm. This corresponds to 0.0121 moles of gas per gram of powder, even without taking account of the possibility that some of the solid products would be vaporized, and some of the gaseous products dissociated, at the temperature of reaction. These calculations show that it is most unlikely that flash powder “generates more gas than black powder”. Flash powder produces a louder bang than black powder, *despite* producing less gas per unit mass, because it reacts faster and at higher temperatures, thus producing a more rapid release of high-pressure gas.

Having found so many errors and misleading statements in so few pages, this reader lost confidence in Dr. Akhavan’s book. The other sections of the book might be models of accuracy; they might also be as unreliable as the statements just discussed.

The statement on the back cover indicates that the book is “ideal for ‘A’ level students and new graduates with no previous knowledge of explosive materials. It will also be useful to anyone needing succinct information on this

subject”.^[1f] Regrettably, one cannot agree with these statements, at least in regard to pyrotechnics. It is to be hoped that a properly revised and edited second edition will be published in due course.

References

- 1) Jacqueline Akhavan, *The Chemistry of Explosives*, The Royal Society of Chemistry, Cambridge, 1998; [a] back of title page; [b] p 1; [c] p 155; [d] p 156; [e] p 157; [f] back cover.
- 2) J. R. Partington, *A History of Greek Fire and Gunpowder*, W. Heffer and Sons, Ltd, Cambridge, 1960, Chapter III. The quote may be found on p 96 of the 1999 edition (The Johns Hopkins University Press, Baltimore and London).
- 3) T. L. Davis, *The Chemistry of Powder and Explosives*, Angriff Press, Hollywood, 1975; [a] p 29; [b] p 43.
- 4) T. Shimizu, *Fireworks, the Art, Science and Technique*, Maruzen, Tokyo, 1981; [a] p 55; [b] pp 57–61.
- 5) A. A. Shidlovskiy, *Principles of Pyrotechnics*, Mashinostroyeniye Press, Moscow, 1964, pp 182–186.
- 6) J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, New York, 1985, pp 150–163.
- 7) R. Lancaster, *Fireworks Principles and Practice*, 3rd edition, Chemical Publishing, New York, 1998, p 246.

Editor’s note: The author was given the opportunity to respond to these two reviews; however, no response has been received.

Events Calendar

Pyrotechnics

NDIA – Insensitive Munitions & Energetic Materials

Nov. 29–Dec. 2 1999, Tampa, FL, USA

Contact: Megan McCrory

National Defense Industrial Assoc. Event #055

2111 Wilson Boulevard, Suite 400

Arlington, VA 22201–3061

e-mail: mmccrory@ndia.org

Web site: www.adpansia.org/interview/register.ndia

Pyrotechnic Chemistry

Instructors: Ken and Bonnie Kosanke

March 6–7, 2000, Gatton, QLD, Australia

Contact: Clive Featherby

Freeport 99, PO Box 1103

Nambour, Qld 4560, Australia

Phone: +61-7-5446-8236

FAX: +61-7-5446-8456

e-mail: jwagner@bigpond.com

Web site: www.kcsfireworks.com.au

5th International Symposium on Fireworks

April 10–14, 2000, Naples, Italy

Contact: Dawn Stewart

Phone: +613-995-1026

FAX: +613-995-1230

e-mail: driche@ncrcan.gc.ca

3rd Seminar “New Trends in Research of Energetic Materials”

April 12–13, 2000, Pardubice, Czech Republic

Contact: Prof. Pavel Vávra

Dept. Theory & Technology of Explosives

University of Pardubice

CZ-532 10 Pardubice, Czech Republic

Phone: +42-40-603-8023

FAX: +42-40-603-8024

e-mail: pavelvavra@upce.cz

Web site: www.intlpyro.org/Czech1/htm

5th Int. Symp. on Special Topics in Chemical Propulsion Combustion of Energetic Mat.

June 19–22, 2000, Stresa, Italy

Contact: Prof. Kenneth K. Kuo, Co-Chair.

140 Research Building East, Bigler Road

Pennsylvania State university

University Park, PA 16802, USA

Phone: +814-863-6270

FAX: +814-863-3203

e-mail: kkkper@entr.psu.edu

Web site: www.me.psu.edu/kup/5-isticp

31st Int. Annual Conf. of ICT “Energetic Materials – Analysis, Diag. and Testing”

June 27–29, 2000, Karlsruhe, Germany

Contact: Manuella Wolff

Fraunhofer-Inst. für Chem. Technologie (ICT)

P. O. Box 1240

D-76318 Pfinztal (Berghausen), Germany

Phone: +49-(0)721-4640-121

FAX: +49-(0)721-4640-111

e-mail: mw@ict.fhg.de

Web site: www.ict.fhg.de

27th International Pyrotechnics Seminar

July 16–21, 2000, Grand Junction, CO, USA

Contact: Alita Raoch, IPS 2000 Coordinator

Los Alamos, NM 87545, USA

Phone: +505-665-6277

FAX: +505-665-3407

e-mail: alita@lanl.gov

Web site: www.ipsusa.org

Chemistry of Pyrotechnics & Explosives

July 23–28, 2000, Chestertown, MD, USA

Advanced Pyrotechnic Seminar: Explosives & Propellants—The Past, Present & Future

Jul. 30–Aug 4, 2000, 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

2nd Int'l Disposal Conference

November 2000

Contact: Mr. Ola Listh, FOA
SE-172

90 Stockholm, Sweden

Phone: +46-8706-3510

FAX: +46-8706-3521

e-mail: listh@sto.foa.se

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

Contact: Manuella Wolff

Fraunhofer-Inst. für Chem. Technologie (ICT)

P. O. Box 1240

D-76318 Pfinztal (Berghausen), Germany

Phone: +49-(0)721-4640-121

FAX: +49-(0)721-4640-111

e-mail: mw@ict.fhg.de

Web site: www.ict.fhg.de

Explosives

Computational Mech. Assoc. Courses—2000

Introduction to Explosives (Mar 6–10)

Detonation: An Engineering Approach
(March 21–24)

Explosive Initiation and Initiators
(April 25–28)

Material Behavior at High Strain Rates
(April 25–28)

Explosive Effects and Applications
(May 16–19)

Fundamentals of Shaped Charges
(June 12–16)

Contact: Computational Mechanics Associates
PO Box 11314,

Baltimore, MD 21239-0314, USA

Phone: +410-532-3260

FAX: +410-532-3261

Fireworks

Pyrotechnics Guild International Conv.

Aug. 7–11, 2000, Muskegon, MI, USA

Contact: Steve Franklin, Chairman

2866 Vandenberg

Muskegon, MI 49444, USA

Phone: +616-737-9903

e-mail: sfsummit@aol.com

Web site: www.pgi.org

11th Western Winter Blast

Feb. 11–13, 2000, Lake Havasu, AZ, USA

Contact: Steve Rhodes

Phone: +906-685-2968

e-mail: remains4u@aol.com

Web site: wpa.pyrotechnics.org

Fireworks Display Operator Training

Instructors: Ken and Bonnie Kosanke

March 8–10, 2000, Gatton, Qld, Australia

Contact: Clive Featherby

Freepost 99, PO Box 1103

Nambour, Qld 4560, Australia

Phone: +61-7-5446-8236

FAX: +61-7-5446-8456

e-mail: firework@dcc.net.au

Web site: www.kcsfireworks.com.au

High Power Rocketry

LDRS 2000

July 1–4, 2000, Orangeburg, SC, USA

Contact: see web site

www.tripoli.org/launchpad/LDRS2000.html

Model Rocketry

NARAM 2000

July 20–Aug. 4, 2000 – SE Colorado, USA

Contact: — see web site for details:

<http://www.naram2000.org>

For launch information visit the NAR Web site: www.nar.org

Journal Sponsors

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

Individual Sponsors:

Ed Brown

P.O. Box 177
Rockvale, CO 81244, USA
Phone: +719-784-4226
e-mail: 34031.3066@compuserve.com

Larry Crump

2001 SE 11th Street
Mineral Wells, TX 76067,
USA

Phone: +940-325-1517
FAX: +972-323-2252
e-mail: lcrump1@wf.net
Web: www.wf.net/~lcrump1

Gerald Laib

17611 Longview Lane
Olney, MD 20832, USA
Phone: +301-744-4358
FAX: +301-744-4784
e-mail: gerald_rlaib@yahoo.com
laibgr@ih.navy.mil

Corporate Sponsors:

Allied Specialty Insurance

David H. Smith
10451 Gulf Blvd.
Treasure Island, FL 33706, USA
Phone: 800-237-3355
FAX: +727-367-1407
e-mail: info@alliedspecialty.com
Web: www.alliedspecialty.com

American Fireworks News

Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328 USA
Phone: +570-828-8417
FAX: +570-828-8695
e-mail: afn@98.net
Web: www.fireworksnews.com

Astro Pyrotechnics

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

blacksky Corporation

Scott Bartel
3179 Roosevelt Street
Carlsbad, CA 92008, USA
Phone: +760-730-3701
Fax: +760-730-3704
e-mail: scott@blacksky.com
Web: www.blacksky.com

Canadian Explosives Research Laboratory

Ron Vandebek
CANMET, 555 Booth St.
Ottawa, ON 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
e-mail: delcor@hotmail.com

Dolliff, Inc. / Insurance

John Allen
6465 Wayzata Blvd., Suite 850
St. Louis Park, MN 55426, USA
Phone: 800-338-3531/+612-593-7418
FAX: +612-593-7444
e-mail: JAllen@dolliff.com

European Pyrotechnics Arts Newsletter – EPAN

Rob Driessen
Van Hoensbroekstraat 16
NL 6071 CN Swalmen
The Netherlands
Phone: +31-475-501-711
FAX: +31-475-501-711
e-mail: driessen@cuci.nl

Fire One

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

Firefox Enterprises Inc.

Gary Purrington
11612 N. Nelson
Pocatello, ID 83202, USA
Phone: +208-237-1976
FAX: +208-237-1976
e-mail: custserv@firefox-fx.com
Web: www.firefox-fx.com

Fireworks Professionals

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

Fireworks

John Bennett
68 Ridgewood Gardens
Bexhill-in-Sea, East Sussex
TN40 1TS, United Kingdom
Phone: +44-1424-733-050
FAX: +44-1424-733-050
e-mail: JFBen@netcomuk.co.uk
Web: www.fireworks.co.uk/
fireworks-journal

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

Fireworks Business

Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: +717-828-8417
FAX: +717-828-8695
e-mail: afn@98.net
Web: www.fireworksnews.com

Fullam's Fireworks, Inc.

Rick Fullam
P.O. Box 1808 CVSR
Moab, UT 84532, USA
Phone: +435-259-2666

Goex, Inc.

Mick Fahringer
PO Box 659
Doyline, LA 71023-0659, USA
Phone: +318-382-9300
FAX: +318-382-9303
e-mail: goexpowder@aol.com
Web: www.shooters.com/goex

High Power Rocketry

Bruce Kelly
PO Box 970009
Orem, UT 84059-0009, USA
Phone: +801-225-3250
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@powernet.net
Web: www.aerotech-rocketry.com
www.specificimpulse.com

Iowa Pyro Supply

Mark Mead
1000 130th St.
Stanwood, IA 52337, USA
Phone: +319-945-6637
FAX: 319-945-0007
e-mail: iowapyro@netins.net
Web: www.netins.net/showcase/
iowapyrosup

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: +608-987-4750
FAX: +608-987-4750
e-mail: kastner@mhtc.net

KC's Fireworks Displays

Clive Featherby
P.O. Box 1103
Nambour, Queens. 4560, Australia
Phone: +61-7-5446-8236
FAX: +61-7-5446-8456
e-mail: firework@dcc.net.au
Web: kcsfireworks.com.au

Lantis Fireworks & Lasers

Ken Lantis
PO Box 491
Draper, UT 84020, USA
Phone: +801-768-2255
FAX: +801-768-2433
e-mail: info@fireworks-lasers.com
Web: www.fireworks-lasers.com

Luna Tech, Inc.

Tom DeWille
148 Moon Drive
Owens Cross Roads, AL 35763, USA
Phone: +256-725-4225
FAX: +256-725-4811
e-mail: PyropakUSA@aol.com
Web: www.pyropak.com

Marutamaya Ogatsu Fireworks Co., Ltd.

1-35-35 Oshitate Fuchu
Tokyo, 183-0012, Japan
Phone: +81-42-363-6251
FAX: +81-42-363-6252
e-mail: moff@za2.so-net.ne.jp

Mighty Mite Marketing

Charlie Weeth
122 S. 17th St.
LaCrosse, WI 546018, USA
Phone: +608-784-3212
FAX: +608-782-2822

Miller Pyrotechnics

Chy Miller
119 North 9th
Sterling, KS 67579, USA
Phone: +316-278-3028
e-mail: millers@awav.net
Web: www.oe-pages.com/BIZ/
Getrich/pyroman

MP Associates Inc.

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

Ontos Pyrotechnics, Inc.

John and Karin Driver
1059 Carter Road
DeLand, FL 32724, USA
Phone: +904-736-8996
FAX: +904-740-0555
e-mail: JWDriver@worldnet.att.net

OXRAL, Inc.

Tom DeWille
P.O. Box 160
Owens Cross Roads, AL 35763, USA
Phone: +256-725-4225
FAX: +256-725-4811
e-mail: oxral@pyropak.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
Web: www.pyro-pro.com

Pyro Shows, Inc.

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

Pyrodigital Consultants

Ken Nixon
1074 Wranglers Trail
Pebble Beach, CA 93953, USA
Phone: +831-375-9489
FAX: +831-375-5225
e-mail: pyrodig@aol.com
Web: www.infinityvisions.com/pyrodigital

PyroLabs, Inc.

Ken Kosanke
1775 Blair Road
Whitewater, CO 81527, USA
Phone: +970-245-0692
FAX: +970-245-0692

Pyrotechnics Guild Int'l., Inc.

Ed Vanasek, Treas.
18021 Baseline Avenue
Jordan, MN 55352, USA
Phone: +612-492-2061
e-mail: edvanasek@aol.com
Web: www.pgi.com

RES Specialty Pyrotechnics

Steve Coman
Route 1, Box 7601
Belle Plaine, MN 56011, USA
Phone: +612-873-3113
FAX: +612-873-2859
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

The Show Factory Pty. Ltd.

Kim Lowes
Factory 3 / 21 Church Street
Abbotsford, Melbourne, Vic.
3067
Australia
Phone: +61-3-9428-7710
FAX: +61-3-9428-0901
e-mail: pyrohead@onthe.net.au

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

Sunset Fireworks Ltd.

Gerald Walker
10476 Sunset Drive
Dittmer, MO 63023, USA
Phone: +314-274-1500
FAX: +314-274-0883
Web: www.sunsetfireworks.com

Sunset Fireworks, Ltd. / Omaha

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

Syd Howard's Fireworks International Pty. Ltd

Syd Howard
420 Halcrows Road, Glenorie
Sydney, NSW 2157, Australia
Phone: +61-29-652-2244
FAX: +61-29-652-1581
e-mail: showard@austpyrotechnics.com.au
Web: www.sydhowardfireworks.com.au

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

TNO Prins Maurits Lab.

Pyrotechnics & Energetic Materials
Rutger Webb
PO Box 45
Rijswijk, NL 2280 AA
The Netherlands
Phone: +31-15-284-3771
FAX: +31-15-284-3974
e-mail: webb@pml.tno.nl
Web: www.tno.nl/instit/pml/pe.htm

Western Pyrotechnics, Inc.

Rudy Schaffner
2796 Casey Road
Holtville, CA 92250, USA
Phone: 760-356-5426
FAX: 760-356-2051
e-mail: renitad@thegrid.net

Sponsorships

- ◆ No advertising as such is printed in the *Journal of Pyrotechnics*. However, a limited number of sponsors have been sought so that the selling price of the Journal can be reduced from the listed cover price.
 - ◆ Sponsorships are \$70 per issue of the Journal, for which the sponsor receives two complimentary copies of the sponsored issue, permanent listing in the sponsored issue, listing on a loose flyer in the issue, plus information on the Sponsor area of the JPyro web site, if desired.
 - ◆ What else do sponsors receive?
 - ⇒ A good feeling for having contributed to the advancement of fireworks by supporting the dissemination of technical information.
 - ⇒ Membership in an exclusive group of several of the most prominent names in the international pyrotechnic industry.
 - ⇒ Our deepest gratitude!
 - ◆ For more information contact Bonnie Kosanke at the Journal of Pyrotechnics.
-

Guidance for Authors of Full Articles

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 or (202) 776-8100.

Manner of Submission:

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

General Writing Style:

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

Format:

In addition to the authors' names, please include an affiliation for 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, not a listing of areas to be addressed.)

Include 3 to 5 keywords (more if necessary) to be used in a reference database. 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 a conversion to the appropriate 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.

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, not alphabetically. A full citation is preferred, including author, title, book or journal, publisher for books, and volume and pages for journals, etc. Examples:

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

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.

More Information:

Contact:

Bonnie Kosanke, Publisher,
Journal of Pyrotechnics, Inc.
1775 Blair Road
Whitewater, CO 81527, USA

Phone/FAX: +970-245-0692

e-mail: bonnie@jpyro.com