

Journal of Pyrotechnics

Issue 8, Winter 1998

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CAUTION

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

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

Table of Contents

Issue Number 8, Winter 1998

Organic Fuels: Composition and Formation Enthalpy Part I — Wood Derivatives, Related Carbohydrates, Exudates, and Rosin Will Meyerriecks	1
Composite Color Stars Scot Anderson	19
Silicone II: A New Fuel and Binder for Fireworks Ken Burdick	31
Determination of the Velocity of Fragments Produced from Exploding Firework Maroon Shells S. G. Myatt	43
Glitter Chemistry Clive Jennings-White	53
Communications: Comment from R. Webb on “High-Nitrogen Pyrotechnic Compositions”, Issue 7	29
Comment from B. Nelson on “Development of a Video Spectrometer”, Issue 7	52
Review by C. Weeth of White’s article “Pollution Caused by Fireworks”	72
Review by M. Rossol of White’s article “Pollution Caused by Fireworks”	74
Errata	17
Events Calendar	18
Guide for Authors	42
Sponsors	77

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

Organic Fuels: Composition and Formation Enthalpy Part I — Wood Derivatives, Related Carbohydrates, Exudates, and Rosin

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ABSTRACT

The utilization of free energy minimization computer programs in areas of combustion research is likely to increase in the future. These programs require the specification of the reactant chemical formulas and their respective formation enthalpies as part of the input data set. Frequently, for common compounds, the values required are readily available in handbooks. Complex organic compounds or poorly characterized mixtures may not have the required data available in a directly usable form. This article evaluates a variety of organic fuels used in pyrotechnics from the perspective of establishing useful chemical formulas and formation enthalpies. Along the way, it is the author's intention to simplify the methods used, to illustrate how many disparate sources of information may be drawn upon to achieve the estimation of the required values, and to demonstrate that each of the methods used is itself relatively easy to perform or calculate.

Keywords: chemical composition, enthalpy of formation, higher heating value (HHV), Benson group, free energy minimization, ultimate analysis, trace elements, wood, monosaccharide, disaccharide, oligosaccharide, polysaccharide, sugar, lactose, sucrose, cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, cellulose nitrate, lignin, starch, gum, gum arabic, gum tragacanth, guar gum, rosin

Introduction

Considerable varieties of organic fuels are available for and are used in pyrotechnic formulations. Choosing the right fuel for the intended application is made all the more difficult if the data required to make an informed decision is incomplete or unavailable. The primary focus of this article is to present chemical formulas and formation enthalpy estimates for common organic fuels that will be useful to the pyrotechnist and energetics chemist.

The author believes that, in the future, the use of free energy minimization software will find wider acceptance as an important tool for use in the combustion products analysis of pyrotechnic formulations. These programs allow the investigator to simulate, study, and optimize the combustion properties of a pyrotechnic formulation prior to actually handling the potential ingredients. This will certainly expedite the formulation development cycle and improve the end product.

These programs require, in part, that the chemical composition and formation enthalpies of the ingredients—the *reactants*—be specified as part of the input data set. The compositions of these fuels range from simple, pure compounds to complex mixtures that are poorly characterized. Many of the fuels have variable compositions. This may be due in part to the source location, climate, collection time of year, or species. In some cases, the chemical compositions are readily available in handbooks. The formation enthalpies, on the other hand, are rarely available, but may be estimated using a variety of methods.

The reference values listed in the following tables are expressed as either *higher heating value* (HHV), *formation enthalpy* ($\Delta_f H^\circ$), or *combustion enthalpy* ($\Delta_c H^\circ$). Units of kilojoule (kJ) or megajoule (MJ) per kilogram (kg) or mole are used for both. Formation enthalpies are for the solid phase unless otherwise indicated. *Molecular weights* (MW) are in gram-moles. The method used for estimating the $\Delta_f H^\circ$ is denoted by superscripted letter(s) following the value:

H	HHV
C	Combustion enthalpy
B	Benson group additivity
PB	Partial Benson group additivity
D	Simple difference method
F	Flame temperature and formulation

Each of these methods is described in "Six Methods for Estimating the Formation Enthalpy of Organic Compounds".^[1] For convenience, the chemical formulas are generally represented using a common basis such that comparisons may be readily made between the different fuels. The author arbitrarily chose a C₆ formula basis because many fuels are derived from simple C₆-based molecules. Chemistry Abstract Service Registry Numbers (CAS numbers) are provided when available.

It is assumed that the reader has some familiarity with basic chemistry. Most of the detailed and often confusing nomenclature used in carbohydrate chemistry will be oversimplified or avoided altogether, perhaps to the distress of the chemistry purist. This nomenclature is generally not relevant to the purpose of this article.

This article covers organic fuels based on wood, its direct derivatives, related carbohydrates, exudates, and rosin.

Part II of this series of articles covers acaroid resin, shellac, destructive distillation of wood: charcoal and pitch; gilsonite; waxes; and a sampling of pure fuels and synthetic polymers.

Wood is the source for many fuels used in pyrotechnics; thus it is the logical starting point.

Wood and Its Derivatives: Wood

Wood, by itself, is generally not used in pyrotechnic formulations. Occasional references, such as Shimizu,^[2] use finely divided sawdust as a fuel. *Hardwoods* are generally characterized as deciduous trees such as oaks, and *softwoods* are coniferous trees such as pines.^[3] A sampling of common tree species is listed in Table 1.

The energy value of wood depends in part on the tree species and the wood material, such as the bark, heartwood, sapwood, etc. These values cannot be defined precisely for a given species, tree or even part of the tree. This is due, in part, to variations in location, climate, season, and soil conditions.^[4] Accumulated data from various labs over many years has yielded average values. Representative ultimate elemental compositions and heating values appear in Table 1.

The three primary polymers that make up the bulk of wood are *cellulose*, *lignin*, and *hemicellulose*. A general compositional analysis reveals the following:^[5]

	Cellulose	Lignin	Hemi-cellulose
Hardwoods	43%	22%	35%
Softwoods	43%	29%	28%

Note: Values are on a dry, extractive free basis.

Wood has a roughly uniform composition with a C₆-based chemical formula of: C₆H_{8.7}O_{3.921}N_{0.012}S_{0.001}, and a corresponding $\Delta_f H^\circ$ of -738.8 kJ/mole^H .

Ash composition is a function of the trace elements present in wood (see Table 2) and is composed primarily of calcium and potassium oxides. Bark has approximately 10–20 times the ash content of wood and is slightly different in trace element composition. This may be due, in part, to extraneous mineral matter being inadvertently picked up during handling.^[7]

Table 1. Ultimate Elemental Compositions and Heating Values of Selected Woods.

	Elemental Analysis (% weight, dry basis)						HHV (MJ/kg)	$\Delta_f H^\circ_{298}$ (MJ/kg ^H)	Ref.
	C	H	O	N	S	Ash			
Hardwoods									
Beech	51.64	6.26	41.45	0.0	0.0	0.65	20.38	-5.427	5
Hickory	49.67	6.49	43.11	0.0	0.0	0.73	20.17	-5.316	5
Oak, Black	48.97	6.04	43.48	0.15	0.02	1.40	18.65	-5.957	6
Maple, Big Leaf	49.89	6.09	43.27	0.14	0.03	0.60	18.86	-6.120	6
Poplar	48.45	5.85	43.69	0.47	0.01	1.33	19.38	-4.788	6
Walnut, Black	49.80	5.82	43.25	0.22	0.01	0.78	19.83	-4.737	6
Willow, Hybrid	48.32	6.09	44.70	0.14	0.08	0.73	19.30	-5.171	6
Average	49.53	6.09	43.28	0.16	0.02	0.89	19.51	-5.359	
Softwoods									
Fir, Douglas	50.64	6.18	43.00	0.06	0.02	0.10	20.37	-4.981	5
Fir, White	49.00	5.98	44.75	0.05	0.01	0.25	19.95	-4.582	5
Hemlock, Western	50.4	5.8	41.4	0.1	0.1	2.2	20.05	-4.706	4
Pine, Ponderosa	49.25	5.99	44.36	0.06	0.03	0.29	20.02	-4.610	5
Redwood	50.64	5.98	42.88	0.05	0.03	0.36	20.72	-4.350	5
Average	49.99	5.99	43.28	0.06	0.04	0.64	20.22	-4.646	
Overall Average:	49.72	6.05	43.28	0.12	0.03	0.79	19.77	-5.062	

Note: Reference 6 included trace amounts of chlorine in the elemental analysis percentages.

Table 2. Trace Element Analysis for Selected Woods.

	Trace Elements (ppm)									
	Ca	K	Mg	P	Mn	Na	Cu	Zn	Fe	Cl
Hardwoods										
Aspen, Quaking ^[a]	950	1050	270	100	35	5	7	17	12	—
Maple, Red ^[a]	750	600	120	30	70	5	5	29	11	18
Oak ^[b]	400	900	170	20	10	33	73	38	30	15
Sweetgum ^[c]	600	350	355	205	70	85	—	21	—	—
Softwoods										
Fir, Balsam ^[a]	850	650	270	—	110	18	17	11	13	—
Hemlock, Eastern ^[a]	950	350	110	120	135	6	5	2	6	—
Pine, Eastern White ^[a]	250	200	70	—	25	9	5	11	10	19
Spruce, Red ^[a]	750	150	70	50	125	8	4	8	14	0.3
Average	688	531	179	88	73	21	17	17	14	13

All values based on moisture-free wood. Data from reference 4. Items designated “—” not used in average.

[a] Average of atomic spectroscopic and neutron activation methods.

[b] Average of White and Southern Red Oak.

[c] Average of Bottomland and Upland Sweetgum.

The trace elements present in wood might adversely affect, for example, the purity of a flame's color. It requires very little sodium to produce the generally undesirable, characteristic yellow 589 nm emission doublet. See Ta-

ble 2. Many of these trace elements find their way into wood derivatives, such as charcoal, or exudates, such as gums.

Carbohydrates

Monosaccharides

Wood-based *polymers* all start with *monomers*. The fundamental monomer building blocks are *monosaccharides*. Many have the general formula $C_6H_{12}O_6$.^[8] They are also known as *simple sugars*, or just *sugars*.^[8] The general formulas of monosaccharides are classified according to the number of carbon atoms they contain. Those that are of importance in this article are *pentoses*, $C_5H_{10}O_5$ and *hexoses*, $C_6H_{12}O_6$.^[9,10] These monosaccharides can form either linear molecules or stable ring structures. The *furanose* ring form is five sided (see D-ribose Figure 1), and *pyranose* is six sided (see D-arabinose Figure 1). On both, one ring position is occupied by an oxygen atom. The ring forms are of the most concern in this article. Figure 1 illustrates a few representative monosaccharides. Table 3 lists a few common monosaccharides and their abbreviated names.

A variety of different molecular representations may be encountered in chemical literature. The author took the liberty of displaying a few common styles in Figure 1: α -D-xylose is shown using both *Fischer* and *Haworth* projections (sometimes referred to as *Haworth hexagonal*).^[11] D-sucrose in Figure 2 uses a *Haworth conformational* style, which better illustrates the *chair* conformation of the ring structures. Solid wedge bonds project toward the viewer from the plane of the paper, and hashed wedge bonds project away from the viewer. Typical of most rendering schemes, hydrogens have been removed for clarity.

From these illustrations and the data presented in Table 3, it is evident that the chemical formulas and their corresponding *molecular weights* (*MW*) are the same for many of the compounds, but the position of the *hydroxyl* (*OH*) group may be above or below the equator of a ring sugar. This leads to, for the $C_6H_{12}O_6$ hexoses as an example, 16 different *stereoisomers*. Each has a different name and properties.

The proper nomenclature to sort this out gets involved.

For combustion purposes the chemical compositions are identical, and the $\Delta_f H^\circ$ is essentially constant for the various stereoisomers—the variations in $\Delta_f H^\circ$ are generally less than 1%. (See Table 3.) For these reasons, this article will dispense with most of the exact carbohydrate nomenclature. Focus is instead directed toward formulating practical estimates of the formation enthalpies and chemical formulas. Average $\Delta_f H^\circ$ values based on the references may be used when specific values are unknown.

Oligosaccharides

Oligosaccharides are polymers composed of from 2 to 10 monosaccharides.^[8] This quantity is an arbitrary number, but fortunately, nature produces very few carbohydrates between 5 and 15 sugar residues.^[9] If the oligosaccharide is composed of two monosaccharides, then it is sometimes referred to as a *disaccharide*.^[16] The individual monosaccharides are linked together with a *glycoside bond*.^[17] (This is also known as an *oxygen bond*.^[18] It may also be a *glucoside* bond depending on the specific monosaccharides involved, etc.^[16] In this article *glycoside* will be used for uniformity.) This bond is formed between the hydroxyl group on the anomeric^[9] (hemi-acetal)^[17] carbon atom of one monosaccharide and any hydroxyl group on the other monosaccharide. Water (H_2O) is eliminated in the process. Figure 2 illustrates the glycoside bond, elimination of water, and two familiar disaccharides that form as a result: *lactose* (“milk sugar”) and *sucrose* (“cane sugar”). Note that sucrose is composed of a pyranose and a furanose sugar.

In a fashion similar to that of the monosaccharides, there are *many* possible oligosaccharides. Note that the chemical compositions are identical ($C_{12}H_{22}O_{11}$) for the oligosaccharides listed in Table 3, and the variations in $\Delta_f H^\circ$ are within 1% of their average.

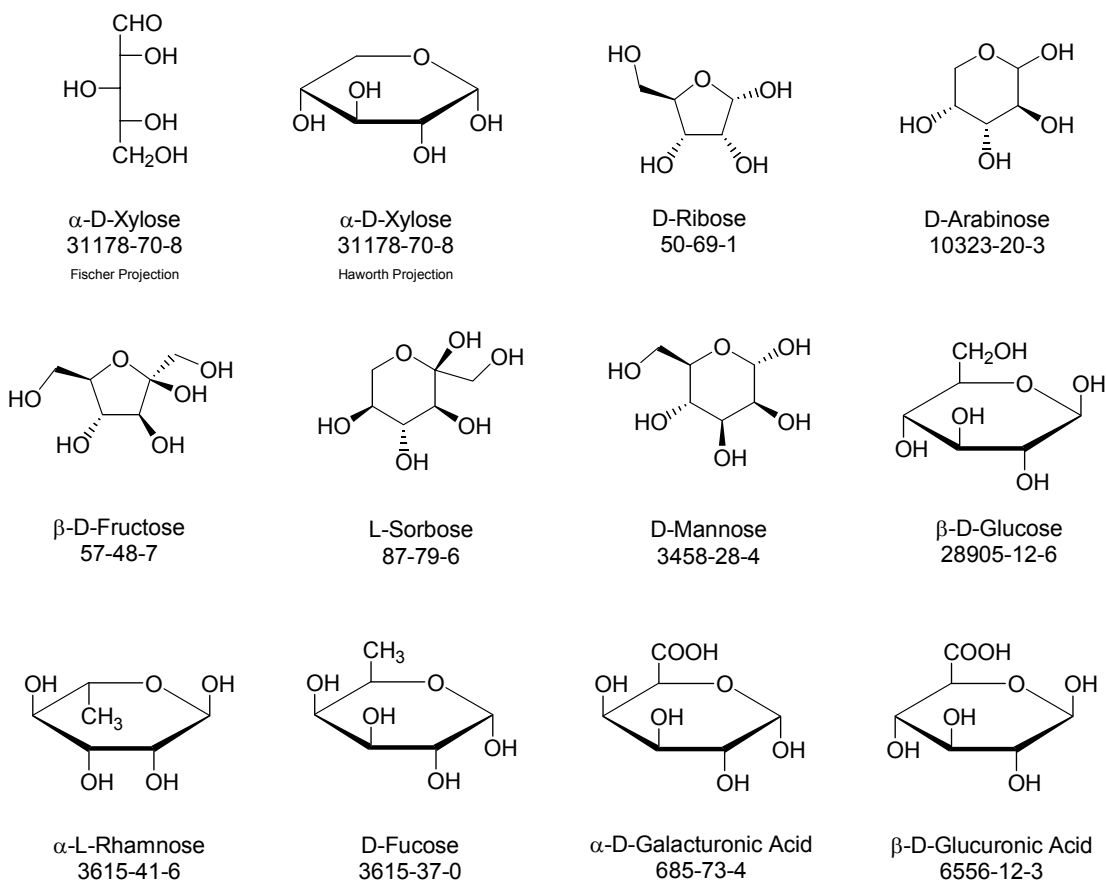


Figure 1. Some representative monosaccharides.

When a disaccharide forms, the resulting $\Delta_f H^\circ$ is not equal to the sum of that of the constituent monosaccharides. This is due, in part, to the rearrangement of the atoms that participate in the glycoside bond and the elimination of water. If the $\Delta_f H^\circ$ of the monosaccharides (reactants) are added, and this sum is then sub-

tracted from the $\Delta_f H^\circ$ of the disaccharide (product), the difference represents the change in enthalpy (*heat of reaction*^[8,10] $\Delta_r H^\circ$) for glycoside bond formation and water elimination. Using the averages from Table 3, see calculation at bottom of next page.

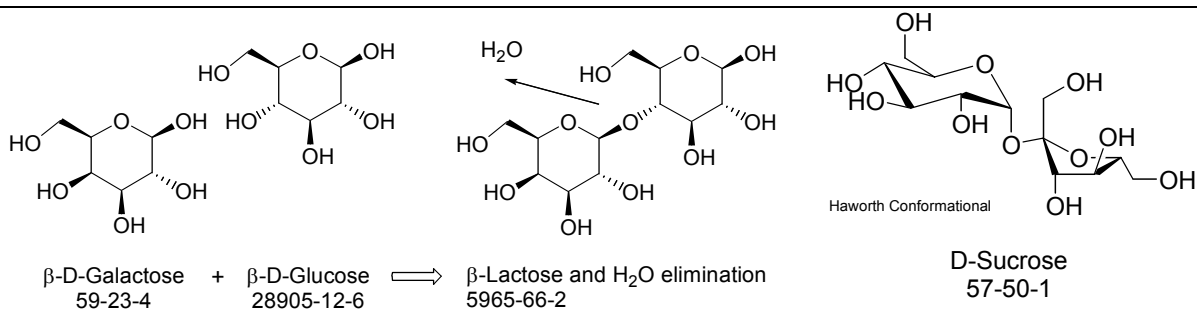


Figure 2. Glycoside bond formed by elimination of water from two monosaccharides; and two familiar disaccharides: β -lactose and D-sucrose.

Table 3. Chemical Formulas, Abbreviations, and Formation Enthalpies for Some Common Mono- and Oligosaccharides.

Name	Abbr. ^[9]	CAS No.	References	$\Delta_f H^\circ$ kJ/mole ^[a]
α -D-xylose	Xyl	31178-70-8	12, 13	-1053.6
D-ribose	Rib	50-69-1	12 – 15	-1053.4
D-arabinose	Ara	10323-20-3	12 – 15	-1056.6
C₅H₁₀O₅	MW 150.13		Average:	-1054.7
L-rhamnose	Rha	3615-41-6	12, 15	-1073.2
D-fucose	Fuc	3615-37-0	12, 15	-1099.1
C₆H₁₂O₅	MW 164.16		Average:	-1086.2
α -D-glucose	Glc	26655-34-5	12 – 15	-1273.8
β -D-glucose	Glc	28905-12-6	13, 14	-1267.5
β -D-fructose	Fru	57-48-7	12 – 15	-1266.4
α -D-galactose	Gal	3646-73-9	12 – 15	-1286.0
L-sorbose	—	87-79-6	12, 13	-1271.1
D-mannose	Man	3458-28-4	12, 13, 15	-1263.1
C₆H₁₂O₆	MW 180.16		Average:	-1271.4
D-sucrose	—	57-50-1	12 – 15	-2223.2
β -lactose	—	5965-66-2	12 – 15	-2236.2
Cellobiose	—	528-50-7	13, 15	-2221.5
Maltose	—	69-79-4	13, 15	-2215.1
C₁₂H₂₂O₁₁	MW 342.30		Average:	-2226.1

[a] All values based on averages of the references.

Each of the two monosaccharides participates in *half* of this bond, so the average respective $\Delta_f H^\circ$ *per monosaccharide* is approximately 158.35 kJ/mole^D. This value will be used in subsequent estimates. The change in MW by elimination of *each* H₂O molecule is -18.02.

Polysaccharides

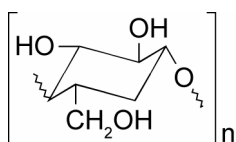
Polysaccharides are polymers where the number of sugar residues is greater than 10.^[17] As with oligosaccharides, the glycoside bond links the monosaccharides together. There are usually two, but sometimes more, glycosidic bonds between the monosaccharides.

One disaccharide	= 1 C ₁₂ H ₂₂ O ₁₁	=	- 2226.1	kJ/mole
Two monosaccharides	= 2 C ₆ H ₁₂ O ₆ = 2 × -1271.4	=	- 2542.8	kJ/2 moles
Glycoside bond formation (<i>average</i>) and H ₂ O elimination		=	$\frac{-2542.8}{2}$	316.7 ^D kJ/mole

Cellulose

Cellulose (9004-34-6) is the main constituent of plant cell walls and is perhaps the most abundant naturally occurring polymer.^[19] See Figure 3. Cellulose is found in its purest natural form in seed hairs, of which cotton is notable. The generally accepted empirical formula for cellulose $(C_6H_{10}O_5)_n$ agrees closely with the elemental analysis for purified cotton cellulose:^[20]

	Cotton	$C_6H_{10}O_5$
Carbon	44.35	44.45
Hydrogen	6.14	6.22
Oxygen	49.51	49.34



Cellulose
9004-34-6

Figure 3. Cellulose.

The *degree of polymerization (DP)*, or “n” in the empirical cellulose formula, denotes the number of repeating monomer units in an *average* polymer. For cotton, the *DP* is between 6200 and 6700, for pine it is 3300, and for wood pulp it ranges from 500 to 2000.^[19] The “squiggly lines” in Figure 3 represent the glycoside bonds that connect adjacent monomers. Polymers of this nature are often referred to as *macromolecules* due to their enormous sizes.^[8]

Cellulose is constructed from glycosidic bonds between adjacent monosaccharides. Each monomer participates in *two* glycoside bonds, with the exception of the monomer “caps” at each end of the chain that participate in only one bond. Considering the *DP* of cellulose, it is reasonable to ignore the “caps” only having a single glycoside bond and to base the cellulose $\Delta_f H^\circ$ estimate on two bonds for all monomers as illustrated in Figure 3 (an infinitely long chain).

One monosaccharide	= $C_6H_{12}O_6$	= -1271.4	kJ/mole
Two glycoside bonds and elimination of H_2O	= 2×158.35	= + 316.7	kJ/2 moles
Cellulose $(C_6H_{10}O_5)_n$		= -954.7 ^D	kJ/mole

The calculation at the bottom of this page agrees well with the $\Delta_f H^\circ$ of -979.0 kJ/mole^C for filter paper cellulose. (See Table 5 near the end of this article.)

Cellulose (paper) may be used, for example, as tubing for pyrotechnic devices, as liners for composite propellant rocket motor grains, or directly as a fuel in hybrid rocket motors.

Lignin

Lignin (9005-53-2) is a polymer of amorphous structure^[8] with an approximate formula of $C_{10}H_{11}O_2$.^[21] It consists of a complex array of bonds between hydroxy- and methoxy-substituted phenylpropane units. The three primary precursors (see Figure 4) are:

p-coumaryl alcohol (3690-05-9, $C_9H_{10}O_2$),
coniferyl alcohol (458-35-5, $C_{10}H_{12}O_3$), and
sinapyl alcohol (537-33-7, $C_{11}H_{14}O_4$)^[18]

The $\Delta_f H^\circ$ of -1153.3 kJ/mole^C will be considered representative. Lignin is not directly utilized in pyrotechnic formulations or rocketry.

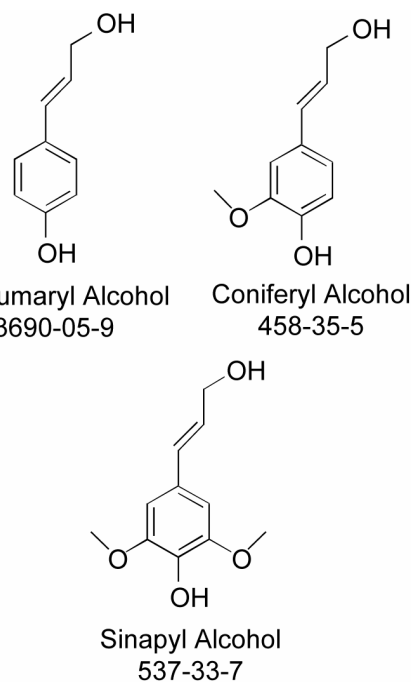


Figure 4. Primary precursors of lignin.

Hemicellulose

The hemicelluloses are polymers related to cellulose and have a *DP* of 150 or less.^[8] Hemicellulose is generally easily hydrolyzed and is a branched and amorphous structure^[22] that is rather ill-defined.^[10] Whereas cellulose is a *homopolysaccharide* based on repeating glucose monomers,^[8] hemicellulose is a *heteropolysaccharide* incorporating other sugars. Softwoods generally have higher concentrations of mannose and galactose, and hardwoods generally have more xylose.^[23]

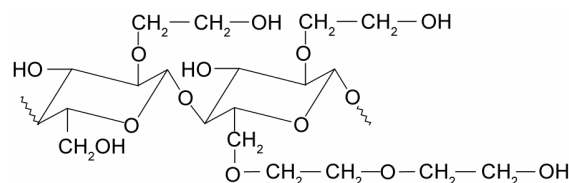
Cellulose Derivatives

Cellulose may be modified into other useful compounds, each with different properties and applications. Most of the modifications involve substituting different functional groups or short polymers for one or more of the hydroxyl groups. The *degree of substitution*, or *DS*, denotes the *average* number of hydroxyl groups that have been substituted per monomer. The *molar substitution*, or *MS*, denotes the *average* number of units substituted per monosaccharide, and this number can be any value equal to or greater than the *DS* depending on the length of these side chains.

Hydroxyethyl Cellulose

Hydroxyethyl cellulose (9004-62-0), (See Figure 5) sometimes called *Cellosize*^[8] or *HEC*,^[24] is a cellulose ether where some of the hydroxyl (OH) groups have been replaced by hydroxyethyl groups (using *ethylene oxide*, 75-21-8, C₂H₄O). The *DS* is variable and ranges from 0.2–0.5 for paper sizing to 1.5 for adhesives.^[17] A *DS* of 0.8–1.5 is usually encountered.^[19,22]

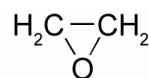
The maximum possible *DS* is 3.0 as there are only three hydroxyls per monosaccharide available for substitution. Typically, the *MS* ranges from 1.4–2.0.^[19] Figure 5 is a simple case where there are 3 substitutions on two monosaccharides, hence the *DS* is 1.5 (3.0 OH substitutions ÷ 2.0 sugar units). There are a total of 4 ethylene oxide units, so the *MS* is 2.0 (4.0 C₂H₄O units ÷ 2.0 sugar units).



Hydroxyethyl Cellulose
9004-62-0

Figure 5. *Hydroxyethyl cellulose.*

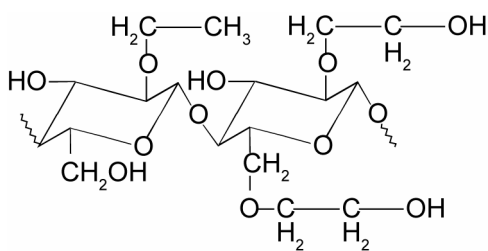
Each ethylene oxide (see Figure 6) unit adds C₂H₄O and a $\Delta_f H^\circ$ of -185.0 kJ/mole^B to the cellulose molecule. In the example illustration, the *MS* of 2.0 per sugar residue adds $2.0 \times -185.0 = -370.0$ kJ/mole and $2.0 \times C_2H_4O = C_4H_8O_2$ to the cellulose formula of C₆H₁₀O₅ and a $\Delta_f H^\circ$ of -954.7 kJ/mole; thus giving this particular (and perhaps typical) hydroxyethyl cellulose molecule a formula of (C₁₀H₁₈O₇)_n and a $\Delta_f H^\circ$ of -1324.7 kJ/mole^{PB}. In C₆ units this would be C₆H_{10.8}O_{4.2} and a $\Delta_f H^\circ$ of -794.8 ^{PB}.



Ethylene Oxide
75-21-8

Figure 6. *Ethylene oxide.*

A similar polymer is *ethyl hydroxyethyl ether cellulose* (9004-58-4),^[25] and it is illustrated^[24] in Figure 7. Both ethyl and hydroxyethyl groups substitute for hydroxyl groups. *DS* equals 1.5, ethyl *MS* equals 0.5, and hydroxyethyl *MS* equals 1.0. As in hydroxyethyl cellulose, each ethylene oxide substituted adds C₂H₄O and a $\Delta_f H^\circ$ of -185.0 kJ/mole. The ethyl group adds C₂H₄ and a corresponding $\Delta_f H^\circ$ of -79.74 kJ/mole^B. Performing the arithmetic gives a formula of (C₆H₉O₆)_n and a $\Delta_f H^\circ$ of -1179.6 kJ/mole^{PB}.



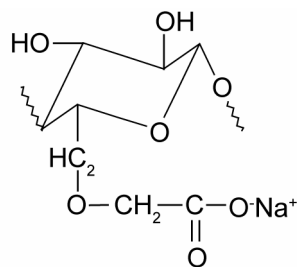
Ethyl Hydroxyethyl Cellulose
9004-58-4

Figure 7. Ethyl hydroxyethyl ether cellulose.

The commercial product is a white fibrous material that contains 1–2% ash that is probably a sodium salt.^[22] Principle uses are a binder, thickening agent, in gel lacquers, and in paper sizing.^[17,19]

Carboxymethyl Cellulose

Carboxymethyl cellulose, or CMC, has some of the hydroxyls substituted with carboxymethyl groups.^[17] Sodium carboxymethyl cellulose (9004-32-4) is illustrated^[19] in Figure 8. It has a *DS* that typically ranges from 0.5–0.85,^[19] and has a sodium cation in place of the hydroxyl's hydrogen. The illustration's chemical formula is $C_8H_{11}NaO_7$. The MW ranges from 21,000–500,000.^[8]



Sodium Carboxymethyl Cellulose
9004-32-4

Figure 8. Sodium carboxymethyl cellulose.

The author could not find $\Delta_f H^\circ$, $\Delta_c H^\circ$, or HHV data for sodium carboxymethyl cellulose, and the required sodium Benson Group values are unavailable for the solid phase.^[26] The author derived a required group value and arrived

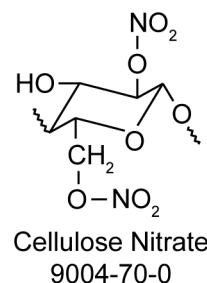
at a tentative $\Delta_f H^\circ$ estimate, for the example illustration, of $-1564 \text{ kJ/mole}^{\text{PB}}$. [Derivation: Crystalline sodium acetate (127-09-3, $C_2H_3NaO_2$) has a $\Delta_f H^\circ$ of -708.8 kJ/mole .^[27] It is composed of three Benson Groups:^[28] (C)-(H)₃(CO) with a $\Delta_f H^\circ$ of -46.74 kJ/mole ; (CO)-(C)(O) with a $\Delta_f H^\circ$ of -153.60 kJ/mole ; and the unknown group O-(Na)(CO). Difference yields an estimated $\Delta_f H^\circ$ of $-508.46 \text{ kJ/mole}_{\text{solid}}^{\text{B}}$ for the O-(Na)(CO) group.]

It is used for paper sizing,^[8] as a binder, and as a thickening agent in pyrotechnics.^[29]

Cellulose Nitrate

Cellulose nitrate (9004-70-0) has some of its hydroxyls substituted with nitro groups.^[19] (See Figure 9.) Frequently the literature uses percent nitrogen instead of *DS*. Typical ranges^[19] of these parameters are:

Nitrogen (%)	DS	DP	Application
10.7–12.3	1.9–2.4	70–850	plastics & lacquers
12.3–13.5	2.4–2.8	3000–5000	explosives & propellants



Cellulose Nitrate
9004-70-0

Figure 9. Cellulose nitrate.

Each nitro group adds NO_2 , eliminates an H and a $\Delta_f H^\circ$ of $75.66 \text{ kJ/mole}^{\text{B}}$. For the sample illustration, the *DS* equals 2.0 and the resulting formula is $C_6H_8N_2O_9$ with a $\Delta_f H^\circ$ of $-803.4 \text{ kJ/mole}^{\text{PB}}$. For a *DS* of 2.5, the resulting formula would be $C_6H_{7.5}N_{2.5}O_{10}$ with a $\Delta_f H^\circ$ of $-765.6 \text{ kJ/mole}^{\text{PB}}$.

Starch

Starch (9005-84-9, *soluble*), sometimes called *dextrin*^[29] or *starch gum*^[8] when partially hydrolyzed, occurs naturally as small granules whose size and shape are characteristic of the plant from which it is obtained. It consists of both *amylose* (9005-82-7) (C₆H₁₀O₅)_n, which is water soluble, and *amylopectin* (9037-22-3), approximate formula (C₆H₁₀O₅)_n, a branched polysaccharide that is water insoluble.^[16] The amount of amylose in starch ranges from less than 2% in waxy maize to 80% in amylo maize, but the majority of starches contain between 15 and 35% amylose.^[9] Twenty percent amylose will be considered representative. Amylose (see Figure 10) is very similar in structure to cellulose and has a *DP* of between 1000 and 4000. In this article its $\Delta_f H^\circ$ will be considered the same as cellulose (-954.7 kJ/mole^D), which compares favorably with a reference value of -955.6 kJ/mole^C. See Table 5.

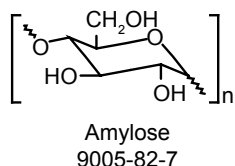


Figure 10. Amylose.

Amylopectin (see Figure 11) has a branched structure slightly more complex than that of amylose. Note the arrow pointing to the oxygen atom. The monomer drawn below this oxygen has three, rather than two, glycoside bonds. Approximately 5% of the monomers in amylopectin have three glycoside bonds rather than two. The length of each amylopectin chain is approximately 20 units.^[16,19] This yields an approximate chemical formula of (C₆H_{9.96}O_{4.96})_n.

The $\Delta_f H^\circ$ may be estimated from this *ideal* structure as in the example at the bottom of this page. Starch (dextrin), the most commonly used binder in pyrotechnic formulations,^[29] is used as an adhesive, in textile sizing, and as a thickener in foods.^[10]

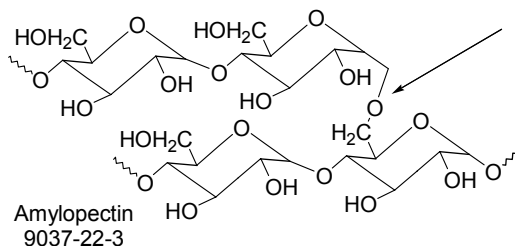


Figure 11. Amylopectin.

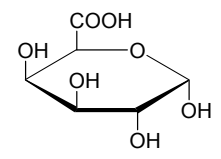
Gums and Resins: Gums

Gums are polysaccharides or their derivatives that hydrate in hot or cold water to form viscous solutions. The source of gums may be microbial, algal, seed endosperm, or plant exudates.^[30] Two plant exudates and one seed gum will be considered in this article, though the methods used apply to all gums. Gums typically consist of from two to five different monosaccharides that are linked by glycosidic bonds in a branched manner.^[31]

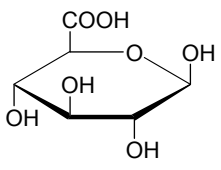
In addition to the monosaccharides that have already been encountered in this article, two additional ones are frequently present in gums: α -D-galacturonic acid and β -D-glucuronic acid. See Figure 12. Note that, for combustion purposes, these two molecules (C₆H₁₀O₇) are fundamentally the same. The $\Delta_f H^\circ$ value of -1468.8 kJ/mole^{PB} will be used for both.

Carbohydrate literature generally simplifies the graphical representation of gum polymers for reasons of brevity and clarity. Abbreviations

Amylose	=	20% of -954.7 [(C ₆ H ₁₀ O ₅) _n , bonds included]	=	-190.94 kJ/mole
Amylopectin	=	80% of -1271.4 [C ₆ H ₁₂ O ₆ monomer]	=	+ -1017.12 kJ/mole
		95% 2 glycoside bonds		
Plus		5% 3 glycoside bonds		
	=	(2 × 0.95) + (3 × 0.05) = 2.05 bonds		
	=	80% of bonds: 0.80 × 2.05 × 158.35	=	+ 259.69 kJ/mole
Starch (C ₆ H _{9.96} O _{4.96})	$\Delta_f H^\circ$		=	-948.4 ^D kJ/mole



α -D-Galacturonic Acid
685-73-4



β -D-Glucuronic Acid
6556-12-3

Figure 12. Two monosaccharides frequently present in gums.

for the constituent monomers are used and numbers indicate which ring positions are taking place in the various glycoside bonds. This article will dispense with the numbering system. The monosaccharide abbreviations (see Table 3) have either a “p” for pyranose or an “f” for furanose appended, and in the case of an acid, an “A” appended after that; thus, the furanose form of arabinose is **Araf**, and the pyranose form of β -D-glucuronic acid is **GlcA**.

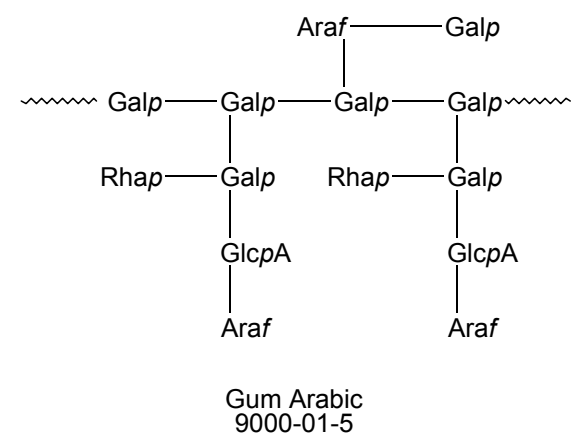
Gum Arabic

Gum arabic (9000-01-5) is an exudate collected from the various species of the thorny, shrub-like tree *Acacia*, including *A. arabica*, *A. senegal*, *A. vereck*,^[32] and *A. seyal*.^[30] When a plant is wounded it often produces a sticky sap-like substance that covers the incision. This fluid dries to a translucent and glassy mass on exposure to air. It is then collected, sorted, possibly cleaned, then crushed to a powder. Commercial grades are most likely mixtures of varying composition and stored under varying conditions.^[33]

Gum arabic is also known by dozens of other names including *Acacia*,^[29] *Abyssinia*, *black wattle* (from *A. mollissima*, *Willd*^[34]), *Ba-*

bool, *Jeddah*, *Senegal*, *Sudan*, *sunt*, *Turic*, and *white gum* just to name a few.^[32]

The generally accepted structure for this gum is illustrated in Figure 13.^[31-34] A recent report^[35] indicates that the branching structure—as determined by a variety of analytical methods—may be slightly more complicated than that used here. The molecular weight has a broad distribution. It has been variously reported as a low of 200,000,^[34] approximately 240,000–250,000,^[32,36] 580,000,^[31,37] and a high of 1,160,000;^[30] 250,000 is considered representative.



Gum Arabic
9000-01-5

Figure 13. Gum Arabic, ideal polysaccharide structure.

Gum arabic is acidic due to the high concentration of glucuronic acids. These acids usually form salts where sodium, calcium, and potassium represent the majority of the cations involved.^[32,34,36,38] Trace amounts of iron and magnesium are present.^[32] Industrial grades of gum arabic contain from 1–3% ash^[32,38] that is mainly sand or dirt,^[34,39] and may contain up to 10% bark.^[39] Discoloration is generally caused by bark tannins.^[32] Foreign matter may be removed by washing-precipitation-filtering cycles using ethanol and water.^[32,34]

The following example estimates the chemical formula and the $\Delta_f H^\circ$ based on the specific monosaccharide average values from Table 3 and the ideal polysaccharide illustrated in Figure 13 and detailed at the top of the next page.

Qty.	Sugar	$\Delta_f H^\circ$ (kJ/mole)		Total (kJ/mole)	Formula	C	H	O
3	Araf	-1056.6	=	-3169.8	$C_5H_{10}O_5$	15	30	15
7	Galp	-1286.0	=	-9002.0	$C_6H_{12}O_6$	42	84	42
2	Rhap	-1073.2	=	-2146.4	$C_6H_{12}O_5$	12	24	10
2	Glc pA	-1468.8	=	-2937.6	$C_6H_{12}O_7$	12	20	14
14			=	-17255.8		81	158	81
26	Bonds	158.35	=	4117.1	$\frac{1}{2} H_2O^{[a]}$	—	-26	-13
	Gum Arabic			-13138.7 ^D	$C_{81}H_{132}O_{68}$	81	132	68

[a] There are 26 “participants” in the bonds, each eliminating *half* a water molecule (13 total water molecules eliminated).

Gum Arabic ($C_{81}H_{132}O_{68}$)_n has a $\Delta_f H^\circ$ of -13138.7 kJ/mole^D. Based on a molecular weight of 250,000, “n” is approximately 114. In C_6 units this is $C_6H_{9.778}O_{5.037}$ with a $\Delta_f H^\circ$ of -973.2 kJ/mole^D. Recalculating using the *representative averages* that appear in Table 3 gives a $\Delta_f H^\circ$ of -967.2^D, less than a 1% difference. The C_6 -based formula and the corresponding $\Delta_f H^\circ$ also agree closely with that of starch ($C_6H_{9.96}O_{4.96}$) with a $\Delta_f H^\circ$ of -948.4 kJ/mole^D. Accounting for the sodium, calcium, and potassium cations present in a commercial food grade gum (1.643% ash), its corresponding caloric value,^[38] and the carbon, hydrogen, and oxygen—based on the ideal polysaccharide—results in a C_6 -based formula of:

$C_6H_{9.778}O_{5.037}Na_{0.035}Ca_{0.036}K_{0.010}$ with a $\Delta_f H^\circ$ of -1353.0 kJ/mole^{C,D}.

Gum Arabic is used as a binder in pyrotechnics,^[29] probably more so in the past than today (see *Starch* above). It is also used as an adhesive in foods,^[10] pharmaceuticals, and cosmetics, and in coatings and inks.^[32]

Gum Tragacanth

Gum tragacanth (9000-65-1) is an exudate from several species of tree of the genus *Astragalus*.^[30] The MW is approximately 840,000.^[25] Solutions of this gum have an extremely high viscosity,^[30,39] heat stability, a long shelf life,^[36]

and are acid resistant.^[39] Gum tragacanth impurities (dirt) are typically 1% maximum,^[39] and ash content is 3%.^[34]

Based on the structure^[9,37] in Figure 14, a chemical formula of $(C_{51}H_{76}O_{46})_n$, and a $\Delta_f H^\circ$ of -8570.8 kJ/mole^D, and “n” equals 448 may be estimated. In C_6 units this is equivalent to $C_6H_{8.941}O_{5.412}$ and a $\Delta_f H^\circ$ of -1008.3 kJ/mole^D. At the time of this writing, no data was readily available to the author regarding the caloric value or concentrations of cations present.

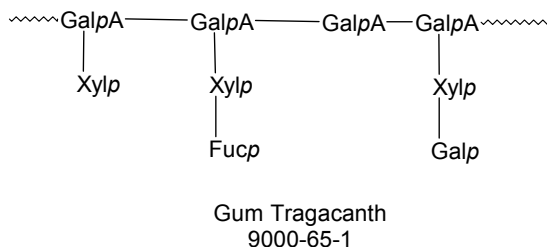


Figure 14. *Gum Tragacanth*.

Gum tragacanth has also found occasional use as an adhesive in fireworks.^[40] At one time it was used in matchhead compositions in conjunction with gum arabic but has been replaced due to its high cost.^[39] Other uses include food applications, pharmaceutical emulsions, cosmetics, and adhesives.^[25,30]

Guar Gum

Guar gum (9000-30-0) is representative of seed gums. It is derived from the endosperm of the guar plant (*Cyanopsis tetragonoloba*).^[8,36] The endosperm comprises approximately 40% of the seed, which is then milled to the final product guar flour.^[30]

Guar gum has an ash content ranging from 0.3^[38] to 1.07%,^[41] 0.67% nitrogen and 0.06% phosphorous.^[41] The MW is approximately 220,000.^[30,36] Guar gum is one of the few natural alternating copolymers.^[9]

Based on this ideal structure,^[9] (see Figure 15) a formula of $(C_{36}H_{60}O_{30})_n$, a $\Delta_f H^\circ$ of $-5724.2 \text{ kJ/mole}^D$, and “n” equals 244 may be estimated. In C_6 units this becomes $C_6H_{10}O_5$ and a $\Delta_f H^\circ$ of -954.0 kJ/mole^D . Accounting for the sodium, calcium, and potassium cations present in a commercial food grade gum (0.308% ash), its corresponding caloric value,^[38] the aforementioned nitrogen and phosphorous, and the carbon, hydrogen, and oxygen—based on the ideal polysaccharide—results in a C_6 -based formula of $C_6H_{10}O_5N_{0.077}P_{0.003}Na_{0.002}Ca_{0.003}K_{0.009}$ and a $\Delta_f H^\circ$ of $-1320.1 \text{ kJ/mole}^{C,D}$.

Guar gum is the most extensively used gum in food and industrial applications: a paper sizing

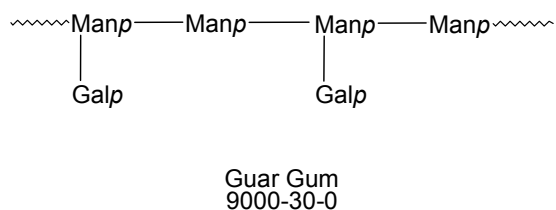


Figure 15. Guar gum.

agent, food stabilizer, gelling agent for slurry explosives, and flocculent in mineral processing to name just a few.^[30]

Rosin

Rosin (8050-09-7), also known as *colophony*,^[22,40] is a natural resin that is obtained from pine trees, chiefly *Pinus palustris* (long-leaf) and *P. caribaea* (Caribbean),^[8,22] but also *P. taeda* (loblolly) and *P. elliotii* (slash).^[42,43] The bulk of rosin comes from the distillation of tall oil^[44] (*tall oil rosin*), though smaller commercial quantities are also extracted from stumps^[17,22] (*wood rosin*) and from the distillation of turpentine^[8,22] (*gum rosin*). (Note: *Tall Oil* is derived from the Swedish word “*talloolja*”, which translates to “*pine oil*”.^[42])

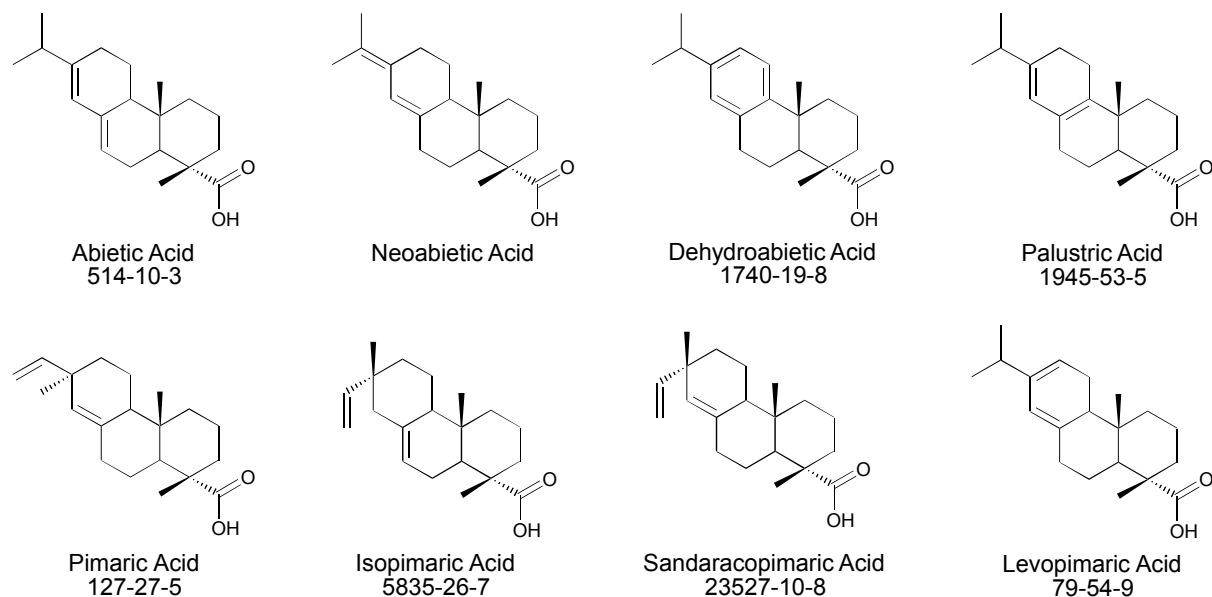


Figure 17. Principle acids found in rosin.

Table 4. Principle Acids Found in Rosin, Their Compositions and $\Delta_f H^\circ$.

Acid ^[a]									
	Abietic	Neo-abietic	Dehydro-abietic	Palustric	Pimaric	Isopimaric	Sandaracopimaric	Other ^[b]	
CAS	514-10-3	N/A	1440-19-8	1945-53-5	127-27-5	5835-26-7	23527-10-8		
$\Delta_f H^\circ$ (kJ/mole ^B)	-686.88	-615.5	-631.1	-635.0	-547.1	-590.1	-547.2		
Pinus Species	Percent of Various Acids								$\Delta_f H^\circ$ (kJ/mole ^B)
<i>taeda</i>	69	4.7	8.1	10	5.5	0.9	0.9	0.9	-663.8
<i>elliottii</i>	19	16	7.2	25	5.5	23	1.8	2.5	-624.5
<i>palustris</i>	18	15	8.6	35	4.8	16	1.6	1.0	-628.2

[a] Only the acid fraction of rosin is considered for the $\Delta_f H^\circ$ estimates. The neutral fraction (approximately 10%) consists of hydrocarbons, terpenes, alcohols,^[22,42] and C₁₈–C₂₆ fatty acids.^[43]

[b] Not included in the $\Delta_f H^\circ$ estimate. May consist, in part, of levopimaric acid (79-54-9, C₂₀H₃₀O₂) with a $\Delta_f H^\circ$ of -683.9 kJ/mole^B.

The principle ingredients are *abietic acid* (514-10-3, C₂₀H₃₀O₂), *pimaric acid* (127-27-5, C₂₀H₃₀O₂), and their isomers,^[8] accounting for approximately 90% of the rosin.^[17,22,42,43]

Table 4 lists the $\Delta_f H^\circ$ for the seven principle acids found in rosin (see Figure 17^[42,44]), the corresponding composition for three species of pine, and their resulting $\Delta_f H^\circ$. An average of the three yields a formula of C₂₀H_{29.84}O₂ and a $\Delta_f H^\circ$ of -638.8 kJ/mole^B. The formula is not exactly C₂₀H₃₀O₂ due to the dehydroabietic acid having a formula of C₂₀H₂₈O₂. In C₆ units this becomes C₆H_{8.952}O_{0.6}, and $\Delta_f H^\circ$ is -191.6 kJ/mole^B. Reference 2 lists an ultimate analysis that converts to a formula of C₂₀H_{27.72}O_{3.04} but unfortunately lists no corresponding $\Delta_f H^\circ$ value.

Rosin is used in fireworks,^[40] paper sizing, adhesives, inks, and chewing gums. Chemically modified rosin finds extensive use in modified styrene-butadiene rubber polymers.^[42,43]

Conclusion

A variety of disparate sources of data, as illustrated above, may be drawn on to gather, reduce, and estimate useful chemical formulas and formation enthalpies for fuels used in pyrotechnics until such time as exact, laboratory measured values become available. In this process of research and discovery, other potentially

useful information may be found. For example, the trace elements present in many of the fuels might cause undesirable coloration of, say, a star's color purity. This ancillary information assists the energetics chemist in making informed decisions. Hopefully the reader has a greater appreciation for the overall simplicity and variety of methods in which useful estimates may be made. The benefit one gets by estimating and using these values certainly outweighs the costs in getting them.

Acknowledgments

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

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Table 5. Chemical Formulas (C₆-Basis) and Formation Enthalpies of Organic Fuels.

Fuel	CAS	Formula	$\Delta_f H^\circ$ (kJ/mole)	Ref
Hardwood		C ₆ H _{8.79} O _{3.94} N _{0.16}	-778.5 ^H	
Softwood		C ₆ H _{8.57} O _{3.90} N _{0.06}	-670.6 ^H	
Cellulose	9004-34-6	C ₆ H ₁₀ O ₅	-954.7 ^D	
Cellulose (filter paper)			-979.0 ^C	21
Lignin, Douglas Fir	9005-53-2	C ₆ H _{6.6} O _{1.2}	-692.0 ^C	21
Cellulose derivatives				
Hydroxyethyl	9004-62-0	C ₆ H _{10.8} O _{4.2}	-794.8 ^{BD}	
Ethyl hydroxyethyl	9004-58-4	C ₆ H ₉ O ₆	-1179.6 ^{BD}	
Sodium carboxymethyl	9004-32-4	C ₆ H _{8.25} Na _{0.75} O _{5.25}	-1173 ^{BD}	
Nitrate, DS = 2.0	9004-70-0	C ₆ H ₈ N ₂ O ₉	-803.4 ^{BD}	
Nitrate, DS = 2.5		C ₆ H _{7.5} N _{2.5} O ₁₀	-765.6 ^{BD}	
Starch	9005-84-9	C ₆ H ₁₀ O ₅	-948.37 ^D	
Starch			-955.62 ^C	15
Starch			-955.37 ^C	45
Gum arabic	9000-01-5	C ₆ H _{9.778} O _{5.037}	-973.2 ^D	
		C ₆ H _{9.778} O _{5.037} Na _{0.035} Ca _{0.036} K _{0.010}	-1353.0 ^{C,D}	
Gum tragacanth	9000-65-1	C ₆ H _{8.941} O _{5.412}	-1008.3 ^D	
Guar gum	9000-30-0	C ₆ H ₁₀ O ₅	-954.0 ^D	
		C ₆ H ₁₀ O ₅ N _{0.077} P _{0.003} Na _{0.002} Ca _{0.003} K _{0.009}	-1320.1 ^{C,D}	
Rosin	8050-09-7	C ₆ H _{8.952} O _{0.6}	-191.6 ^B	

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(05/98)

Errata — Issue 7

Page 2, left column, 2 lines from bottom: "Figure 1. A 1-1/2" long section of pipe (the"
The "1-1/2" " should be "1/2" ".

Events Calendar

Pyrotechnics

Pyrotechnic Chemistry Course—UK

Spring 1999, Sevenoaks, Kent, UK

Contact: Ken Kosanke, PyroLabs
1775 Blair Road

Whitewater, CO 81527, USA

Phone: 970-245-0692

FAX: 970-245-0692

e-mail: bonnie@jpyro.com

Web site: www.98.net/jop

17th Symposium on Explosives & Pyrotechnics

April 27–29, 1999, Essington, PA, USA

Contact:

Franklin Applied Physics, Inc.

Phone: +610-666-6645

FAX: +610-666-0173

Grunelagen Pyrotechnik (Fundamentals of Pyrotechnics)

May 17–22, 1999, Weil-am-Rhein, Germany

Contact: Dr. G. A. Schröder

Carl-cranz-Gesellschaft e. V.

79576 Weil-am Rhein, Germany

Phone: +49-7621-75091

FAX: +49-7621-793026

7th International Seminar—Groupe de Travail de Pyrotechnie—EuroPyro 99 and 25th International Pyrotechnics Seminar

June 7–11, 1999, Ensietia Brest, France

Contact: Association Francaise de Pyrotechnie
EuroPyro 99

B.P. No. 121

45240 La Ferte

St. Aubin, France

FAX: +33-238-516-822

Web site: www.intlpyro.org

30th International Annual Conference of ICT

June 29–July 2 1999

Contact: Mrs. Gesa Langer, Chair

Franuhofer-Institut für Chemische Technologie

Attn: Manuella Wolff

PO Box 1240

D-76318 Pinfzthal (Berghausen)

Federal Republic of 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

The Chemistry of Pyrotechnics & Explosives

July 25–30, 1999, Chestertown, MD, USA

Advanced Pyrotechnic Seminar: Pyrotechnics in the 21st Century —A Review of the State-of-the Art in 1999

Aug. 1–6, 1999, Chestertown, MD, USA

Contact: John Conkling

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American Pyrotechnics Association Conv.

Fall 1999 [date to be determined]

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(Continued on Page 70)

Composite Color Stars

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ABSTRACT

Ammonium perchlorate has long been used to produce high-quality color stars and lances. In this article the author uses the basic ingredients of composite rocket propellants to generate colored flame suitable for pyrotechnic display. The use of composite materials has several advantages over classic formulations in that the material is handled in a semi-liquid state prior to cross-linking, produces little smoke, exhibits vibrant color, and uses no water in the manufacturing process. Several formulations are discussed along with visual observations from ground burn and star gun tests.

Keywords: composite rocket propellant, ammonium perchlorate, color stars, hydroxy terminated polybutadiene, HTPB, chromaticity, prime, formulation

Introduction

Ammonium perchlorate has long been used as the principal oxidizer in solid composite rocket motor propellants. A tremendous amount of research by both commercial and military laboratories is available regarding the burning characteristics of these composite materials.^[1-3] Ammonium perchlorate has also found some use in pyrotechnics because of its excellent color production and low smoke output.^[4,5] The author's interest in composite rocket motor propellants initiated the research outlined in this paper.

Generally speaking, rocket motor propellants have different formulations and requirements than pyrotechnic mixtures. Characteristics such as burn rate, energy content, geometric configuration, and even opacity are usually carefully controlled to produce the desired ballistic performance in a given rocket motor design.

Copper chromite ($\text{Cu}_2\text{Cr}_2\text{O}_4$) has been used as a burn rate modifier in ammonium perchlorate composite rocket motors.^[1,2] Copper chromite is both expensive and difficult to procure so copper(II) oxide was used in its place. As it turned out, copper(II) oxide performed as a satisfactory burn rate modifier for the author's rocket motor research and had the unexpected benefit of giving the flame a magenta coloration. It should be noted that copper(II) oxide and copper metal act as catalysts for hydroxy terminated polybutadiene (HTPB) further cross-linking the resin, thereby causing a loss of elasticity in the finished product over time. This would be a concern for the long term storage of rocket motor grains but should cause little trouble with fireworks stars.^[6] The magenta formulation used during this test was not applicable to this paper, but the coloration was produced by 0.1 weight percent of copper(II) oxide! This concentration is ridiculously low when compared with most pyrotechnic color compositions. Many contain 10% or more copper(II) oxide to produce a satisfactory blue; older formulations sometimes called for nearly 20% Paris green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$)* to generate rather poor blues.^[4,7]

Why investigate new color formulations? Composite materials have several properties that typical color star formulations lack. In particular, the material is handled in its semi-liquid state, allowing new, perhaps safer, manufacturing processes, such as extrusion and casting. The process involves no water or other ionic solvent. This eliminates one of the common dangers of fireworks manufacture, ion exchange during processing and drying. Further, the cured product is relatively safe, waterproof, and not prone to accidental ignition. Indeed successful ignition in a shell burst is one of the difficulties

* This formula is from the *Handbook of Chemistry and Physics*, 61st ed. CRC Press 1980-1981.

encountered with composite stars. The finished product produces a voluminous, almost transparent flame from very tiny stars. These stars do not dry but cure by cross-linking in 24 hours and do not require heat or evaporative cooling to cure. Finally, the colors produced with these formulations are among the best the author has seen. Indeed, many people have indicated that the red, orange and green formulations are as pure as any ever witnessed. This observation has been borne out with chromaticity and spectral testing.^[8,9] It has been noted that the burning characteristics of polybutadiene closely resembles that of shellac, perhaps even surpassing it, in flame clarity. Many readers will no doubt envision formulations the author has not tried or conceived.

Colored flames are generally produced by the spectral emission bands of metal monochlorides excited by the high temperature flame developed from the combustion of a fuel with an oxidizer. In many color star formulations, chlorinated fuels such as polyvinyl chloride (PVC), Parlon[®], or Saran[®] resin are added to ensure a sufficient quantity of chlorine to form the desired metal monochlorides. The metals in most common use are strontium, sodium, barium, and copper. Occasionally other metals such as zinc and calcium have been used. The oxidizer, ammonium perchlorate, has an abundance of chlorine that becomes available during the decomposition of the oxidizer. This, no doubt, is a primary reason that the color star compositions researched in this work produce such exemplary colors. In addition, ammonium perchlorate decomposes to all gaseous products, reducing solid particle incandescence.

When this work was initiated, only a few questions were really considered. Would composite materials lend themselves to fireworks? Could colors suitable for display fireworks be obtained from these compositions? Could composite color stars compete with the state of the art found in modern color star formulations? As this research has continued, these simple questions have been answered in the affirmative. Of course, this has led to the asking of many more questions. Hopefully, this paper outlines the journey of discovery and will spur yet more research into this fascinating subject.

Cautionary Notes

The resin used for this work was R45 hydroxy terminated polybutadiene (HTPB). The resin is very sticky and has a characteristic odor. Care should be taken to provide adequate ventilation. The effects of prolonged breathing of vapors are not listed as harmful in the Material Safety Data Sheet (MSDS) but reasonable care should be exercised in any case. The author always used disposable gloves when handling resin components and was careful to avoid skin contact.

All catalysts and hardeners should be treated with the respect due any active chemical. Diphenyl methane diisocyanate (MDI) was used as the curative for these experiments. It has been suggested that this material is hazardous and should be kept in a safe place and used in small quantities. The MSDS indicates that the vapors should not be inhaled nor should the material be allowed to come into contact with the skin. The MSDS also indicates that the material is a strong irritant to skin and mucous membranes as well as being a sensitizer. MDI decomposes spontaneously in the presence of water or excessive heat; so care should be taken to keep it dry and between 50 and 95 °F. It has also been suggested, and the author concurs, that other, low vapor pressure, cross-linking agents such as diisophorone diisocyanate be tried to avoid some of the potential risks associated with MDI.^[6]

Dioctyl adipate (DOA) was used as a plasticizer. DOA is used in vinyl tubing, Saran[®] resins, and PVC sheeting. The MSDS lists only irritation to the skin and mucous membranes as the immediate health dangers associated with DOA. Long term effects are less clearly known, but there is evidence that DOA is a carcinogen. Personal protective equipment should be worn, and the material should be handled in areas with plenty of ventilation. DOA is a strong plasticizer, however, and tends to soften or dissolve vinyl gloves and utensils; so care should be exercised in selection of protective equipment and materials.

Salts used as color agents pose their own risks, especially soluble barium compounds. Care should be taken to avoid breathing the dust from these chemicals. Barium perchlorate

is also a strong desiccant and will cause a chemical burn to unprotected skin and eyes. Because the color agents are typically fine powders, they pose an additional inhalation risk. Dust filter respirators should be used by persons using these chemicals. The author used a high quality nose and mouth dust mask with replaceable filter cartridges and full eye protection when working with these chemicals.

The mixed resin-oxidizer system will burn vigorously in the uncured state. While this makes testing of new formulations easy, it poses some danger during manufacture. As always, care should be taken to avoid sources of ignition during mixing and curing. When the mixed product is burned, either in the cured or uncured state, copious quantities of hydrogen chloride gas are released. DO NOT breathe the smoke from burning composites or ignite them in a confined area. While this prevents using these compositions indoors, composite formulations are burned in hobby solid propellant rocket motors frequently, so their use in outdoor fireworks poses few risks except downwind. One final note, the burning material is often propulsive and can easily skitter across a flat surface. As with all pyrotechnics, care should be taken to remove other combustibles from the testing area.

Fuel and Oxidizer

The oxidizer used for these tests was solid propellant grade ammonium perchlorate from either Kosanke Services^[10] or Pacific Engineering^[11]. The oxidizer was purchased as rotary-rounded, 200-micron spheroids. Experiments on mixing have shown that fine powder is very hard to mix into the final composition. The nascent fuel-oxidizer mix (sans color agent) contains 85% by weight ammonium perchlorate and 15% by weight HTPB. The maximum volume that can be filled with perfect spheres is 64% for the cubic arrangement and 74% for hexagonal close pack. The density of ammonium perchlorate is 1.95 g/cc, and the density of the uncured HTPB is 0.9 g/cc; thus under ideal conditions, the mixture should contain few voids. However, because of the hand mixing and the lack of vacuum degassing, the mixture discussed in this work contains significant

voids. While this would prove disastrous for solid rocket propellant, it is quite acceptable for color star compositions.

The fuel used was hydroxy-terminated-polybutadiene (HTPB), R45 from Sartomer Corp.^[12] This resin is a clear viscous fluid and has a strong characteristic odor. A syringe was employed to dispense the resin, and acetone was used for cleaning the uncured resin from mixing bowls and utensils.

The dioctyl adipate used was purchased from BASF^[13] under the trade name Palatinol[®]. DOA was added to the resin as a plasticizer to facilitate hand mixing with the oxidizer. It readily dissolves PVC's and some polyurethanes; thus polyethylene, nylon, or stainless utensils are needed.

The cross-linking agent used was diphenylmethane diisocyanate (MDI) from Dow Chemical.^[14] MDI is a clear yellow liquid with no detectable odor. It should be stored under controlled temperature conditions; however, the author's supply has not been maintained under temperature control, is several years old, and still works well.

Table 1 lists the fuel mixture by component. The weights listed provide sufficient fuel for two 100 gram batches of mixed composition. As a practical matter the colorants were typically added to the mixed fuel prior to adding the oxidizer. Once mixed, the fuel has a useful pot life of about 2 hours, though at the end of this time it is noticeably more viscous. During the cure process, the fuel is sensitive to atmospheric water, and a foam will form in high humidity regions. This work was done where relative humidity seldom exceeds 20%; so this was not a concern. The weight percent of the ingredients listed in Table 1 were determined empirically and are not meant to be taken as stoichiometric or optimized quantities.

Table 1. Base Fuel Mixture for Composite Color Stars.

Ingredient	Weight (g) *	Weight %
HTPB	24	80
MDI	2.9	9.7
DOA	3.1	10.3
Total	30	100

* Weight for 200 grams of mixed composition.

To mix 100 grams of composition, the above fuel was divided into two 15-gram batches. The desired color agent was added to the liquid resin and thoroughly mixed. This resin mixture was then added to 85 grams of ammonium perchlorate to make about 100 grams of mixed fuel-oxidizer-colorant. Mixing was performed in a bowl by hand; no mechanical mixing was employed. The mixed propellant formed a soft dough, similar to cookie dough. Once well mixed, the composition can be processed in a number of ways to make stars. This includes flattening to make cut stars, pumping and extruding to make pumped stars, or even molding into round or other shapes. The author commonly pumped the dough into a 1/4" tube and pressed it out with a wooden dowel, forming 3" long cylinders. Curing was performed on waxed paper sheets at 25 °C and took about 24 hours to complete. When cured, the composition was tough and flexible, resembling an art-gum eraser, and could be easily cut or broken into appropriate sized stars, star cores, or lances. No special drying screens or equipment were required.

A System of Colors

As this research progressed, it was realized that the colors produced with this system were exceptional. This being so, it became a goal to produce a system of colors that could be mixed to produce virtually any color. Thus, the ultimate goal was to produce an additive color system whereby the shell maker could pick a set of color coordinates, convert this to colorant amounts, mix a standard batch of composition, and produce stars of the desired color. This process was envisioned to be much like commercial paint mixing, and would provide easily reproducible designer colors. Such systems are not new and have been proposed and compounded by others.^[5,14-16] The final formulations are listed in Table 4.

Figure 1 shows the standard CIE Chromaticity Diagram for the human eye.^[18-21] Note that the author used the 1964 CIE supplemental standard observer because it was determined using 10 degree field of view. The 1931 CIE standard observer used a 2 degree field of view. In the author's opinion, the wider field of view is more likely to represent a spectator's perception of the entire shell; it may not represent the color perceived from a single star in the central visual field. The black dots are the approximate location for the Red, Orange, Green, Blue and Purple starting with the red corner and progressing counterclockwise. As may be seen, the red and orange are essentially pure colors. The green is not fully pure. The blue is more cyan and is also not pure. During a weekend investigation of color stars, Clive Jennings-White provided a Minolta XY-1 chromaticity meter. Data presented in Figure 1 were taken using this instrument and show the quality of color, especially for the red and orange. These data indicate that the colors produced by these formulations have the highest purity seen for red, orange, and green.^[8] A handheld Zeiss spectroscope and several spectrometers were also used to make a detailed qualitative analysis of the burning composition. The outcome of this analysis will be presented with the full discussion of the colors.^[9] The dark lines between the chromaticity coordinates represent the gamut of colors that may be obtained using the composite formulations described here. As is clearly

CIE Chromaticity Diagram

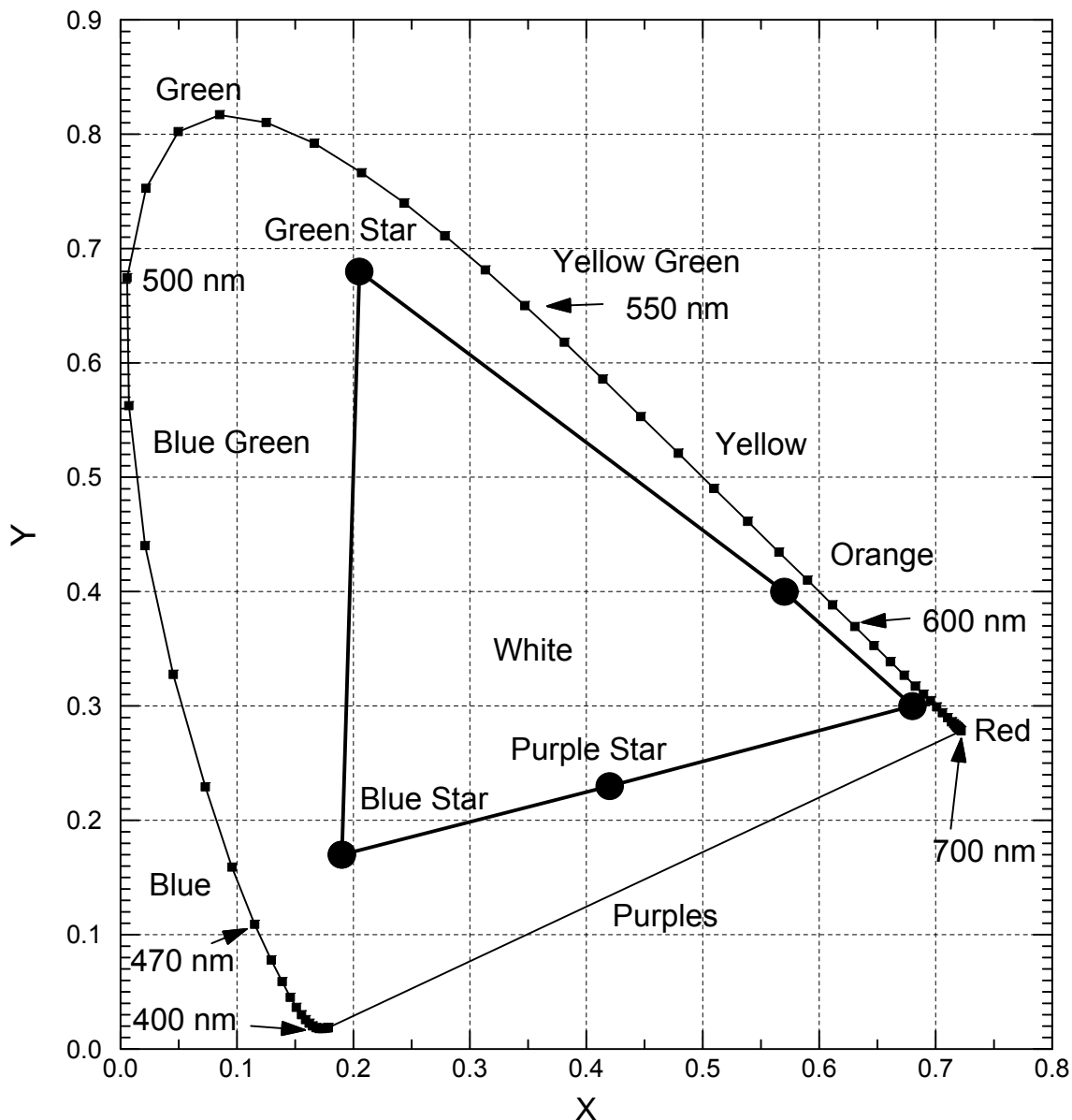


Figure 1. CIE Chromaticity diagram (1964 data) showing the color gamut for composite color stars.^[21]

shown, the lack of purity in the blue and green limit the quality of colors that may be obtained by a simple mixture of the two. Deeply saturated blue green is not possible at this time. Work is continuing on this subject and will be presented in a future paper.

Red

Strontium carbonate or strontium nitrate was used to produce red. Both compounds produced a very deep, saturated red when added as an additional 5% (e.g., 5 grams added to a 100 gram batch of neutral composition). The flame had a striking translucent quality, producing an outstanding red. Strontium, in either form, appears to be a burn rate catalyst, accelerating the

burn rate above that of the neutral mixture. The fast burn rate of this composition makes it suitable for aerial shells and display set pieces. As shown in the chromaticity diagram, the flame is essentially pure; so no further improvement in color is needed. Further, the eye is not very sensitive to spectral shifts at these wavelengths; so a deeper red seems unlikely at this time.

Spectrographic analysis of the flame showed an abundance of red spectral bands. These are most likely caused by the presence of strontium monochloride in the flame, but the spectroscope used had insufficient resolution to determine this absolutely. To the eye, there was very little difference in color between the longest and shortest of these spectral bands. No serious black body continuous spectra were evident in the flame, which explains the observed translucent quality. There was evidence of both calcium and sodium lines in the flame. The source of these lines is detailed in the discussion of green as they cause no difficulty with the red.^[9]

Orange

Calcium sulfate (anhydrous), as an additional 5%, produced a very pure orange red. The flame had similar characteristics to that of strontium, except that the burn rate does not appear accelerated. The flame was also more opaque, possibly indicating the presence of incandescence. The color produced is most unusual but is not really orange. A quick look at the chromaticity diagram indicates that, for a better orange, the color must be shifted toward the yellow.

Shifting toward the yellow could be done with either sodium or barium. After several experiments, barium was found to produce an exceptional orange flame. Spectroscopic analysis revealed the presence of both calcium and barium monochloride; as expected, it also revealed sodium. The chromaticity meter showed a fully saturated color. As with red, further work with this color is not going to yield major improvements. One note, the sodium tended to be a strong color agent, and it produced similar shifts to the yellow at lower concentrations, thus with less fidelity than barium.

Yellow

Sodium chloride produces the strong, characteristic color of sodium. Color saturation is very high, almost monochromatic. Again, the flame has the transparent quality characteristic of this color system. Since sodium yellow is really slightly red, the addition of barium could be used to shift the color to a more pleasing canary yellow color. No spectral analysis of these colors has yet been performed.

Green

The addition of 5% barium nitrate to the neutral composite star mixture produced a yellow flame of low purity. Even when this amount was doubled to 10%, the color was neither pure nor aesthetically pleasing. Although spectroscopic analysis of these colors has not been performed, the author suspects incandescence and contamination to be the primary faults. The difficulty with green was solved after many debates and consultations.

Historically, the best green colors were produced using barium chlorate.^[4] Aside from the sensitive nature of barium chlorate, mixing it with ammonium perchlorate could be highly dangerous.* However, a close examination of several, so-called, exhibition green formulations showed an extraordinarily high concentration of barium salts. For example, Weingart's exhibition green calls for almost 90% barium chlorate and 10% shellac.^[7] At first, it was hypothesized that the high molecular weight of barium might be reducing the ion concentration in the flame thus reducing the number of emission sources. An analysis of atomic concentration for barium compared to strontium and calcium showed that if low ion concentration was the cause, the 10% formulation should have worked. It did not.

* A double-base decomposition reaction could form explosive ammonium chlorate, even in the non-aqueous bound stars discussed in this article. The effect of even microscopic concentrations of ammonium chlorate on these compositions is unknown and considered too dangerous to study. In any case, formulations utilizing chlorates and perchlorates would not be suitable for display fireworks.

The first requirement, however, was to get a good green formula. Charley Wilson suggested that the barium nitrate be increased to 35% based on Lancaster's green fire 'B', substituting HTPB for the red gum.^[4] Wilson showed that this formulation produced a good green using shellac instead of red gum. To compensate for the added oxidizer the amount of ammonium perchlorate was reduced. Table 2 shows this green formulation.

Table 2. Exceptional Green Color Formulation.

Ingredient	Weight (g)
Ammonium perchlorate	50
Barium nitrate	35
Mixed resin	15
Total	100

This green was of high quality, certainly as good as the barium chlorate green of old. However, chromaticity analysis showed that while this green was the purest green having yet been measured, it could be improved. The spectroscope still showed the annoying calcium and sodium lines evident in the other colors. It was suspected that the presence of the contamination was causing the green color to be shifted to the whiter region of the chromaticity diagram. Since calcium and barium are chemically very similar, it seemed likely that the calcium was a natural contaminant of the barium nitrate. Sodium was ubiquitous; so its source could be anywhere. Spectroscopic analysis of the component chemicals revealed, surprisingly, that the ammonium perchlorate was contaminated with both sodium and calcium. Some research showed that this might not be so odd since ammonium perchlorate is produced by the electrolysis of aqueous sodium chloride. The calcium may be present as a trace element in the water used during processing.

While the barium nitrate produced an excellent green, it burned very slowly. Simulated wind tests and star gun tests showed that the finished product would not stay lit in high speed air. Indeed, throwing a lit star would sometimes extinguish it.^[15,16] Various schemes were tried to improve the burning speed of the

barium nitrate based green, some of which have not been fully explored. The final formulation given in Table 3 was developed by Charley Wilson and used anhydrous barium perchlorate.^[15]

Normally anhydrous barium perchlorate would not be used in fireworks because it is very hygroscopic. The non-aqueous composite binder coupled with the fact that the stars are essentially encased in rubber after curing, allowed its use here. These stars burned very quickly and produced an exceptional green. Stars using barium perchlorate have been stored in an open container for several weeks with no apparent loss of color or the appearance of pools of liquid even at cut edges.

Table 3. Green Formulation.

Compound	Weight (g)
Ammonium perchlorate	45
Barium perchlorate	40
Mixed resin	15
Total	100

The lack of purity was still troubling, however, not so much that the color was poor, but because as a part of a color system, it excluded the color palette on the blue-green side of the chromaticity diagram.

During the course of this investigation a formulation of 85% barium perchlorate and 15% HTPB was tried. This high barium concentration produced a less vivid green with an abundance of smoke. Some of the lack of saturation is certainly due to incandescent barium byproducts in the flame. The low concentration of metal salts in the other colors might keep the incandescence at a low enough level that it does not significantly affect the resultant color. Barium green colors may also be more sensitive to impurities in the constituent salts. This hypothesis will be tested in future research using high purity chemicals. Further, as shown in Figure 1, the chromaticity diagram indicates that the eye is exquisitely sensitive to very small shifts in wavelength and saturation level

at green wavelengths.* The problem may simply be that the high concentration of barium metal in the flame limits saturation by incandescence, compounded by the human eye being more sensitive at these wavelengths.

Blue

Copper(II) oxide, used as a burn rate modifier, initially started this whole investigation by producing a colored flame. Close examination of stationary burning blue composite stars showed red flame tips. This was true of most, if not all, blue formulations. Some investigators have indicated that the addition of certain non-hydrocarbon fuels reduces the effect of red flame tips on blue colors.^[15] Since the basic research involves HTPB, the elimination of hydrocarbons was not considered. Other than the tips, the flame was quite blue and was one of the better ones the author has seen.

The chromaticity meter, however, indicated a less than pure cyan. The loss of purity might be explained by the red from the flame tips. It required spectroscopic analysis to get to the bottom of the cyan color. The spectroscope revealed a plethora of blue bands, just what one would expect from copper monochloride; but it also indicated strong green bands. The source of the green was not known, but copper hydroxide or copper oxide was strongly suspected. The presence of green shifted the blue to a region of the chromaticity diagram where the eye is, again, very sensitive to wavelength variations. Clearly to deepen the blue, the green band intensities should be reduced.

How to reduce the green intensities is unknown and will be the subject of future research. One of the first attempts will be to try

* The small squares on the chromaticity diagram in Figure 1 are spaced at 5 nm intervals. The closeness of sequential points at red and blue indicate that the eye is less sensitive to spectral shifts at these wavelengths. Green (540 nm), however, has the squares spaced far apart indicating high spectral resolution by the eye. The human eye is most sensitive at green wavelengths and is capable of discerning small changes in purity. This is indicated by the relatively large distance between white and the spectrally pure greens. For more information see references 18–20.

anhydrous copper(II) perchlorate. Copper perchlorate is strongly deliquescent; so it is not usually considered for pyrotechnic mixtures. This system, however, does allow the use of more hygroscopic materials such as barium perchlorate. Purifying the blue, in the color system, would also enhance the quality of color available on the blue green side of the spectrum.

The author notes that most blue and green formulations are not pure, and this may explain the lack of good aqua colors. Zinc has been used to fill this gap but has not been tried in this color system. A quick look at Pearse and Gaydon^[22] indicated that zinc chlorides do not emit in the blue or green.

In the author's experience, blue is a very difficult color to produce. Some compositions that perform well in a static test near the observer do not perform nearly as well at a distance while moving. Similarly, good blues in aerial displays sometimes appear weak when burned on the ground. Air temperature, as well as, flame temperature also appears to have strong effects on the quality of blue stars. Star gun testing has shown this composite blue can hold its own against others, but the real test will be how it performs in a shell and that has not yet been tested.

Purple

Violet and purple are not spectral colors and must be produced by the combination of red and blue. As expected, the purples that can be produced fall on the line between the blue and red coordinates in Figure 1. The purple is quite good and can be dialed in as desired. One should note the very low concentration of color agents and the low concentration of copper(II) oxide (2%). The chromaticity diagram explains why. The line between the blue and red passes near white. As more strontium is added to a blue flame composition, the color first moves toward white and becomes pinkish; it then passes into more pure purple colors yielding a deep satisfying color. It is a strong statement that the blue emission bands can compete satisfactorily with red at these low concentrations.

Prime

Historically, an outer coating of a material that easily takes fire and then transfers fire to the actual star composition is called prime. Most fireworks stars are primed to improve ignition efficiency during the violent shell burst. Composite star formulations, like their progenitor propellants, are notoriously difficult to ignite. Research into priming compositions and methods showed that strobe stars are also difficult to ignite and pointed the way to successful priming of the composite stars.

The poor ignition properties of composite materials are due, in part, to the higher activation energies of the constituent components. It is also, in large part, due to the inhibition caused by the rubber coating on the ammonium perchlorate spheroids in the cured composition. Finally, the rubber coating on the star may not take a water-based prime effectively, increasing the difficulty of finding a workable prime formulation. Water-based primes may also produce undesirable double-base decomposition reactions between the ammonium perchlorate and the other salts used in the star composition or the prime itself; thereby, significantly altering the performance of the finished star.

A suitable prime was found in Takeo Shimizu's seminal article on strobe stars.^[23] Primed stars prepared by Charley Wilson showed 100% ignition when primed with Shimizu's "First Ignition Composition". The prime was prepared with 10% nitrocellulose and thinned to a slurry with acetone. The composite stars were then dipped into the slurry and allowed to dry.

Conclusions

Composite color stars are not only feasible but produce some of the purest colors available to the pyrotechnician. The semi-liquid state of the formulations allows novel processing techniques that may lead to safer, more automated manufacture. The stars produced during this research, 1/4" diameter extruded stars, burned long enough to be useful in 3" and possibly 4" shells. Thus the vibrant color could be combined with dense star patterns. The highly propulsive nature of these stars also lends them to shell special effects such as go-getter, hummer, stickless rocket, serpent, etc. The formulations discussed in this article are presented in Table 4.

Research will continue on the green formulation to improve the color purity and enhance the color gamut available. Further research is

Table 4. Composite Color Star Formulations. (These formulations are based on adding an additional 5% of coloring agent to the standard 85% ammonium perchlorate, 15% HTPB propellant.)

	Color	Colorant 1	Wt %	Colorant 2	Wt %	Comments
1	Red	SrCO ₃	5	—	—	Outstanding red, transparent flame, slightly propulsive
2	Red	Sr(NO ₃) ₂	5	—	—	Outstanding red, transparent flame, slightly propulsive
3	Red-Orange	CaSO ₄	5	—	—	Unusual red-orange, transparent flame
4	Orange	CaSO ₄	2.5	Ba(NO ₃) ₂	7.5	Outstanding color, pumpkin orange, transparent flame
5	Green	*	*			Very good green, as good as barium chlorate
6	Blue	CuO	5	—	—	Good color, slightly cyan, propulsive
7	Purple	CuO	2	SrCO ₃	3	Good color, transparent flame, propulsive

* Formulation is found in Table 3.

indicated to improve the blue compositions as well. Many new pyrotechnic ingredients are possible with these formulations as evidenced by the barium perchlorate green.

Acknowledgments

The author wishes to gratefully acknowledge the urging and help from Charley Wilson, without whom this paper would never have been completed.

The author also wishes to thank Ken and Bonnie Kosanke for making their laboratory and equipment available, enabling many of the improvements presented in this paper. Gratitude also goes to Clive Jennings-White for making his chromaticity meter available and sharing this most useful data. Also thanks and kudos to the many pyrotechnicians whom I have talked with during the last few years and who have supported and contributed to this research.

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(03/98)

Communications

Brief technical articles, comments on prior articles and book reviews

Comment on:

High-Nitrogen Pyrotechnic Compositions, Summer 1998, Issue 7.

Rutger Webb posed the following questions:

1. Did you measure the color (spectra) of the flames? Or was the color quality determined by visual comparison?
2. Why was increased burn rate of most copper salts undesirable? Did it "wash out" the color?
3. Did you try copper(I) chloride (CuCl) as a color agent? It is, as far as I know, the only desired emitter that does not have to be formed *in situ*.
4. Do you have more detail on the stability of the Hz₂Tz compositions?

Michael Hiskey's Reply:

Thanks for your inquiry, and I'll be glad to tell you what we know so far about our pyrotechnic compositions. First, all color quality determinations were done with the naked eye and compared to the color of traditional formulations. Since we wrote the paper last fall, we have made some improvements.

Reds are now using nontoxic Li₂CO₃; orange CaCO₃, which give much better depth of color compared to sodium; green uses H₃BO₃, which is superior to Ba(NO₃)₂ and is also nontoxic; and very nice canary yellows utilize NaNO₃ and H₃BO₃. Hot pink uses orange with smaller amounts of green and blue. Blues and purples still use copper as sulfide or oxide. As you are probably aware, hydrazine is used as a monopropellant by spraying through a palladium or platinum gauze. Other transition metals have varying degrees of activity; so it is not too surprising that copper acts as a burn rate catalyst for our substituted hydrazine. Very fine Fe₂O₃ (i.e., nanocat) is exceptional in this regard and increases the burn rate by at least an

order of magnitude with only 1% added. The blue colors with CuS or CuO are good. When stars are burned stationary, they have orange tips, but while flying through the air in an indoor mine, the blue is very nice with no flame tip discoloration. However, we must make these stars slightly larger as they burn faster. The increase in burn rate does not wash out the color. Regarding the stability of di-hydrazino-tetrazine, we have found that as long as the mixtures containing copper salts are dry, they age quite well. We make cut stars by first wetting the formulations with water into a mud-like mass and cutting small pieces. Large stars made by this method air-dry very quickly in New Mexico. Again, the stars have shown no decomposition as long as they remain dry. When copper mixtures are wet for extended periods, the situation is not good. Discoloration and gassing occur after several hours. At your suggestion, we mixed up some star composition containing 2% CuCl. The blue was very nice, but not significantly superior to what we already have, and the burn rate was faster than with CuS. It was worth a try; thanks for the suggestions.

We have currently not found a viable replacement for copper; we tried CsCl and Ni(NH₃)₆Cl₂ with no luck. The replacement of copper for blues and purples would definitely be an advancement as this is the only toxic (although not very toxic) metal left in our formulations. We are currently thinking about the possibilities of low or even zero signature rocket propellants utilizing di-hydrazino-tetrazine. As mentioned above, nanocat is an extremely powerful burn rate catalyst, and this may allow us to use ammonium nitrate as an oxidant in a non-aluminized propellant and still achieve reasonable burn rates. Please keep in mind that we plan to publish our most recent observations in the *Journal of Pyrotechnics* in the near future.

Follow-up from Rutger Webb:

I'm curious. In the article you wrote that you had examined a large number of materials, such

as nitroguanidine, guanidine nitrate, etc. How did you evaluate their “degree of usefulness”? Did you create color compositions containing guanidine nitrate? How did these compare to those made with Hz_2Tz ?

In your reply above, you mention “... we tried CsCl and $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ with no luck.” Interesting! Atomic emission of cesium is used in covert infrared (IR) illuminant flares, as you probably know. Yes, that is not of any use for color compositions, but there seems to be demand for it. If I may suggest, try to measure the IR/VIS (visible) spectrum of your compositions, too. [See: C.W. Lohkamp, “Black Nite Flare”, AD-A030713 (NWSC/CR/RDTR-39), 2 Sep 1996 and C.W. Lohkamp, “Black Nite Flare”, 5th *IPS Proceedings* (1976)pp 307–315.]

What desired emitting species were you aiming for with $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$?

In your reply above, you mention “...Please keep in mind that we plan to publish our most recent observations in the *Journal of Pyrotechnics* in the near future.” Would it be possible that I could have a preview of your article? I’d really appreciate it. Please ask me anything in return. As you see, your article made me very curious.

Mike Hiskey’s reply to the above:

We had problems with the burn rate of the other high-nitrogen energetic materials. They burned slow and smoky, even when mixed with oxidizer. The real advantage of Hz_2Tz is zero signature and reasonable burn rate, even when using ammonium nitrate as an oxidizer.

With regard to $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, we thought that NiCl^+ could possibly give interesting color, but it was not acceptable. Other more exotic colorants have been examined with some degree of success, for instance AgNO_3 gave an acceptable purple and Au_2O_3 gave a nice green. There’s a whole periodic table out there and most of it is metals, and I don’t think the final word has been written on coloring pyrotechnic flames.

With regard to “... preview of your article ...”, Not a problem, you must realize that I’m a terrible writer, and I haven’t even started to put this paper together in my head yet. Our pyrotechnic work has been done essentially with no funding, and therefore only in our spare time, which is almost non-existent these days.

(The Communications Section continues on page 52.)

Silicone II: A New Fuel and Binder for Fireworks

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ABSTRACT

This paper presents some initial work on the use of silicones including GE Silicone II (GE280 and GE5000) as a fuel and binder in fireworks. Some of the pros and cons of silicones are covered, as well as a partial list of safety concerns. A brief review of silicone chemistry is included as a background for the choice of suitable silicone materials. This is followed by some pyrotechnic chemistry, including observations, methods, and ideas for how to use silicone compositions in fireworks. Silicones show great promise for certain applications and may prove to be safer and less costly than some of the materials they could replace.

Keywords: silicone, fuel, binder, rocketry, potassium perchlorate, ammonium perchlorate

Advantages and Disadvantages of Silicones

Except for the military illumination flare mentioned by Stanbridge,^[1] there seems to be no published material on the use of silicone in fireworks. Yet, like Parlon®, silicone rubber can serve as both a fuel and a binder.

Perhaps the most striking advantage of silicones, sometimes known as Room Temperature Vulcanizing rubbers (RTVs), is that they are almost unreactive at normal ambient temperatures. This makes working with them relatively safe. Most silicones are totally stable at 300 °F and some as high as 500 °F. In fact, it is somewhat surprising that they burn at all. Indeed, some formulations are difficult to ignite, while others take fire readily. Most are fairly energetic fuels in pyrotechnic compositions.

Unlike Parlon®, a chlorinated rubber, silicone rubbers generally lack the color enhancing

halogens—chlorine or fluorine. All tested varieties also appear to be free of sodium, which would interfere with color purity. Silicones burn colorlessly and somewhat luminously, like metals.

The chemical properties of silicone seem to reduce the sensitivity of compositions during and after manufacture. The water-resistant nature of the silicone serves to encapsulate the grains of the composition, not only protecting them from moisture, but also slowing such reactions as ion exchange between salts.

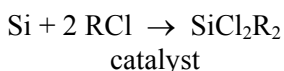
The physical properties of better silicone pyrotechnic mixes are also favorable. Silicones require no solvents to facilitate mixing. Ten to 15% silicone compositions tend to have a dry, crumbly texture and can be pressed into objects that hold their shape during and after cure. Compositions with 15 to 25% silicone usually have a workable, putty-like, plastic texture, and can probably be pumped. These properties would lend themselves well to low-cost, high-volume automated productions. After curing, the compositions can be bent and struck without losing physical integrity. The lubricity of the uncured material allows devices, such as rockets, to be removed easily from forming tools.

On the negative side, many compositions—but not all—generate large amounts of smoke. Silicone also has a no-stick property like Teflon®, so it is difficult to find materials that will adhere to it. This makes the priming of cured stars extremely difficult. The water resistance and chemical stability also assure that any unconsumed items such as unlit stars will remain as reactive pyrotechnic compositions indefinitely.

Chemistry of Silicone Manufacture

The manufacture of silicones is a multi-stage process, in which several foreign materials may be introduced into the finished product. Some are beneficial for pyrotechnic purposes; others are not. There are many processes. According to Rochow^[2] the following is typical.

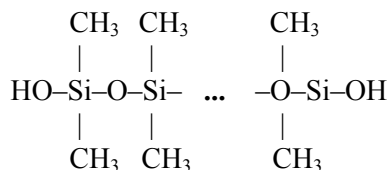
Elemental silicon (Si) is reacted with chlorinated hydrocarbons (RCl) in the presence of a catalyst to form a substance that can be polymerized. This reaction forms compounds with a varying degree of chlorine saturation. The resulting mixture is distilled to obtain the desired product in purified form.



The "R" in the equation represents a hydrocarbon radical such as $-\text{CH}_3$. The type or types of radicals chosen for R ultimately determine chemical and physical properties of the silicone because the R groups become the side chains of the final polymer. If the methyl group is chosen, for example, the result is dimethyldichlorosilane. Copper is typically the catalyst used in this reaction.

The dimethyldichlorosilane, or other starting material, is then hydrolyzed by adding water, forming short chains and rings, and evolving hydrochloric acid.

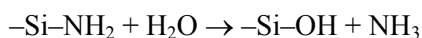
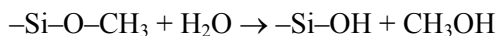
In the next step, the rings are broken and the chains further polymerized with the help of an additional catalyst. Strong acids like sulfuric and nitric, strong bases like sodium hydroxide, amides and other materials are used for this purpose. The result is called a silicone oil or grease. Its chains are terminated with hydroxyl groups. These terminal groups may be replaced to alter the curing chemistry. But for some purposes, this is the final product. A typical result is



Silicone Rubber Curing Chemistry

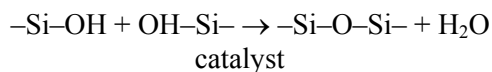
The curing of silicone rubber is similar to the building of Tinkertoys®. The chains described above are the sticks, except that they are quite long and flexible. The round Tinkertoys connectors correspond to molecules of cross-linking material added to the silicone. These molecules are typically composed of one silicon atom with three or four reactive groups attached, corresponding to Tinkertoys connectors with only three or four holes. During curing, the sticks become attached to the connectors until very few ends remain unattached. Failure to react most of the chains with cross-linkers could affect the chemical and physical properties of the product.

The cure reaction of GE Silicone II and other one-part silicones, as they are called, is initiated by atmospheric water vapor. The reaction releases various acids, bases, esters, alcohols or other chemicals as byproducts. The particular byproducts give a silicone its characteristic odor, for example:



The first equation generates methanol as a byproduct; the second, ammonia. These may be the source of the methanol-ammonia odor present in GE Silicone II (GE280). Note that both reactions leave hydroxyl groups attached to the exposed silicon atoms.

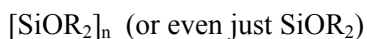
The hydroxyl groups then react, under the influence of a catalyst, to yield water. This catalyst is problematic to the pyrotechnician because it is often listed as a trade secret ingredient by the manufacturer, and derivatives of it may remain in the cured product.



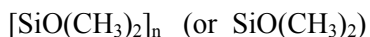
The cured product is typically free of the carbon-carbon bonds or reactive groups that cause instability in other binder-fuels. Thus silicones are unaffected by strong chemicals, excessive heat or UV light. However, possibly undesirable chemicals may still remain in the cured product, for example:

- catalysts, including copper
- HCl, H₂SO₄, NaOH, KOH, etc.
- unreacted organic groups from the cross-linkers
- cure reaction byproducts (ammonia and methanol for GE280, acetic acid for traditional RTV)
- any possible reaction products of the above

The cured product is mostly composed of long-chained, silicon-oxygen backbones, with side groups attached. The cross-links and terminations make up only a small portion of the molecule and can be ignored for stoichiometric purposes. This allows the silicone material to be represented in a simplified way in chemical equations:



For most silicone elastomers, the side groups are methyl radicals. Thus, this becomes



Characteristics of Pyrotechnic Formulations

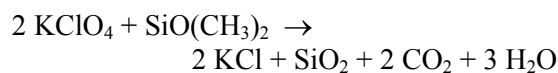
Tests were made with GE280 and GE5000. For oxidizers, only potassium and ammonium perchlorates were investigated in any detail. Potassium nitrate simply did not produce compositions that burned well. Other nitrates were not tried. Chlorates were tested for sensitivity but were otherwise avoided altogether because of the risk of forming highly sensitive or spontaneously combustible mixtures.

The chlorate mixes would snap when pounded on an anvil with a force that might be used to drive a large finishing nail. Nitrate mixes required a severe blow to cause a reaction but were nearly refractory in combustion. Apparently nitrate is not a strong enough oxidizer with silicone.

Potassium Perchlorate

Potassium perchlorate created slow-burning compositions that might be suitable for micro-stars or lance; although smoke tended to be a problem. Excellent blues and good yellows were created with simple compositions. Some blues were tested as comets and in aerial shells, but they tended to wash out to a purplish blue and did not look quite as good as they did on the ground.

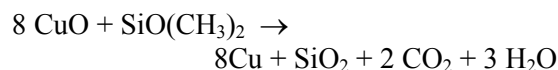
The simplified stoichiometric reaction of potassium perchlorate with silicone is



That represents a 78.9 to 21.1% weight ratio.

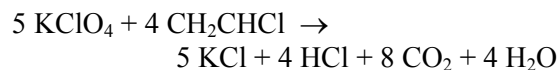
When burned, the silicon accepts a second oxygen-creating silicon dioxide (silica) mostly in a molten state, forming a slag. The potassium tends to hold onto its chlorine, so a chlorine donor is needed. During burning, it is plausible that methyl groups and/or hydrogen are initially left unreacted, leaving the slag as a gas. They can burn in the atmosphere without consuming oxygen from the oxidizer. This means that higher fuel loadings should be possible.

For blue compositions, copper(II) oxide serves as an optional oxidizer, sometimes being reduced, and sometimes not. The presence of elemental copper can easily be detected in the ash of a test, indicating that the copper(II) oxide is being reduced. The reaction when copper(II) oxide is fully reduced is



giving a 89.8 to 10.2% weight ratio.

Polyvinyl chloride (PVC) was used for the chlorine donor. The simplified stoichiometric reaction of potassium perchlorate with PVC is



giving a 73.5 to 26.5% weight ratio.

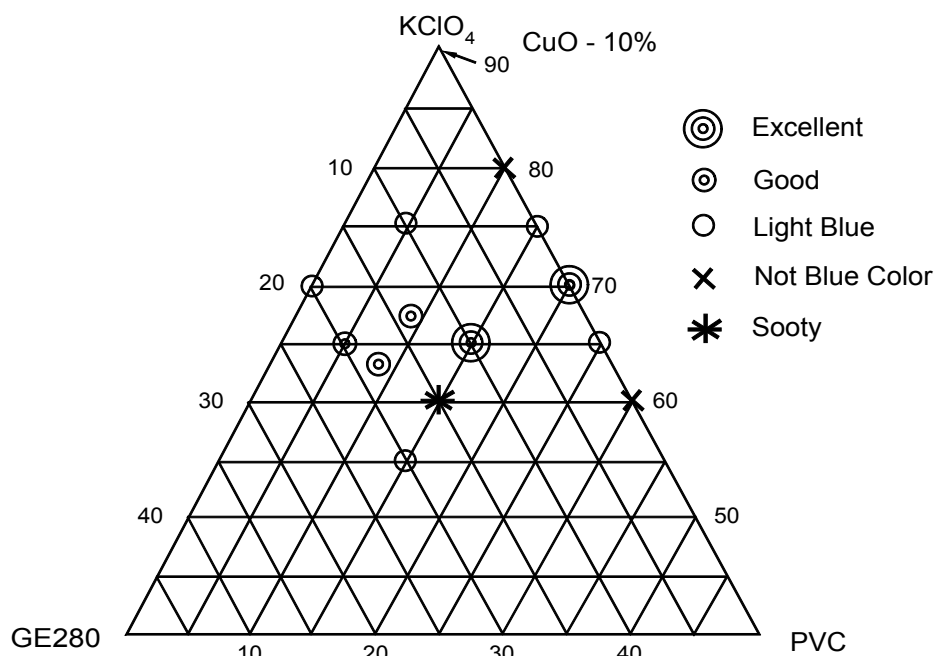


Figure 1. Good slow-burning blue mixtures can be produced using potassium perchlorate, PVC and up to 20 % silicone.

The triangle diagram in Figure 1 shows the range of blue color generation with 10% copper(II) oxide content. Five percent copper(II) oxide was also tested yielding a similar pattern but with inferior color quality. The nomenclature of Shimizu in Pyrotechnica VI^[3] was used, and his formula B11 (see Table 2) was used as a standard to judge results. Shimizu's data correspond with the right hand edge of the triangle, where the silicone content is zero. His results are shown for reference.

Little data was taken on burn rates. Formula KB33 with 75% oxidizer (see Table 2), burned at 36 s/in, while compositions with lower percentages of oxidizer burned slower.

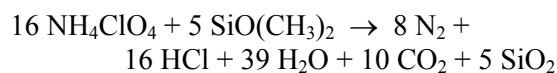
A few formulations were tried for yellow. Attempts to correct the color using barium sulfate were not successful. The mixture KY07 produces a good sodium yellow using sodium benzoate. The burn rate was an impressive 14.5 s/in. (Note that potassium perchlorate plus sodium benzoate is basically a whistle mix. A safe procedure would be to mix in the sodium ben-

zoate after the other ingredients have been combined with the silicone.)

Ammonium Perchlorate

Ammonium perchlorate seemed to be the oxidizer most suited for use with silicone. It burns fast, acts as a chlorine donor, and has a tendency to strobe. The compositions also take fire more readily than those made with potassium perchlorate.

The simplified stoichiometric reaction of ammonium perchlorate with silicone is



giving a 83.5 to 16.5% weight ratio. If the hydrogen is not oxidized, the ratio becomes 66.5 to 33.5%. The oxidizer releases its chlorine largely as HCl gas, which is good for color generation. If PVC is added as a chlorine donor, the stoichiometric formulation is NH_4ClO_4 (79.3%) and PVC (20.7%).

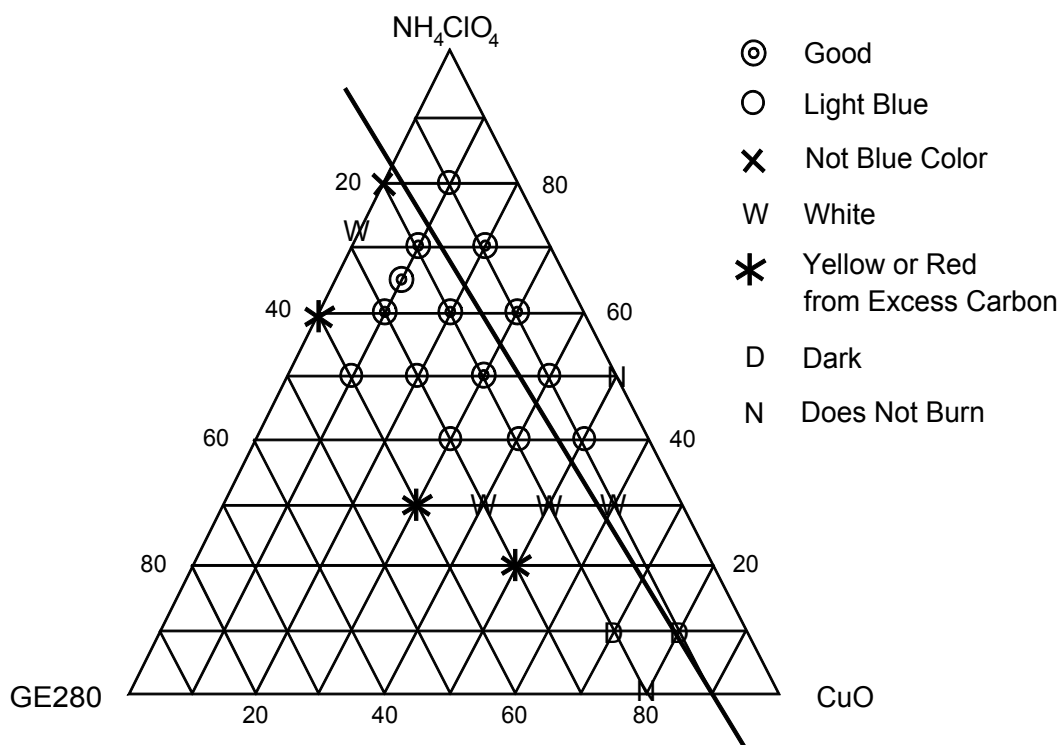


Figure 2. Blue colors using ammonium perchlorate may contain a large excess of fuel (left of sloping line).

Copper(II) oxide is used as the color agent in formulations to make blues. Copper(II) oxide also serves as a catalyst and sensitizer as summarized in Table 1. Three samples with a constant 72:28 ratio of ammonium perchlorate to silicone and a varying percent of copper(II) oxide were tested. Ignition was tested by placing a thin layer of 5FA Black Powder on the surface and igniting it quickly with a propane torch. As the copper content increased, so did the burn rate and ease of ignition.

Table 1. Effect of Copper(II) Oxide.

Mixture	NH ₄ ClO ₄ : Silicone 72:28	CuO (%)	Ignition with 5FA	Burn Rate (s/in.)
NH4W01	100	0	0/3	14.8
NH4B01	95	5	1/2	13.8
NH4B02	90	10	2/2	13.5

The triangle diagram in Figure 2 shows the combination of ammonium perchlorate, silicone and copper(II) oxide. No chlorine donors were added. Some samples showed moderate sensitivity when hammered on an anvil; others were quite insensitive. The line drawn across the diagram represents complete oxidation and reduction per the theoretical stoichiometric reactions. Note that good colors can be found well on the fuel-heavy side of the line.

The triangle diagram in Figure 3 shows burn rate as measured in a 1" long by 5/16" diameter lance tube. There is a large area of nearly constant burn rate that roughly corresponds with blue color generation. There is probably some physical process such as melting of the oxidizer that is controlling this rate.

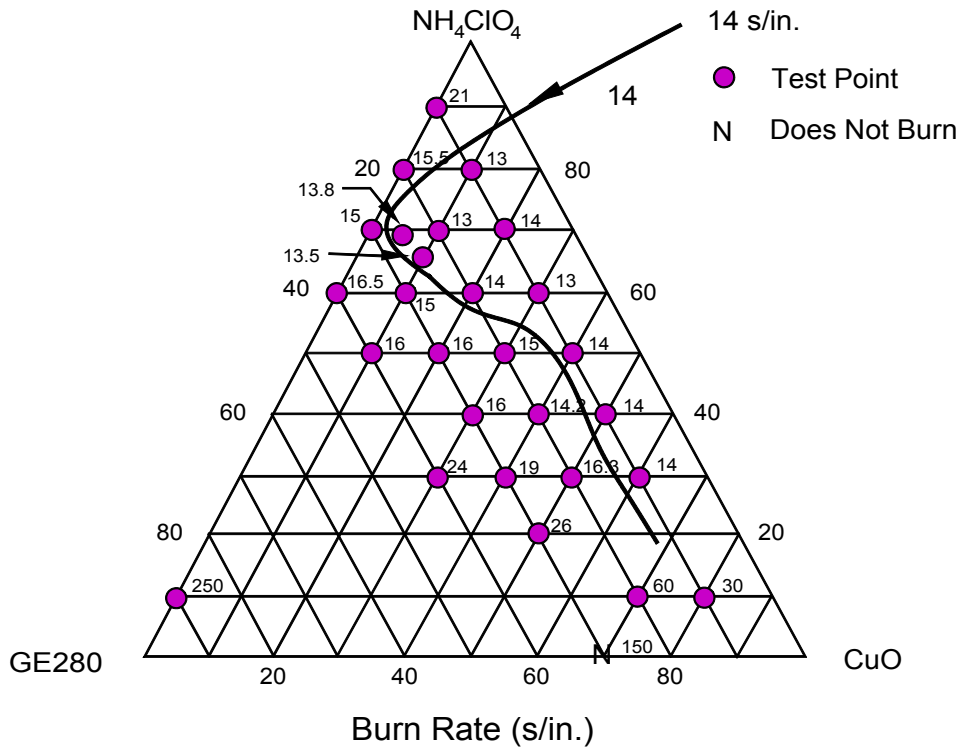


Figure 3. In the area of blue color generation, burn rate is nearly constant for a given percentage of silicone.

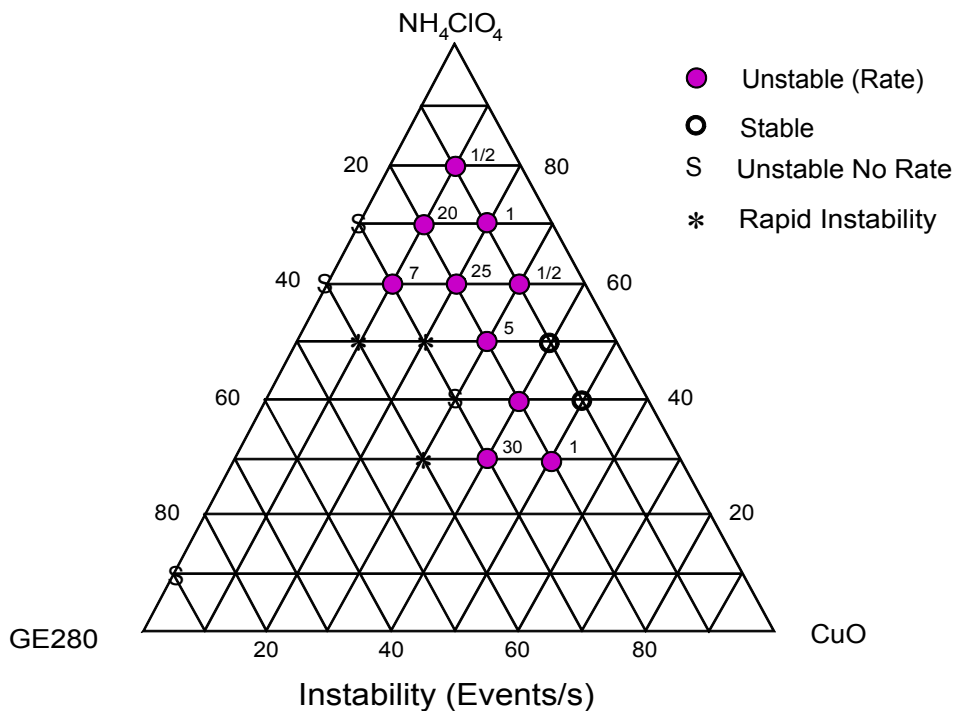


Figure 4. Somewhat strobe-like instability in open air may indicate mixtures that strobe when confined. Numbers next to points indicate strobe rate.

Table 2. Formulations.

Name	NH ₄ ClO ₄ (%)	KClO ₄ (%)	CuO (%)	GE280 (%)	PVC (%)	Other (%)
NH4W01	72	0	0	28	0	
NH4B01	68.4	0	5	26.6	0	
NH4B02	64.8	0	10	25.2	0	
NH4B06	63	0	10	22	5	
NH4B10	20	0	50	30	0	
NH4B19	30	0	40	30	0	
KB33	0	75	5	10	10	
KB40	0	65	10	10	15	
B11(Shimizu)	0	68.5	15	0	9	Accroides resin:7.5 Starch: +5
KY07	0	70	0	15	0	Sodium benzoate:10 Charcoal, air float:5

The triangle diagram in Figure 4 shows unstable burning characteristics observed during small sample testing in lance tubes. Samples that exhibited noticeably unstable burning are marked with "S" for strobe. Where there seemed to be a strobe rate, the strobe rate is indicated by the number next to the test point. It is doubtful that any of these would pass for a blue strobe star, and no aerial shell testing was done. The strobe effect only appeared to be strong and repeatable when there was some degree of confinement, as in rocket motors. One mixture containing PVC (NH4B06) was pressed into several rockets, producing a strobe rate of 5 to 10 per second. The data on the diagram provides a rough guide for where to look for good strobe mixtures.

Some samples left a long, rigid, snake-like ash when burned in the uncured state. Data on this property is sketchy, but some mixes that behaved this way were NH4B01, NH4B10, and NH4B19. These had the drawback that large volumes of HCl gas are generated. Perhaps a mixture using potassium perchlorate, copper(II) oxide, silicone grease and a substance that evolves additional gas can be found that does not generate HCl.

Some compositions generated a large amount of smoke, while others generate relatively little. This seemed to depend on the amount of silica that remained in the slag. A good low-smoke lance may be possible.

Mixing Methods

The following methods were found suitable for small batches. For larger amounts, appropriate precautions should be taken.^[4]

The dry ingredients were sifted together two or three times through a fine screen. The silicone was then combined with the dry ingredients. Highly reactive auxiliary fuels like benzoate were added after the oxidizer was combined with the silicone.

It is important to note that silicone pyrotechnic compositions, unlike typical moist pyrotechnic mixes, burn hot and fast in the uncured "wet" state. And they can be readily ignited. It is a serious miscalculation to assume that "wet" compositions are benign until cured.

Small test batches, around 10 grams, were mixed by folding the material over on itself and pressing it flat, at first with a wooden spatula, then by hand. The spatula was scraped clean once or twice to avoid losing silicone from the mix.

Larger batches, around 200 grams, were placed in a zip-closure food storage bag and kneaded. The bags with the plastic closure shuttle in the one-gallon size worked best. The mixed dry ingredients were dropped in first, then the silicone was added by wiping it from the weighing paper onto one side of the bag, keeping it away from the corners and the zip-

per. A moderate amount of air was left in the bag, so that the two sides could touch together easily in the middle. The powder was worked into the silicone (by pulling the material apart, exposing fresh silicone, and covering that area with powder) until all was dampened. After most of the powder was mixed in, the material sticking to the surface of the bag was removed by rubbing other composition across it. When all of the material was consolidated, it was removed and hand-kneaded further to complete the mixing process. Upon opening the bag, an alarming odor of ammonia was detected. This was largely due to the cure process of the silicone. (One should remain vigilant when detecting ammonia, however, as it may indicate breakdown of ammonium perchlorate and an impending disaster.)

Rocket Construction

Preliminary work showed that ammonium perchlorate-silicone blues work well as strobe rockets. The color was good and the lift was moderate. Limited rocket building skill and experience nevertheless produced nineteen successful launches out of nineteen, with only one rocket deviating significantly from the expected trajectory. Neither formulation nor construction detail seemed to be critical to achieve success. But there is plenty of room for experimentation and improvement.

Most of the experience was with the formula NH4B06, which contains PVC. This mixture was not the result of any exhaustive optimization; rather, it was chosen from the middle of the "good" area in Figure 2, and it worked on the first try! Although PVC was added to improve color, no visible difference was found later when compared to a similar mixture that replaced the PVC with silicone. These mixtures are quite fuel-rich compared to stoichiometric oxidation-reduction. The first motor used the

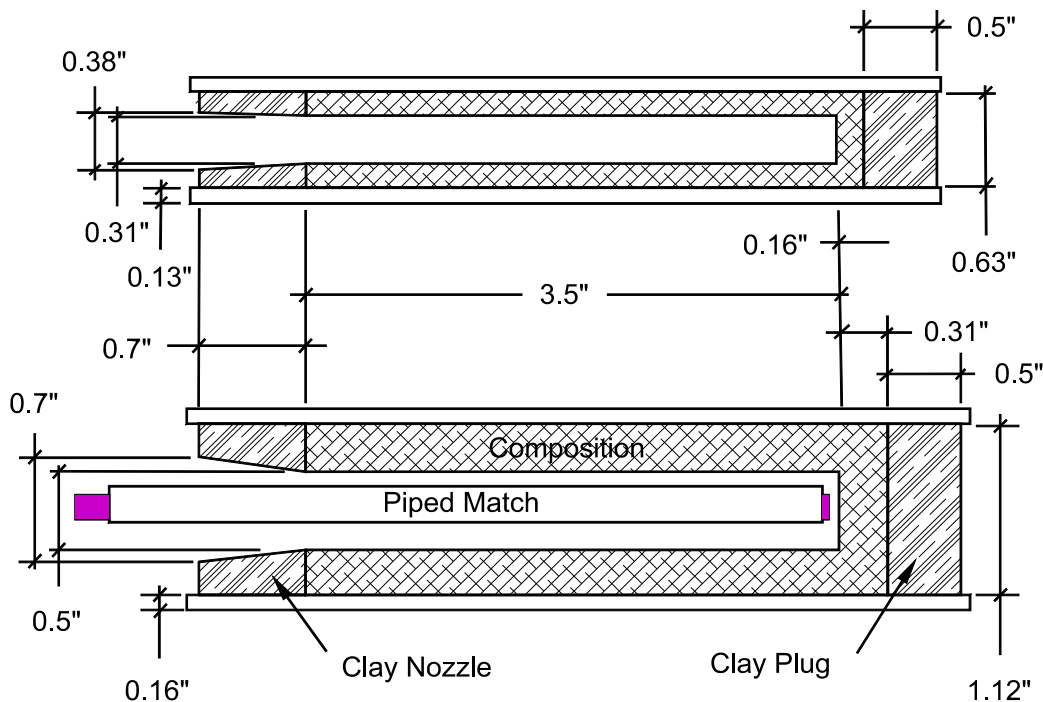


Figure 5. Sketch of rocket designs.

more expensive GE280, and the remaining used GE5000. The lower molecular weight GE280 seemed to give better lift, but the sample size (only one) was very small so this is not conclusive. Equivalent results are probably achievable using the GE5000.

These rocket compositions required a hollow core to achieve good lift and a strobing effect. Otherwise, the details seemed to be non-critical. Five-eighths-inch dia. Roman candle tubes with 1/8" walls and 30 mm Ruggieri display candle tubes were used for the casings. These were built using the dimensions in Figure 5. Longer versions of the 5/8" model (up to a 4.5" long core) were constructed in an unsuccessful attempt to find the core length at which the burn rate became explosive. The results were less beautiful but more amusing because of the resulting erratic strobe rate.

Most of the rockets had clay nozzles. If the nozzle was omitted, the rocket still flew, but stopped strobing about 50 feet above the ground. The choice of nozzle material seems to be unimportant, but materials with a high sodium content might wash out the color. Powdered clay with 25% grog works well. Also up to 10% silicone can be added to the mix, which makes the nozzle less likely to break up in handling and easier to remove from the spindle. Pullout strength [the static axial force required to dislodge the nozzle from the tube] is reduced by about one-third, however.

Because of the workability of the silicone, tooling can be much simpler than for conventional rockets. The ramming force required is much lower than for dry mixes, so no outside support is required to keep the casing from rupturing. The spindle and rammer are also simpler than for black powder motors. The nozzle portion of the spindle is the only part that must be made of metal such as aluminum or brass. Otherwise, the whole tool may be made of hardwood like maple or cherry. The silicone compound is easily removed from the spindle, so essentially no taper is required above the nozzle. This makes the tools easy to build, and also results in all of the composition burning out at the same time. The spindles used in this study had brass nozzles and aluminum shafts with a di-

ameter taper of about 0.02" over the 3/2" length.

Only two ramming tools are necessary, one with a long straight bore, and the other with no bore at all. For safety, the long rammer is designed with enough clearance (about 0.06") so that it can never come in contact with the spindle, and is made of wood as an extra precaution. (Normal rocket tools, which can make contact metal-to-metal, should not be used.)

The composition was made in a food storage bag as described above. It was then broken into pieces small enough to pass freely between the spindle and the tube. This reduced the amount of composition resting on top of the spindle. Such composition can cause air voids in the finished motor or pack into the rammer. Dicing the composition with a plastic knife on wooden cutting board is an effective, but slow method. The composition remains workable for an hour or two after mixing. In fact, allowing it to sit out in the granulated state for a half an hour may aid the curing process through absorption of moisture from the air.

The nozzle is rammed without side support, and ramming is stopped when slight deformation of the tube is observed. This is done with only the nozzle former in place and the rest of the spindle removed. The clay will not consolidate above the top of the nozzle former, automatically creating a nozzle of the correct height. The tube's rotational position is marked with a pen; then it is removed from the tool for inspection and for cure if it contains silicone. The spindle portion is then screwed on, the rocket tube replaced, and the fuel rammed. This is an unorthodox method, but it does not cause problems with these motors.

Before the fuel is rammed, the outside of the case is marked at the point where the composition is to end. The thickness of the fuel above the top of the spindle is made equal to the distance between the spindle and the tube. This gives zero delay from end of lift to burn-through.

Increments of fuel are kept small to avoid trapping large air pockets between areas of consolidated composition. The material does not need to be rammed hard. It takes a certain

amount of time for the air to leak out between the grains, and ramming hard does not help. A long series of light taps drives out the air and leaves the composition solid. Composition adhering to the inside of the rammer is evidence that the increment was fully rammed. Remove this material from the rammer after each increment. When the fuel is level with the top of the spindle, add a generous increment, and switch to the solid rammer. Complete the fuel loading to the marked height, and finish off with clay at the top. Old-fashioned kitty litter (9 mesh) works when sealed after ramming with a bit of white glue. The lack of external support prevents the top clay plug from being consolidated as thoroughly as is normally done with black powder motors. This concession to safety does not appear to affect operation.

The completed motor should be removed immediately from the tool. This is easily done, except for the fact that a partial vacuum will form at the top of the spindle. If pulled too rapidly, the suction will cause large movement of the composition, ruining the motor. A large amount of spinning (clockwise) with a small amount of pulling will allow air to work its way into the space. A small hole bored through the length of the spindle or more taper would probably facilitate removal.

These motors need to cure at least one day, but three days is better, to allow the methanol and ammonia to escape. Afterwards, an electric igniter or piped match is pushed all the way to the top of the motor to achieve proper ignition. An appropriate stick for stabilization is attached before launch (see reference 6). A small amount of white glue plus two wraps of fiberglass tape works well to secure the stick. These motors will not carry large loads predictably.

Silicones for Future Development

While only GE280 and GE5000 were used in these tests, there is a wide variety of silicone materials to choose from. These range from greases and oils to elastomers to casting resins. Each has its own manufacturing process and chemistry, and they should not be assumed to be interchangeable for pyrotechnic use. What follows are some guidelines for the development of new silicone-based compositions.

The manufacturer's Material Safety Data Sheet (MSDS), the manufacturer's technical application support engineers, and basic silicone chemistry texts should be used to gain information about the chemistry of a material. The MSDS is very useful because it gives the ingredients in a product, although some may be listed as "industry secret". The chemistry of the particular silicone should then be considered in respect to the other ingredients before mixing anything together.

Because of the possible reactions when oxidizers are combined with acids, silicones that evolve acids during cure should not be used. Do not use silicones that give off a vinegar odor. Silicones that give off weak bases like ammonia are interesting because they buffer the mixture to about pH10 during cure and can neutralize any acids that might be present in the unreacted silicone. Silicones that evolve alcohols are probably least reactive and should be sought out. (GE280 gives off both methyl alcohol and ammonia.) Those made for electronic circuit assembly are promising for future research in this respect. Avoid any silicone that, during cure, gives off amides, ketones or species with double bonds.

Silicone casting compounds are chemically more complex than other silicones. They may contain carbon-carbon bonds or other opportunities for chemical reactions, making them less stable.

Silicone greases, especially electronic or medical grades, offer the promise of a totally predictable fuel. However, they have no cure process, which means they will not serve as a strong binder. They may work in rockets in spite of this.

Gasoline resistant grades may contain side chains loaded with halogens—fluorine most likely—that can be used for color enhancement as suggested by Kosanke.^[5] Note that combustion products of halogenated organic compounds can sometimes be extremely toxic.

Users unable to understand the chemistry and unequipped to handle spontaneous combustion should restrict their choices to materials with some history of use (currently GE280 and GE5000). This, however, is no guarantee of safety.

Other Ingredients

Other fuels should be chosen carefully to avoid unwanted oxidation–reduction reactions with the oxidizers. Metals, sulfur, or nitrogen-bearing fuels are high-risk choices. Polymers such as Parlon®, PVC and polyethylene fall at the other end of the risk spectrum.

Chlorate oxidizers should be avoided. Chlorate samples made for preliminary safety testing were more sensitive to hammer blow on an anvil than perchlorates. The burn rate for potassium chlorate compositions was actually equal to or slower than that for equivalent ammonium perchlorate mixes.

Sulfates are the safest color donors but did not generate good colors in limited testing. It is unknown why these did not work; possibly there was insufficient temperature, or the metal oxides generated dissolved into the slag forming a glass. Copper(II) oxide (black—CuO) and sodium benzoate can hardly be considered safe, but they work. The copper(II) oxide used was ceramics grade (very fine powder). It is not known with which process it was made, but it was free of acid when tested with pH paper.

Chlorine donors should be restricted to polymers (PVC and Parlon®) plus totally halogenated hydrocarbons. Avoid chlorides and oxychlorides.

Acknowledgments

I want to thank Charlie Hill, Al Klumak and John Vico for help in many, many ways that made this article possible. I would also like to thank all those who provided constructive input, particularly, Barry Sturman and Wes Smith for their generous assistance in preparation of the final version.

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Determination of the Velocity of Fragments Produced from Exploding Firework Maroon Shells

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ABSTRACT

This paper describes a method for determining the velocity of fragments produced when firework maroon shells explode. Fragment velocities for shells fired in free air and in steel mortar tubes (causing them to rupture) are reported. The maximum velocity of plastic shell casing fragments that was recorded (964 m/s) was substantially higher than that measured for steel mortar fragments (512 m/s). The magnitude of the velocities measured indicates the potential hazard associated with these fragments and the need to consider methods of reducing such hazards.

Keywords: mortar, firework, shell, maroon, steel, velocity, fragment, salute, report, exploding, explosion

Introduction

After an accident in 1988, at the Glasgow Garden Festival as a result of which a firework display operator had to have his leg amputated^[1] and a member of the general public was seriously injured,^[2] the UK Health and Safety Executive examined the extent of current knowledge relating to the safe use of mortar tubes. Little published material was available at that time and therefore a programme of research was initiated to provide information on the fragmentation characteristics of different mortar tube types and the effectiveness of mitigation measures such as mortar tube burial and sand-bagging. The need for the work was reinforced by subsequent accidents in Japan^[1] and reports of prematurely exploding shells from the USA in 1992,^[3] 1994,^[4] and 1995.^[5] It is envisaged that safety-related information of this type could

form an important input to the development of guidance for firework display operators.

A survey of factors relating to the use of mortars at firework displays^[6] provided information on the types of shells and mortar tubes commonly used in the UK. This enabled an experimental programme to be designed to investigate the fragmentation behaviour of a range of steel mortar tubes when various types of firework shells were exploded in them.

An important measure of fragment hazard is the velocity with which fragments are projected. This paper reports on the range of initial projectile velocities likely to be encountered when firework shells explode prematurely, shattering the surrounding mortar tube. The possible safety implications of the results are also briefly discussed. Maroon shells, also known as salutes or aerial reports, were used in all the tests. Future analyses of fragment velocities in conjunction with fragment dimensions, mass, and trajectory will enable flight distances for fragments to be estimated.^[7]

Experimental

Time, mass and linear distance measurements recorded during this work can be traced to National Standards.

Experiments were undertaken in a Blast Cell that had wooden walls lined with plastic sheeting. This allowed low kinetic energy fragments to cut or mark the plastic sheet and enabled high kinetic energy fragments to penetrate into the wooden lining. The system has been described more fully in previous work.^[8]

Seamless and spiral-wound steel tubes with 3 mm thick steel baseplates were used for 75 mm calibre mortars. Spiral-wound tubes

with 6 mm thick baseplates were used for 152 mm calibre mortars. Baseplates were fitted inside the tube wall and continuously welded into place using a Metal Inert Gas (MIG) welding technique. Seamless tubes complied with British Standard 6323 Pt4 CFS 3BK. Spiral-wound tubes were formed from a mild steel strip using a four-ply lockseam. All the tube types were available from general engineering companies.

The shells used were 70 mm diameter cylindrical and 150 mm diameter spherical shells for use in 75 and 152 mm calibre mortar tubes, respectively. The 70 mm diameter shells contained 120 g of flash composition; the 150 mm diameter shells contained 400 g of a similar composition.

Three types of test were performed:

1) Explosion of maroon shell charges, which had been removed from their shell casings, in thin-walled, spiral-wound steel mortar tubes (<2.00 mm wall thickness). The removal of the shell casing meant that only steel mortar tube fragment velocities were measured. This simulated the effects of a maroon shell exploding prematurely in a steel mortar tube.

- 2) Explosion of maroon shells in thick-walled steel tubes (>2.6 mm wall thickness) to measure the velocity of fragments of plastic shell casing produced when the mortar splits open but does not produce many steel fragments.
- 3) Explosion of maroon shells in free air to measure the velocity of plastic shell casing fragments that had not been affected by the presence of a mortar tube.

Experiments involving the fragmentation of steel mortar tubes by exploding firework maroon shells in them would expose velocity measuring equipment to a hostile environment. As a consequence, the velocity measuring system was designed to be inexpensive and disposable. Wooden frames with wire screens on the front and back faces were used (Figure 1). The wire screens were made using 0.315±0.004 mm diameter insulated copper wire that was connected through an electronic circuit to an oscilloscope, which recorded the time that the front and back screens were broken (Figure 2). Four frames were arranged in a square with the mortar tube positioned at the centre. The distance from the mortar tube to each frame was 450 mm for 75 mm calibre tubes and 1000 mm for 152 mm calibre tubes. These distances were sufficient to prevent the wire screens from being broken by the blast wave when maroon charges in plastic

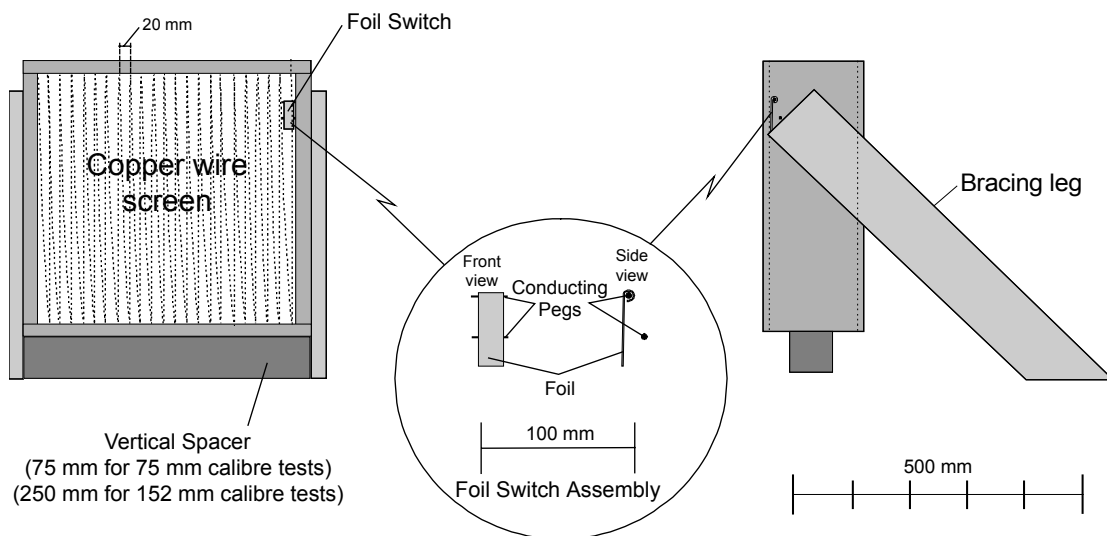


Figure 1. Diagram of wooden frames used to measure the velocity of projectiles generated from prematurely exploding firework maroon shells.

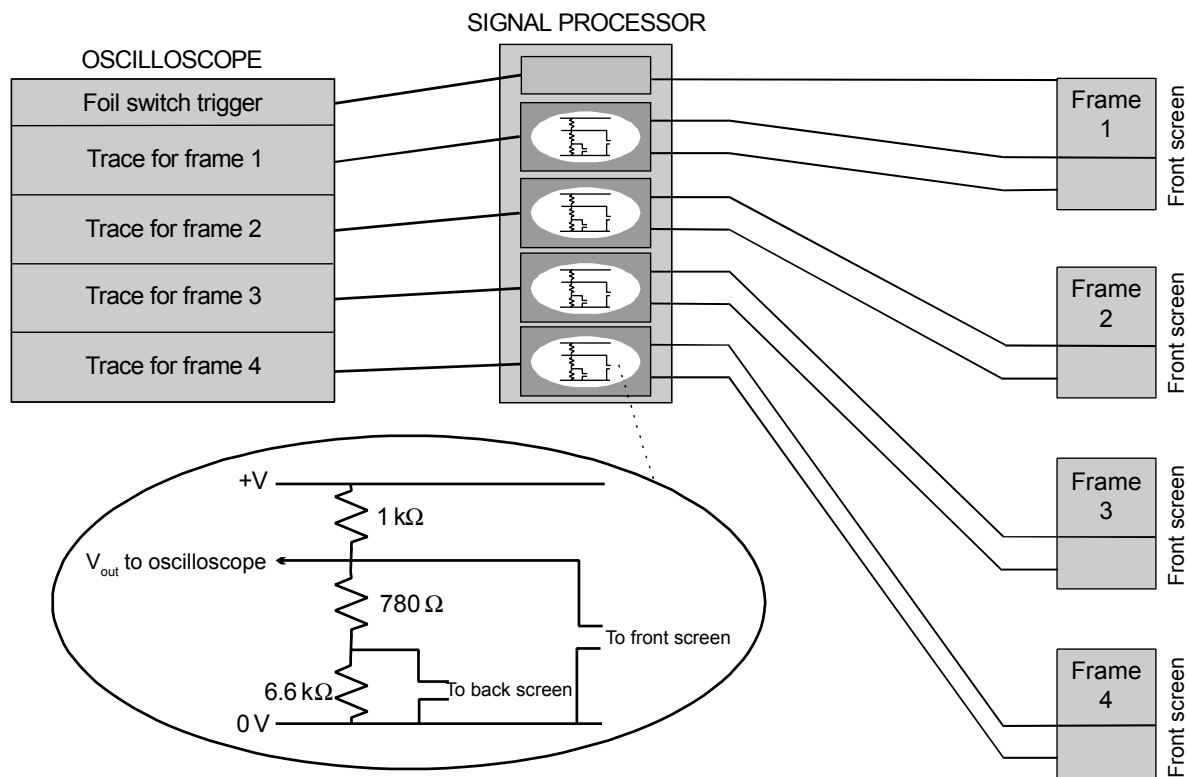


Figure 2. Schematic diagram of the fragment velocity data recording system.

bags were exploded. One of the four screens had a foil switch located directly behind the front screen (Figure 1). This made a circuit as the blast wave passed and activated the oscilloscope recording system to all four frames. A 10% pre-trigger setting was used. A voltage change occurred when a wire screen was broken, and therefore, in those cases in which both the front and back screens of a frame were broken by a projectile, the time interval between the events could be measured. Since the distance between screens on a frame was 150 mm, it was possible to calculate the average velocity of a projectile over this distance from the measured time interval.

Velocity verification experiments, which compared the wire screen system with a more accurate high speed photographic system, showed that the calculated wire screen velocity values were likely to be accurate to $\pm 10\%$.^[9]

Mortar fragment velocity experiments were carried out as indicated in Table 1.

In tests designed to measure the velocity of fragments from steel mortar tubes (test type 1),

the explosive charge was removed from its shell casing and placed in a plastic bag. This prevented plastic shell fragments from interfering with steel fragment velocity measurements. Preliminary experiments had shown that removal of the charge from its casing reduced fragment numbers by up to 10% for 75 mm calibre thin-walled (1.65 mm wall thickness) mortar tubes and by 37% for 152 mm calibre (2 mm wall thickness) mortar tubes.

In tests using thicker walled (2.65 mm) seamless tubes (test type 2) that did not produce many steel fragments, the shell, including the plastic shell casing were exploded to study the velocity of the plastic fragments that passed through splits in the mortar tube.

Shell explosions carried out in free air, without a mortar tube present (test type 3), simulated the effect of a maroon shell lifting out of the mortar tube and bursting directly above it as it ascended (a 'low-burst' or 'muzzle break'). This provided velocity data on the plastic fragments produced.

Table 1. Summary of Fragment Velocity Experiments.

Shell Height (mm)	Distance from Frames to Explosion Point (mm)	Mortar Calibre (mm)	Shell Description	Tube Description (Type/ wall thickness in mm)
300	450	75	Maroon main charge removed from shell casing	Spiral wound/ 1.65
				Seamless/ 1.63
			Maroon main charge in shell casing	Seamless/ 2.65
		N/A	Maroon main charge in shell casing	N/A
500	1000	152	Maroon main charge removed from shell casing	Spiral wound/ 2.00
		N/A	Maroon main charge in shell casing	N/A

Note: N/A refers to experiments in free air.

This provided velocity data on the plastic fragments produced.

Wherever possible, measured velocities were associated with individually identified fragments. This was done by inspecting the walls directly behind the wooden frames to locate fragments that had penetrated into the wooden lining of the Blast Cell. The line of flight of the fragments was projected back to the explosion point to see if the break points on the wire screens could be linked to specific fragments. Where fragments had not penetrated into the wood, those fragments on the floor in the vicinity of the impact point were inspected to see if any could be matched with the impression or cut made in the plastic liner. In cases where more than one fragment could be attributed to a specific velocity measurement, all the masses of likely fragments were recorded.

Experiments where the shell was exploded in free air generated a large number of very small plastic shell casing fragments. It was not possible to match an individual fragment with the velocity measurement; therefore fragments were not weighed.

Results

A typical oscilloscope trace produced from steel mortar tube fragments is reproduced in Figure 3. It shows four traces corresponding to the four frames used for the test and the typical step profile produced as the front and back wires on a frame are broken in sequence. Fragments passed through frames 1, 2 and 3 while the wires on frame 4 remained intact.

Velocity and mass measurements for steel mortar fragments are summarised in Table 2. These show that for the 75 mm calibre spiral-wound and seamless tubes, the maximum velocity recorded was 450 metres per second (m/s) and the minimum velocities were 54 and 19 m/s, respectively. The calculated mean velocities of fragments from these tubes were similar (i.e., 230 and 250 m/s, respectively). Fragments from the 152 mm calibre spiral-wound mortar tubes that could be confidently associated with a measured velocity, or where the mass difference between two possible fragments for a given measured velocity was small, gave a velocity range of 147–512 m/s and a mean velocity of 310 m/s.

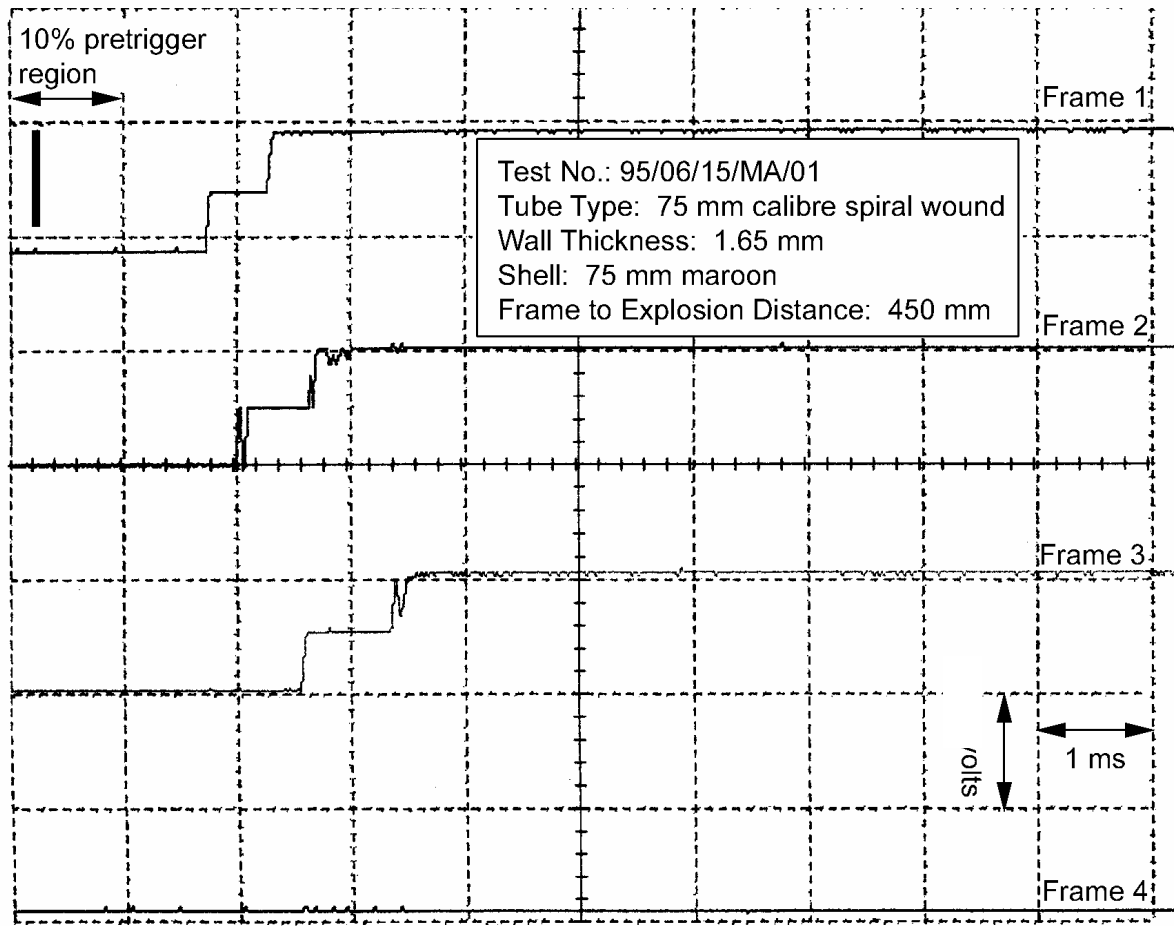


Figure 3. Oscilloscope traces showing the step voltages typical of those generated by fragments when a maroon shell main charge is exploded in a steel tube.

Examination of the relationship between mass and velocity for the steel fragments produced in the tests showed that there was a wide variation in fragment mass for a similar velocity. For example, during tests using seamless 75 mm calibre tubes, three fragments were recorded with a velocity of 450 m/s and masses in the range 0.6–41.0 g. No clear trends could be detected between fragment mass and velocity for the 75 or 152 mm calibre tube tests.

Results for the velocities of plastic shell casings are shown in Table 3. They show that plastic casing fragments ejected from ruptured 75 mm, 2.65 mm wall-thickness mortars, had velocities in the range 135–540 m/s with a mean velocity of 310 m/s. The mass range of the fragments (0.7–7.1 g) was substantially lower than that recorded for steel fragments.

Plastic shell casing fragments from maroon shells suspended between the wooden frames with no mortar tube present showed that the velocities obtained were significantly higher than the velocities recorded for plastic fragments ejected from within ruptured mortar tubes. A maximum velocity of 900 m/s was recorded for shells normally fired from 75 mm mortar tubes and the corresponding maximum velocity from shells normally fired from 152 mm calibre tubes was 964 m/s. Association of individual fragments with the velocities recorded was precluded because of the large number of small fragments produced.

Table 2. Velocity and Mass Measurements for Mortar Tube Fragments Produced Using Maroon Main Charges Removed from their Shell Casings.

Mortar Calibre (mm)	Distance from Frames to Mortar Tube (mm)	Tube Description (Type/ Wall thickness)	Fragment Mass (g)	Velocity (m/s)
75	450	Spiral wound/ 1.65 mm	30.7	450
			—	113
			—	54
			194.9 or 96.8	61
			3.7	318
			16.2	93
			24.2	386
			32.4	386
			28.6	225
			6.1	270
		18.6	193	
		—	246	
		Seamless/ 1.63 mm	69.5	225
			45.1	19
			0.6	450
			38.2 or 41.0	450
			3.1	108
			2.0 or 2.8	450
			51.7	208
			16.5	135
20.3	235			
3.8 or 9.8	415			
22.7	270			
407.9	44			
152	1000	Spiral wound/ 2.0 mm	56.0	386
			—	338
			85.0	245
			191.0	180
			70.5 or 36.5	304
			262.4	371
			52.1 or 54.5	512
			110.6 or 111.9	325
			141.5	253
			—	264
			72.5 or 68.7	147
			78.9	410
107.5 or 56.0	256			

Discussion

An inexpensive and easy to manufacture means of measuring steel fragment velocities was developed. It can be modified to provide velocity data on fragments from plastic shell

casings that are ejected from thicker walled tubes (2.65 mm) that split but do not produce many mortar fragments. It can also measure the velocity of plastic shell casing fragments produced when shells explode in free air. The reduction in the number of fragments generated when the maroon explosive charge is exploded

Table 3. Velocity and Mass Measurements for Plastic Shell Casing Fragments Produced from Maroon Main Charges.

Shell Diameter (mm)	Distance from Frames to Explosion Point (mm)	Test Description	Fragment Mass (g)	Fragment Velocity (m/s)
70	450	Shell fired in seamless, 2.65 mm wall thickness, 75 mm calibre tube, causing rupture of the tube but little fragmentation	0.8 or 0.7	216
			1.0	135
			1.10	540
			2.0	415
			1.0	245
			1.60	235
			7.10	360
		—	300	
		Shell fired while suspended 300 mm above floor between frames	—	771
			—	900
			—	900
			—	900
			—	900
			—	711
—	900			
150	1000	Shell fired while suspended 500 mm above floor between frames	—	794
			—	844
			—	964
			—	587

without its shell casing suggests that the rate of energy release is less than for the cased equivalent and that the fragment velocities measured are likely to be a conservative estimate.

This study has suggested three categories of fragments that would correspond to hazards that may pose different risks to firework operators and spectators when shells explode prematurely. These are:

- 1) Fragments produced from the mortar tube that can have a large mass (407.9 g has been recorded in this study) and velocities in the range 19 to 450 m/s. This means that their kinetic energy is high in comparison with shell plastic case fragments. Such fragments could travel large distances and would pose a hazard to firework operators and spectators.
- 2) Plastic shell casing fragments that emanate from splits in a rupturing mortar tube. These fragments have velocities similar to mortar fragments but are of significantly lower mass

(approx. 1–7 g) and have a correspondingly reduced kinetic energy. The low density of these fragments suggests that air drag would prevent them from travelling far, suggesting that the primary threat is to the firework operator.

- 3) Plastic shell casing fragments produced in free air, which are small and have low mass, but have high velocity in comparison to category 2. These fragments have high kinetic energy that may have the potential to cause injury. Ballistic properties are likely to be similar to category 2 resulting in hazards primarily to the firework operator when a shell bursts low.

The velocity data generated do not represent the maximum velocity of the fastest fragment produced during a test. By its design, the system samples an area of the expanding projectile cloud and therefore provides a range of maximum velocities for projectiles that are travelling

in a direction that will result in their passing through the wire screens.

The velocities of the steel mortar fragments cover a wide range (19–512 m/s), which suggests that a number of factors could affect the velocity of fragments as they leave the explosion point. Factors that could be important are:

- 1) Fragment mass, which will vary and will affect fragment inertia. More massive fragments will require more acceleration energy, which will mean that their resultant velocity is less than lighter fragments.
- 2) Fragment shape, which will affect air drag coefficients. This will affect the rate at which the fragment is decelerated.
- 3) The perimeter of the fragment (i.e., the fracture surface). The larger the perimeter is the more energy will be needed to break the fragment from the main body of the mortar tube, and therefore the less energy there will be to accelerate the fragment.
- 4) The original location of the fragment. Some fragments are produced from areas adjacent to the explosion point while others are produced from areas farther away. This will lead to different amounts of energy being transferred to the fragments.

The velocity of plastic fragments generated from shells exploded in mortar tubes was substantially less than similar fragments generated by shells exploded in free air. This is likely to be due to the mortar tube interfering with the flight of the shell case fragments. The faster plastic fragments will catch up with the mortar tube as it ruptures and collisions will occur. Therefore, it is unlikely that plastic fragments in a mortar tube will attain their full velocity unless their trajectory is along the major axis of the mortar tube (i.e., nearly vertical). The plastic fragments produced were of low mass and had directional trajectories due to the limited number of splits produced in the mortar tube. This type of fragment is considered to be of importance when assessing the safety of firework operators because they might be close to the launch tube when shells are being fired.

Velocities of fragments produced from 152 mm calibre mortars and from plastic fragments from shells of this size exploded in free

air were measured at approximately twice the distance from the explosion point as fragment velocities for the equivalent 75 mm calibre tests. This suggests that the velocities for 152 mm calibre tube tests may have been higher had it been possible to take measurements at the same distance from the explosion point as the 75 mm calibre tests. Tests at closer distances were not possible because the frames were destroyed by the explosion before meaningful velocity data could be recorded.

Conclusions

The main conclusions from this study are:

- 1) The wire screen system for measuring fragment velocity provides data that are likely to be accurate to within $\pm 10\%$. This is adequate for estimating flight distances in future work, provided that fragment trajectory, mass and air drag are also known.
- 2) The use of maroon main charges removed from their shell casings marginally reduces the number of fragments produced from thin-walled mortar tubes. This effect becomes more pronounced as mortar calibres increase, indicating that fragment velocities could be conservative estimates.
- 3) The measured velocities for the fragments generated by this study indicate that some of the types of projectiles produced as a result of the premature explosion of firework shells in or close to mortars will have substantial kinetic energy.
- 4) Data generated by this series of experiments will be useful in helping to assess the hazard posed by different types of fragments at various distances from the explosion point assuming that no mitigation methods are used.

Acknowledgements

The author would like to thank Dr. R. K. Wharton, Head of Explosives Section, Health and Safety Laboratory and Dr. A. W. Train of the Explosives Inspectorate of the Health and Safety Executive for guidance during the course

of the work; Mr. S. A. Formby and Mr. I. M. Howard of the Health and Safety Laboratory for experimental assistance; and the Health and Safety Executive for financial support of the project.

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- 6) S. G. Myatt and R. K. Wharton, "A Survey of Factors Relating to the Use of Mortars at Firework Displays in the UK", *Pyrotechnica XVI*, 1995, pp 50–56.
- 7) M. R. Edwards, S. G. Myatt, and S. Ellis, to be published.
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- 9) S. G. Myatt, "An Experimental Study of the Fragmentation of Steel Firework Mortar Tubes and Methods of Reducing the Resulting Hazard", *M Phil Thesis, Cranfield University*, 1997, pp 96–106.

Communications

Brief technical articles, comments on prior articles and book reviews

Comment on:

Development of a Video Spectrometer, Summer 1998, Issue 7.

I just read your article on the spectrometer. I have a few comments/suggestions for further research.

You might try using a higher color temperature lamp for your incandescent spectrum. Lamps are available with a temp rating of 3200 K. It would be interesting to see if this more closely approximated the radiant energy curve that we would expect.

However, I suspect that a good share of the problem is the sensitivity of the camera to the various colors. This problem will even exist with a black and white CCD, maybe even more so. Another problem is that, just like our eyes, the CCD sensitivity curve varies somewhat, depending on the intensity of the light.

For equalizing filters, Roscolux #356 might be the best—according to my Designers sample book. Others you might try are #51, #54 and #55. In GamColor, you might try #970 or #990. There is also a “minus green” series, #1580 through #1583.

I found your Original/Improved spectra discussion interesting, and have some ideas on why you saw what you did. First, note that the red is reduced. When you mix red and green light,

you get an approximation of yellow. Second, note that the blue is increased on the improved formulation. When you mix blue and yellow, you get white. So, the green would be improved, but the color might be washed out somewhat.

A continuous spectra will not reduce the purity, although it will decrease the saturation of the colors. Mix all the colors, and you get white. Note that the continuous spectrum is heavily weighted toward the blue/green end.

The increased intensity of the green spectra probably accounts for most of the difference. The percentage of yellow and red are lower; so they will be less perceptible to the eye. (The yellow is reduced due to blue being present). Note that if you integrate the area under the green curve portion, it may be as much as twice that from the original curve.

Just some thoughts, from my work doing theatre lighting design. It may shed some light on your results.

One thing to be careful about is getting your slits too narrow. That can cause diffraction—resulting in blurring of the lines. Probably not a problem unless you are interested in identifying various atomic lines. If that were the case, you would probably want to use a high quality glass grating.

Bill Nelson

(The Communications section continues on Page 72.)

Glitter Chemistry

Clive Jennings-White

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ABSTRACT

Pyrotechnic glitter is characterized by a liquid spark terminating in a delayed flash. The chemical mechanisms responsible for the delay and the flash are not known with certitude. Several pyrotechnists have proposed hypothetical mechanisms to account for the phenomena. The different proposals engender different predictions regarding how a glitter performs as a function of its composition. Consequently the behavior of experimental glitter compositions sheds light on the validity of the various proposals.

Although experiments on colored glitter are hitherto disappointing, with the exception of yellow, further work may yet yield useful results.

The most significant safety concern that glitter compositions present is a potential exotherm upon dampening. This can largely be avoided by careful selection of the combination of metal and glitter additives.

Keywords: glitter, formulation, potassium, nitrate, barium, theory

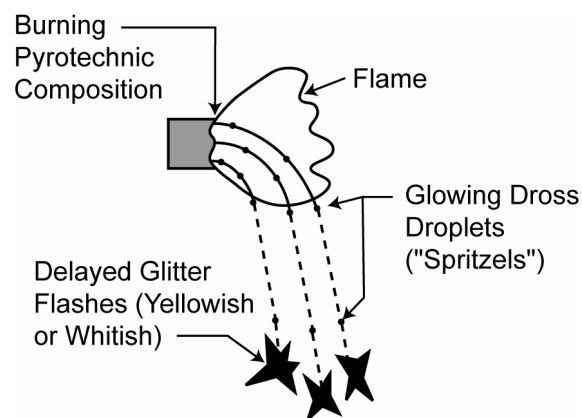


Figure 1. Pyrotechnic glitter.

Introduction

The characteristic property of a burning glitter composition is that it produces rather dim sparks, which suddenly undergo a short lived but tremendous increase in light output. This is illustrated in Figure 1. The glowing of the sparks prior to the glitter flash may not always be obvious when observing a glitter effect in fireworks, but is readily apparent in photographs. Thus there must be at least two different kinds of spark chemistry occurring after the spark has left the burning pyrotechnic composition.

The first phase of a glitter spark resembles that of a classic golden streamer composition utilizing charcoal, not only in color and brightness, but also in that they have both been shown to consist of liquid droplets. The flash phase of a glitter spark, by contrast, resembles the functioning of a pyrotechnic flash powder. Somehow these two disparate elements have been hybridized in the essence of a glitter composition.

An excellent golden streamer formulation, given by Freeman,^[1] is shown as formulation 1 in Table 1. The green powder component is a simple intimate mixture of finely powdered potassium nitrate, charcoal, and sulfur, in proportions 75:15:10, without any milling or wet processing. The use of green powder in this composition, and in the glitter compositions discussed later, is not essential, and it may be replaced by its components or sometimes by commercial meal powder without substantially affecting the chemistry involved. However, it is convenient to discuss glitter chemistry by considering the green powder components collectively as an independent chemical entity.

A pyrotechnic flash powder, which is compatible with the golden streamer components, is shown as formulation 2 in Table 1. The observations discussed so far lead one to think that

one may be able to make glitter by replacing the additional charcoal content of the golden streamer composition with the flash powder, as shown in formulation 3. Remarkably enough, given the rather naive assumptions and the lack of more sophisticated formulation development, this composition does indeed produce quite good

glitter stars, of the short delay type known as "pearl".^[2]

So far the chemistry that may be involved in glitter reactions has not been considered, and for this we must turn to various glitter mechanism theories which pyrotechnists have proposed.

Table 1. Formulations.

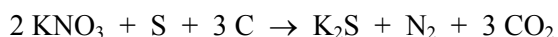
Ingredients	1	2	3	4	5	6	7	8	9	10	11	12	13
Green powder	65		65	75	65	64				65	70	65	65
Barium nitrate		55	11										
Sodium nitrate							50						
Rubidium nitrate								55					
Potassium perchlorate									48				
Sulfur	10		10		10		12	10	19			5	5
Charcoal (air float)	20						11	10	9				
Dextrin	5		5	5	5	5	4	5	4	5		5	5
Aluminum (atomized, 120–140 mesh)				10		9			7	10			
Aluminum (atomized, 325 mesh)											7		
Magnalium (20:80, 200 mesh)		10	2										
Magnalium (50:50, –60 mesh)		35	7		10		10	10				10	10
Titanium (20–40 mesh)						3							
Antimony sulfide (fine powder)				10	10	14	8	10		10			10
Strontium oxalate						5							
Barium sulfate										10			
Molybdenum sulfide											13		
Sodium oxalate							5				10		
Indium sulfide												15	
Sodium bicarbonate									13				5

Key to Formulations:

- | | |
|--|---|
| <ol style="list-style-type: none"> 1. Golden Streamer 2. Flash Powder compatible with Golden Streamer (better to use –200 mesh magnalium for flash powder) 3. Pearl Glitter (short delay) 4. Silver Glitter 5. Bright Silver Glitter (long delay) 6. Silver Glitter Fountain | <ol style="list-style-type: none"> 7. Sodium Nitrate Glitter (not very useful in practice) 8. Potassium-free Bright Silver Glitter (excellent but expensive) 9. Perchlorate Glitter 10. Silver Glitter (good) 11. Glitter Fountain (off-white color of glitter flashes is aesthetically displeasing) 12. Bright Silver Glitter (very expensive) 13. Vivid Yellow Glitter |
|--|---|

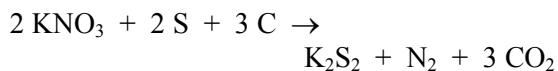
Lloyd Scott Oglesby: Potassium Sulfide Theory^[2,3]

The vast majority of glitter compositions contain potassium nitrate, charcoal, and sulfur, many of them in the proportions present in Black Powder or green powder. One may therefore reasonably suppose that the first chemistry to occur is the combustion of such materials. According to Partington,^[4] "The proportions of the constituents and the main products of combustion correspond roughly with the following equation:

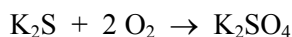
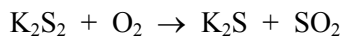


Carbon monoxide, however, is also evolved, and the residue contains potassium carbonate and sulfate." Note that the equation is only a first approximation to the combustion of gunpowder. However, glitter is substantially more complex than gunpowder, and so consideration of all the equations pertinent to the combustion of gunpowder may hinder rather than aid the understanding of glitter.

The pearl glitter composition, formulation 3, contains an excess of sulfur. This extra sulfur can participate in a slight modification of the gunpowder reaction to produce potassium disulfide:



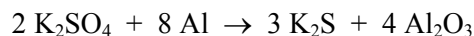
Oglesby describes reactions such as this, occurring in the reacting layer of a glitter star, as "on board reactions". Potassium disulfide has a melting point of 470 °C and is thus formed as liquid droplets that Oglesby calls "spritzeles". Accordingly, the subsequent set of reactions, occurring in these glitter droplets, can be called "spritzele reactions". Oglesby suggests a two stage oxidation of the spritzeles using atmospheric oxygen:



There is precedent for this sequence of reactions. These are the reactions that are thought to occur in high-sulfur golden streamer compositions, such as formulation 1, as well as in "senkohanabi".^[5] In such compositions the liquid po-

tassium disulfide forms a matrix in which the unreacted charcoal is suspended. These droplets of potassium disulfide together with charcoal are commonly referred to as "charcoal sparks". Not only does the charcoal gradually oxidize from atmospheric oxygen, but so does the potassium disulfide, first to potassium monosulfide and then to potassium sulfate. All of these reactions generate heat.

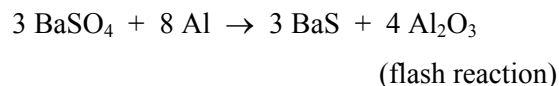
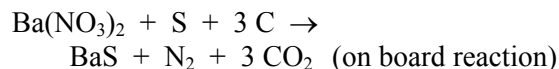
Meanwhile, what becomes of the aluminum, present in some form in almost all types of glitter? According to Oglesby the aluminum has remained chemically unchanged so far in the process and is present as a suspension in the spritzeles. Then as the potassium sulfate concentration increases, a critical point is reached when the glitter flash reaction occurs:



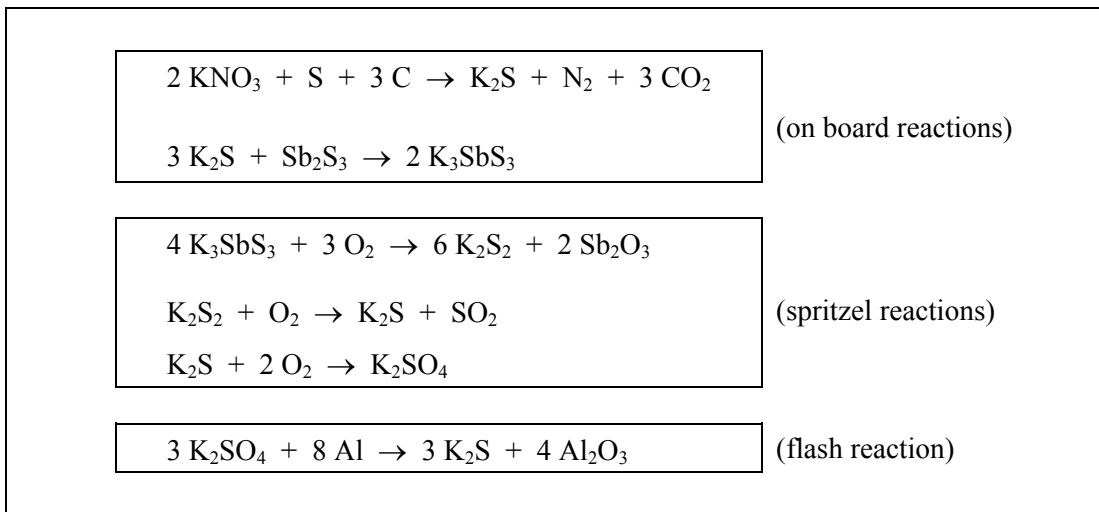
Again, there is precedent for such a reaction. Sulfates are known to function as oxidizers in pyrotechnic flash powders.^[6,7]

The set of four reactions depicted above form the core of Oglesby's theory of glitter chemistry. Yet they are not sufficient. The ingredients potassium nitrate, sulfur, charcoal, and aluminum alone do not produce an effective glitter composition. Something else is needed.

The glitter composition, formulation 3, contains barium nitrate, and this indeed suffices as an extra ingredient to make the glitter work. Oglesby suggests that barium nitrate undergoes a sequence of reactions analogous to those of potassium nitrate:



Why does this make a difference if the reactions are so similar? The difference is that potassium sulfate (m.p. 1069 °C) is a liquid at the spritzele temperature, whereas barium sulfate (m.p. 1580 °C) is a solid. If the flash reaction is initiated by a critical concentration of sulfate oxidizer present as a solution in potassium sulfide, then barium sulfate plays no part in *initiat-*



ing the flash reaction. There are two consequences of this. Firstly, barium sulfide takes up some of the oxygen available to the spritzel, and so the potassium sulfate concentration builds up more slowly. Consequently there will be a greater delay time until the initiation of the flash reaction. Secondly, the total amount of oxidizer available for the flash reaction is increased, resulting in a brighter flash.

Barium nitrate is neither the most common, nor the most effective glitter additive. That honor goes to antimony sulfide. Any theory of glitter must take into account the role of antimony sulfide.

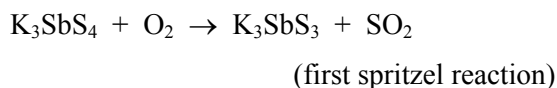
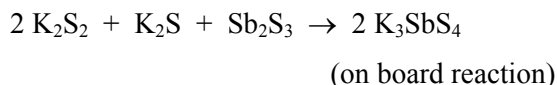
Spur fire, the characteristic composition used in the fountain called a flower pot, also frequently contains antimony sulfide.^[8] These fountains produce large and long-lasting spark droplets with much fire-branching, each droplet a senko-hanabi. When viewed at short range, the effect is incredibly beautiful.

Oglesby suggests the series of reactions (at the top of this page) when antimony sulfide is used in glitter.

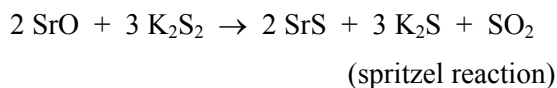
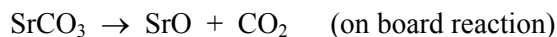
Notice that this mechanism does not require any extra sulfur, as reflected in formulation 4, and so the first step is the standard gunpowder reaction. There are two key steps resulting from the use of antimony sulfide. Firstly, the formation of potassium thioantimonite (K_3SbS_3). Secondly, the oxidative decomposition of this in the spritzel to produce potassium disulfide and antimony oxide (Sb_2O_3). The latter is a relatively volatile material and may be partially lost

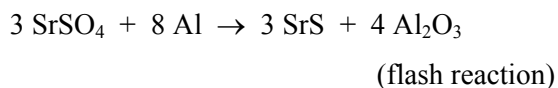
lost from the spritzel as it falls through the air. The more extensive sequence of spritzel reactions allows for a greater delay until the flash reaction.

One can go further and combine the use of additional sulfur together with antimony sulfide, such as in formulation 5. In this case the potassium sulfides can combine with antimony sulfide to form potassium thioantimonate (K_3SbS_4). Oxidative loss of sulfur in the spritzel can then give potassium thioantimonite, and the reactions proceed as before. The key parts of the sequence are depicted below:



As one might expect, the addition of yet another spritzel reaction to the sequence allows particularly long delays to be achieved. Formulation 6, for a glitter fountain based on Lancaster's white glitter star formulation,^[9] introduces yet another glitter additive, strontium oxalate. Oglesby suggests that such materials function in a way described by the following equations:





The initial decompositions of strontium oxalate consume heat, thereby slowing down concurrent reactions and adding to the delay, perhaps by allowing larger spritzel size. The melting point of strontium sulfate (1605 °C) is comparable to that of barium sulfate, and so there is a similar additional contribution to the delay and to the flash brightness.

Strontium oxalate is but one of a range of carbonates and oxalates with utility as glitter delay agents. (See Table 2.) Carbonates function in a similar way, as can be seen by their intermediacy in the oxalate reaction sequence.

Table 2. The Role of Carbonates and Oxalates.

	Oxalate	Carbonate	Bicarbonate
Barium	x	x	
Strontium	x	x	
Calcium	x	x	
Magnesium	x	x	
Lithium	x	x	
Sodium	x		x
Potassium	x		x
Antimony	x		

x = useful materials

Note that the postulated mechanism for the functioning of these materials requires the presence of potassium disulfide. Consequently, such glitter delay agents cannot function as such by themselves, but only in the presence of additional sulfur or antimony sulfide.

Note that formulation 6 retains dextrin even though it is for a dry fountain composition. Oglesby suggests that carbohydrates, such as dextrin, serve a function in glitter beyond that of binding, by furnishing water as a combustion product, which affects the spritzel viscosity and “enhances the formation of sulfides rather than carbonates in glitter mixtures”. Lancaster also concurs stating “Dextrin is quite useful in the right proportions and we actually put it in some

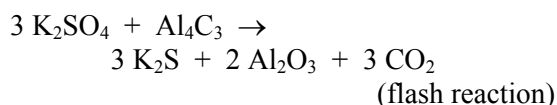
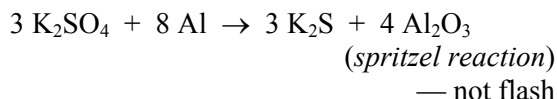
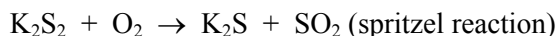
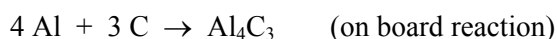
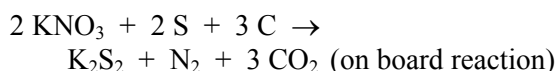
dry mixes, which it tends to make rather ‘bubbly’”.^[10]

Ferric oxide is a glitter additive that does not fall within the categories discussed so far. Oglesby suggests that it is reduced to iron and iron sulfides as on board reactions; then “The iron serves as a low energy fuel after the spritz [ejection of spritzels] and as a simple physical barrier to fluid motion in the spritzel.”

Oglesby’s theory is expounded in more depth in reference 2.

Myke Stanbridge: Aluminum Carbide Theory^[11]

This theory is analogous to Oglesby’s theory except for the key role proposed for aluminum carbide. The theory may be summarized by the following set of equations:



The easiest way to understand what is going on is to consider the differences between this and Oglesby’s theory. Firstly, a portion of the aluminum is postulated to be converted to aluminum carbide as an on board reaction. The remaining aluminum reacts with potassium sulfate as soon as the latter is formed in the spritzel flying through the air. Note that, for Stanbridge, Oglesby’s flash reaction is part of the delay mechanism. When all the aluminum is consumed, the concentration of potassium sulfate rises until criticality is reached, and the flash reaction proceeds with aluminum carbide as the fuel.

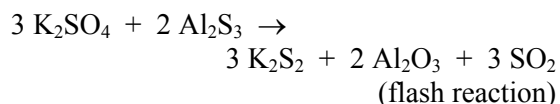
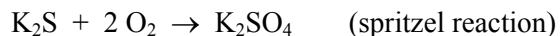
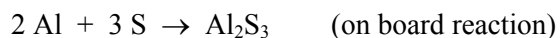
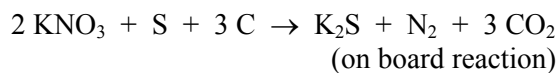
The reader is referred to the articles by Stanbridge for the more subtle points of the theory.

theory. There do not appear to be any major points of departure from Oglesby's theory other than those mentioned here.

Troy Fish: Aluminum Sulfide Theory^[12]

This theory is quite similar to that of Stanbridge with the critical difference of aluminum sulfide formation in place of aluminum carbide formation. A quote from Ellern exemplifies the principle behind this theory: "An extremely potent, but seemingly very little known, mixture is the one of flake aluminum and sulfur in approximately stoichiometric ratio of about one to two parts. It can be ignited with an ordinary match and reacts slowly with brilliant white glow, forming beads of aluminum sulfide".^[13] Under certain conditions the reaction can be quite violent.^[14] Stanbridge makes thermodynamic arguments that either aluminum carbide or aluminum sulfide, but not aluminum, could be the fuel in the flash reaction.

Fish does not describe the theory in detail and provides no equations. The author has therefore taken the liberty of interpreting the theory in the form of the equations that follow:

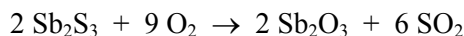


Fish makes use of this theory in formulating glitter compositions. The first two equations are taken to represent "base fires", which are then mixed with the other glitter components. The first equation simply represents green powder. The second equation represents the stoichiometric mixture of aluminum and sulfur. Fish actually uses a slight excess of sulfur in this second base fire, presumably to allow for some loss due to its volatility at high temperatures.

A key point of departure for this theory, compared with the others, is that the excess sulfur commonly present in glitter compositions is

not considered to react to form potassium disulfide. Aluminum sulfide is formed instead, with potassium monosulfide as the other sulfur-containing primary-reaction product. Note that each of the theories discussed so far proposes a different fuel for the flash reaction.

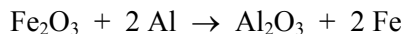
Fish considers the delay effect of antimony sulfide to be firstly physical, on account of its high latent heat of fusion. The process of melting absorbs heat, thereby retarding the on board reactions. Then in the spritzel the following delay reaction occurs:



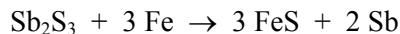
This reaction generates heat and retards potassium sulfate formation by virtue of its oxygen consumption.

Michael Swisher: Thermitic Theory^[15]

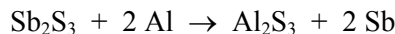
None of the theories presented so far provides a good explanation of the role of ferric oxide in certain glitter compositions. The most familiar combination of ferric oxide and aluminum is the thermitic reaction:



Swisher postulates this as the flash reaction in such glitter compositions. How does this idea relate to more common compositions that do not contain ferric oxide? The classic preparation of metallic antimony involves heating antimony sulfide with iron.^[16]

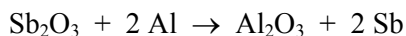


One may immediately recognize this as being closely analogous to the standard thermitic reaction. Thus, Swisher postulates a similar reaction with aluminum as the flash reaction for glitter compositions containing antimony sulfide:



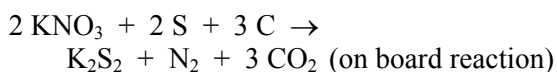
It is interesting to contrast the idea of aluminum sulfide being a product of the flash reaction with that of Troy Fish's theory, where aluminum sulfide is consumed in the flash reaction. Note that the suggestion of Fish that antimony sulfide is converted to the oxide prior to

the flash reaction is also consistent with the latter being thermitic in nature:

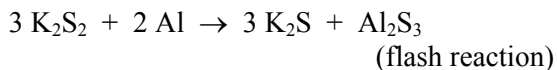


Takeo Shimizu: Polysulfide Reduction Theory^[17]

Shimizu concurs with the formation of potassium sulfides, as previously described:



However, for Shimizu these sulfides are the oxidizing agent for the flash reaction: "The bloom is produced by the reaction of the aluminum with the K_2S_x ."



Thus Shimizu is in agreement with Swisher in proposing that aluminum sulfide may be the product of the flash reaction, but at odds with Fish and Stanbridge who suggest that aluminum sulfide may be a fuel for the flash reaction. Oglesby suggests no role for aluminum sulfide in glitter chemistry.

Note that no specific spritzel reaction is key to the production of flash reactants in Shimizu's theory. Indeed Shimizu acknowledges that sulfur is lost from the potassium sulfides during the spritzel phase. Rather, the flash reaction is initiated upon reaching a critical temperature: "when small particles of molten residue pass through the air, they increase in temperature while being oxidized by atmospheric oxygen. If they achieve a sufficiently high temperature, then blooms are produced". Presumably, this feature is also common to Swisher's theory, in contrast to the other three theories all of which require a build up of critical concentration of potassium sulfate in order to initiate the flash reaction, though perhaps also via a temperature rise mechanism.

Experimental Observations

The different theories of glitter chemistry outlined in this paper were developed by the respective authors in response to their own ob-

servations and theoretical considerations. This constitutes the first two stages of the scientific process. The next step is to distinguish between the validity of different theories by means of experiments. Fortunately all the theories were couched in such a way as to allow testable predictions of changes in the behavior of glitter as a result of changes in compositions. (Theories that do not allow for testable predictions are not in the realm of science).

Experiments will not necessarily lead us to conclude that one of the theories is "correct". Some theories (notably Oglesby's) are so extensive that they may be found to be "partially correct". Also, the theories are not entirely mutually incompatible. Indeed there are common features shared between some of them. Finally it is possible that all of the theories could be shown to be incorrect, in which case we should all have to think again.

In general, the theories postulate the formation of certain transient chemical intermediates that are then destroyed in a later stage of the glitter process. Thus one cannot simply analyze combustion products to determine which path the reaction took. One can, with substantial difficulty, quench the glitter reaction at an intermediate stage, such as the spritzel, and analyze the mixture for the proposed intermediates.

Both Oglesby and Stanbridge provide some micro analytical data to support their theories but, as Oglesby points out, "Some of the sulfide melts studied were not stable for more than one half second after capture". Similarly, Shimizu states "It is difficult to establish the mechanism of the flash solely through chemical analysis". Ultimately the success of the theories must depend on their ability to predict the actual behavior of glitter compositions.

The author's glitter star tests used pumped stars of 7/16" diameter fired from 1/2" i.d. roman candles and observed visually.

1. The Necessity for Potassium

Several of the glitter theories postulate the formation of potassium sulfides, K_2S_x , as key intermediates in the process of glitter. Indeed, Oglesby states "Potassium sulfide is therefore a necessity from the theoretical view and has

been experimentally determined to be necessary".^[2] If this is strictly correct, one would predict that a composition devoid of potassium will not function as a glitter. One of the obvious ways to attempt a yellow glitter is to replace the potassium nitrate content of a white glitter with sodium nitrate. Sodium is the element directly above potassium in the periodic table and so the substitution is chemically analogous.

The author prepared a variety of star compositions consisting of sodium nitrate, sulfur, charcoal, antimony sulfide, aluminum, and dextrin. The results were invariably a bright yellow star with no sign of the glitter effect.

It is interesting to put oneself in the mind of a chemically oriented pyrotechnist one hundred years ago, when aluminum was being introduced as a firework material. Such a pyrotechnist might well have predicted the yellow illumination star described above, but surely would never have guessed what would happen with potassium nitrate as the oxidizer.

On the other hand Winokur has been able to devise a composition utilizing sodium nitrate as the sole oxidizer (formulation 7) which can function as a glitter under certain conditions.^[18] Following Winokur's suggestions the author confirmed that five grams of the composition burnt in a loose pile ejected numerous short delay flashes with excellent yellow color, along with a large yellow flame. In addition Winokur exactly described the burning behavior of the composition pressed in an unchoked 1/2" i.d. tube as starting with an excellent yellow glitter, shortly degenerating into a yellow flame. The composition does not function as a glitter when used for stars. Despite its lack of much practical utility, this composition is of theoretical importance for it shows that the glitter effect can take place without any potassium salts, albeit under very limited circumstances.

It would appear then that the complete replacement of potassium with sodium does allow a glitter to function, but only marginally so. Oglesby is explicit about what is required of potassium: "Potassium sulfide melts below the melting point of potassium sulfate and that is what it takes to make glitter". The melting points are 840 °C for potassium sulfide and 1069 °C for potassium sulfate. By contrast the

melting points of sodium sulfide and sodium sulfate are 1180 and 884 °C, respectively, in the reverse order from the potassium salts. Thus Oglesby's theory predicts that sodium nitrate cannot function as a replacement for potassium nitrate in most glitter compositions.

The element most closely related to potassium in the opposite direction from sodium is rubidium, situated directly beneath potassium in the periodic table. The author prepared potassium-free compositions utilizing rubidium nitrate as the oxidizer, such as formulation 8. In contrast to the experience with sodium nitrate, the rubidium nitrate composition produced truly excellent glitter stars. The requirement for potassium is unambiguously disproved. However, before completely rejecting the theory, one should note that the melting point of rubidium sulfide is 530 °C, compared with 1060 °C for the sulfate. Thus the success of rubidium as a replacement for potassium is actually in accord with the predictions of Oglesby's theory. Rubidium glitters have no discernable color imparted to the glitter flashes. The element below rubidium in the periodic table is cesium. The author found that cesium nitrate can also function as the sole oxidizer in a glitter composition, in this case producing a particularly impressive terminal delay (the final large droplet produced by a burning glitter star resulting in a particularly large and delayed flash^[19]).

2. The Necessity for Sulfur

The potassium sulfide intermediates require not only the presence of potassium (or other alkali metal) but also the presence of sulfur. The prediction is that one cannot make a glitter composition devoid of sulfur. Winokur has succeeded in making a good glitter composition devoid of elemental sulfur,^[19] but it contains antimony sulfide and it is quite reasonable to assume that potassium sulfides may still be formed in this circumstance.

If one adopts the same approach of chemical analogy taken for potassium, then one should examine the elements directly above and below the sulfur in the periodic table, namely oxygen and selenium. Oxygen, of course, is already present in the glitter composition, as a component of potassium nitrate, as well as in the sur-

rounding air as the element. Consequently the expedient of removing sulfur, in both elemental and combined form, from a glitter composition should allow the production of potassium oxides, K_2O and K_2O_2 , in place of the corresponding sulfides. To the author's knowledge no-one has succeeded in producing a glitter in the absence of sulfur although Winokur has specifically attempted such a feat.^[19]

The use of selenium in a glitter composition has also been tested by Winokur and found to be ineffective.^[19] Thus it would appear that glitter compositions have a requirement for sulfur.

3. The Necessity for Nitrate

Almost all published glitter formulations use potassium nitrate as the principal oxidizer. The necessity for potassium was examined above. Another question is the necessity for a nitrate oxidizer. Von Baum has discussed glitter compositions containing potassium perchlorate as the sole oxidizer,^[20] such as his "A1" shown in Table 1 as formulation 9 with amounts rounded to the nearest percent. This composition, pressed into a lance tube, as suggested by von Baum, or into an unchoked 1/2" i.d. tube, does indeed produce a very beautiful effect with the appearance of being a true glitter, albeit quite distinctive.

It is generally considered that the byproduct of using potassium perchlorate as an oxidizer is potassium chloride. This would be inconsistent with most of the proposed glitter theories. However, one cannot rule out the possibility that in a high-sulfur composition, such as this, sufficient potassium sulfide is generated so as to allow any of the proposed glitter mechanisms.

Von Baum notes that both charcoal and sulfur are necessary in these compositions, with antimony sulfide being ineffective as a substitute for sulfur.^[20] Also, magnalium cannot substitute for aluminum, and ammonium perchlorate cannot substitute for potassium perchlorate. While none of the current glitter theories can fully explain these observations, none of them can be eliminated on this basis.

4. The Necessity for Aluminum

The glitter theories all postulate a key role for aluminum, but the role is different for each of the theories. If it were possible to replace aluminum with a different element then, depending on the element, some, but not all, theories may be able to explain the observation. Following the same rationale as before, the elements above and below aluminum in the periodic table are boron and gallium, respectively.

The addition of even small percentages of boron to a glitter composition destroys the glitter effect.^[21] Gallium inconveniently melts on a warm day (30 °C, 86 °F), but this could be circumvented by the use of an alloy such as gallium antimonide. The author is unaware of any glitter experiments with these materials. Next below gallium in the periodic table is indium, which the author has found to be an ineffective substitute for aluminum in glitter compositions.^[22]

In addition to the kinship among elements of the same column in the periodic table, there also exists the so-called "diagonal relationship", particularly within the first two rows. The element so related to aluminum is beryllium. Feher has tested beryllium in a glitter composition, in place of aluminum, and found it to be quite effective.^[23] Thus aluminum is not an essential component of a glitter composition. The chemistry of beryllium is quite similar to that of aluminum, including the existence of an analogous carbide, Be_2C . The observation of an effective beryllium glitter is therefore consistent with the Stanbridge theory. However, there also exists an analogous sulfide consistent with the Fish theory. The electronegativity of beryllium is virtually identical to that of aluminum, and so it should serve as a fuel in the flash reaction, consistent with any of the theories which postulate aluminum in such a role. Thus the interesting observation of a functioning beryllium glitter sheds no light on the relative viability of the different theories of glitter. However, note that beryllium is extraordinarily toxic. Its use in fireworks should be limited to research by those with the requisite experience.

The theory of Stanbridge allows for the possibility of using manganese in place of aluminum in a glitter composition, on account of the fa-

avorable thermodynamic properties of manganese carbide.^[11] The author has tested manganese as a replacement for aluminum in glitter compositions without success. Although these experiments bear unfavorably on the prediction of manganese as a potential glitter material, they should not be interpreted too strongly as evidence against the Stanbridge carbide theory in general.

Stanbridge also suggests that aluminum carbide may be used as a component in glitter compositions. However, the present author's experiments along the lines recommended resulted in no glitter flashes at all. In addition, aluminum carbide was tested by the author as the sole aluminum source in glitter compositions for fountains. Only orange sparks with no trace of glitter effect were observed. This result is consistent with all of the glitter theories including that of Stanbridge.

Aluminum may be present in alloyed form, for example with magnesium, iron, or cobalt.^[19,24,25] By contrast certain other alloys of aluminum, for example with zinc or zirconium, have not been found to function in glitter compositions.^[2,22] Alloys with copper and nickel appear to be marginal cases of little use for glitter.^[19] A comprehensive theory explaining why certain alloys of aluminum are effective, while others are not, has yet to be proposed.

5. The Role of Barium Salts

Only Oglesby has provided a detailed explanation of the mechanism by which barium salts benefit a glitter composition. Regardless of whether the glitter additive is barium carbonate, barium nitrate, or barium oxalate, delay reactions are proposed leading eventually to barium sulfate. The barium sulfate then acts as a co-oxidizer in the flash reaction, enhancing the brightness of the flash.

This theory is capable of making specific predictions. For example if barium sulfate itself were to be used as a glitter additive there should be no delay reactions associated with it, and the delay should therefore not be increased. However, it should still participate in the flash reaction, enhancing its brightness. These predictions were tested by the author using formulations such as number 10 in Table 1. It was

found that the flash brightness was indeed enhanced relative to the composition without any barium salt. Moreover, the delay was not increased, unlike the behavior when other barium salts are used. The theoretical predictions were exactly born out, in confirmation of Oglesby's theory. The barium sulfate composition is excellent in fact, and recommended for practical use.

6. The Role of Antimony Sulfide

Oglesby gives antimony sulfide a special role in its reaction with potassium sulfides to give potassium thioantimonate as a spritzel intermediate. In searching for analogous materials the author came across potassium thiomolybdate, which could be formed from potassium disulfide and molybdenum sulfide as below:



Thus, in principle, Oglesby's theory predicts that molybdenum sulfide could be used in place of antimony sulfide in glitter compositions. Most glitter additives are effective only when additional sulfur is present such that potassium disulfide could be formed. Antimony sulfide is unique in requiring no additional sulfur, producing potassium thioantimonite in this case. Thus a more stringent test of the ability of molybdenum sulfide to replace antimony sulfide would be in a composition that contains no additional sulfur. Formulation 11 was tested in a 5/8" fountain by the author and found to produce an excellent off-white glitter. Oglesby's theory is again vindicated since it can specifically accommodate the function of molybdenum sulfide as a glitter additive. By contrast, the proposal of Troy Fish that antimony sulfide functions as a heat sink by virtue of its low melting point (550 °C) is inconsistent with the success of molybdenum sulfide whose melting point of 1185 °C is much higher. Thus it seems that antimony sulfide plays a chemical role rather than a physical role in glitter.

The author also tested indium sulfide in glitters. The lack of stable potassium thio-salts of indium leads Oglesby's theory to predict that this material cannot be used as a replacement for antimony sulfide. In fact good glitters such as formulation 12 can be made using indium

sulfide, although the glitter flashes have absolutely no hint of the potential blue coloration from indium emissions. This composition is a vast improvement on simple mixtures of green powder, magnalium, sulfur and dextrin. However, three similar experiments in which the indium sulfide was not accompanied in the composition by additional sulfur resulted in no glitter effect whatsoever. This is exactly as predicted by Oglesby's theory: regardless of the presence of other glitter additives, a necessary requirement for a good glitter is that the composition contains either additional sulfur to allow for the formation of potassium disulfide, or else a material such as antimony sulfide or molybdenum sulfide that allows the formation of a stable potassium thio-salt.

Winokur tested the sulfides of arsenic, mercury, lead, bismuth, barium, copper, and iron.^[19] It is clear from the published descriptions that none of these can function as effectively as molybdenum sulfide. Thus the particular function proposed for antimony sulfide by Oglesby is supported by the specificity of what can be used as a replacement.

7. Tests of Swisher's Thermite Theory

In order for a thermite reaction to take place, the glitter composition must contain a compound of a metal whose electronegativity is greater than that of aluminum. While this condition is met by many glitter compositions, it is not met by all. Consequently the thermite theory is not a candidate for the explanation of all kinds of glitter compositions. However, the thermite mechanism may still operate in specific cases. Note, in particular, that the other theories do not provide a satisfactory explanation for the function of ferric oxide.

Swisher suggests that antimony sulfide may take part in a thermite reaction with aluminum. The author tested the stoichiometric mixture of antimony sulfide and 30 micron atomized aluminum. Five grams of this mixture, pressed in a 1/2" i.d. tube, was hard to light but could be initiated with a standard ferric oxide thermite mixture. The light output was very weak and the mixture was slow burning. A regulus of antimony remained. Although it must be admitted that the result bore little resemblance to a glitter

flash reaction, it should be remembered that the conditions experienced by a spritzel flying through the air are rather different from those pertaining to this experiment. Moreover, the proposal of Troy Fish that antimony sulfide may be converted to antimony oxide in the spritzel would allow for a more energetic thermite reaction.

A specific prediction of the thermite theory is that other oxides and sulfides capable of a thermite reaction with aluminum should be useful glitter additives. Chromic oxide (Cr_2O_3) is another material known to undergo thermite reaction with aluminum and Swisher reports making excellent glitters using it.^[15] The author has found that bismuth subnitrate is a useful glitter additive, and this too can engender a thermite reaction after initial decomposition to bismuth oxide (Bi_2O_3). The effectiveness of molybdenum sulfide is also consistent with the thermite theory.

In contrast with these experiments, Winokur has reported using manganese dioxide (MnO_2) and lead oxide (Pb_3O_4),^[19] both known to undergo thermite reaction with aluminum,^[13] and found them to be useless. Thus the evidence regarding the thermite theory of glitter is mixed at this point.

8. What Is the Fuel in the Flash Reaction?

Three of the theories of glitter postulate that the aluminum component of a glitter composition constitutes the fuel for the flash reaction. The other two theories postulate that the aluminum undergoes a chemical reaction prior to the flash reaction. The two different postulates give rise to two different predictions as to the way the nature of the glitter flash depends on the nature of the aluminum used in the glitter composition. Specifically, if aluminum is the fuel in the flash reaction, then the particle size and alloying of the aluminum component could markedly affect the flash reaction. Conversely, if the aluminum undergoes chemical reaction prior to the flash reaction, the information about its original form should be lost, and the nature of the flash reaction should be relatively constant in regards to this variable. Note, however, that all theories allow for the possibility of excess coarse aluminum being flung burning from the

the glitter flash, thus excluding such effects from distinguishing between the theories.

A flash parameter that can be used for comparison between compositions is the color of the flash when a sodium salt is used as a glitter additive. The author visually compared the colors produced by using aluminum (atomized, 120–140 mesh), aluminum (atomized, 325 mesh), ferro-aluminum (35:65, –60 mesh), cobalt-aluminum (31:69, –100 mesh), and magnalium (50:50, –60 mesh). The aluminum carbide and aluminum sulfide theories predict that the flash color should be essentially invariant. The other theories allow for the possibility that the flash color may vary between the different compositions.

The results of the experiments are as follows. With the coarser aluminum, ferro-aluminum or cobalt-aluminum alloys, only pure white flashes were produced despite the presence of the sodium salt. The finer aluminum produced pale yellow glitter flashes and the magnalium produced vivid yellow glitter flashes. Similar observations have also been reported by Winkur.^[19]

The results are consistent with the theories of Oglesby, Shimizu, and Swisher, but are poorly accounted for by the aluminum carbide and aluminum sulfide theories.

It should be possible to reproduce a flash reaction by mixing the postulated chemicals involved and determining the behavior upon ignition. Both Oglesby and Shimizu state that a mixture of potassium sulfate and aluminum does not ignite to produce a simulation of a glitter flash. Stanbridge goes further, implying that this reaction can be ruled out on theoretical thermodynamic grounds.

In contrast to the opinion of these several pyrotechnists, a 50:50 mixture of potassium sulfate and aluminum (2 μ), when heated in a deflagrating spoon with a Bunsen burner, does indeed produce a very convincing and vigorous flash reaction accompanied by a moderate explosion.^[26] This reaction is clearly a viable candidate for the glitter flash mechanism. The additional presence of sulfides, as suggested by Oglesby, is not a necessary condition for the occurrence of the flash reaction.

This experiment negates the supposed “disproofs” of Oglesby’s theory by Stanbridge and Shimizu. However, the author found that a similar mixture of potassium sulfate and aluminum carbide also undergoes a flash reaction upon heating, albeit less bright and less vigorous than with aluminum. The residue produces hydrogen sulfide upon dampening, thereby demonstrating the oxidative role of potassium sulfate in the reaction. Thus both aluminum and aluminum carbide are capable of acting as fuel in combination with potassium sulfate.

Stanbridge postulates a role for aluminum as a fuel in the delay mechanism as opposed to the flash reaction. Thus his theory predicts that not only will a simple mixture of green powder and aluminum produce glitter, but that the glitter delay should increase with the amount of aluminum in the composition. None of the other theories predicts this relationship between the amount of aluminum and the glitter delay. Consequently an experiment to measure the length of glitter delay as a function of aluminum content can unambiguously determine the viability of Stanbridge’s theory relative to the other theories.

Such an experiment has been performed by photographing stationary glitter stars in a wind tunnel and measuring the number of glitter flashes within one foot increments of the glitter star.^[27] The compositions used were made according to a standard gold glitter formulation,^[28] with the aluminum content being 5, 7 or 10%. The result was that the glitter delay *decreased* as the amount of aluminum was increased. This effect is the opposite of that predicted by Stanbridge’s aluminum carbide theory, but is consistent with the other four glitter theories. Moreover, Oglesby provides an explanation for the observed relationship: “When a glitter formula is overloaded with aluminum, the spritzels produced will have insufficient sulfide melt material to cover and chemically isolate the aluminum from air ... A thin layer of potassium sulfide on aluminum is insufficient to cause delay.” Oglesby’s explanation is also consistent with the observation that decreasing the aluminum particle size causes a decrease in the glitter delay.^[27, 29]

9. Physical Observations

Presumably in referring to Shimizu's theory, Stanbridge states "Reactions based only on K_2S_x are too slow to meet the observed duration of the glitter flash..."^[11] However, Stanbridge's postulated glitter flash duration of one millisecond may be as much as an order of magnitude shorter than flash durations determined experimentally.^[27] Certain glitter flashes, such as those from some compositions utilizing bismuth subnitrate as a glitter additive, have the appearance of being very much longer in duration. Thus, the argument against Shimizu's theory based on flash duration may be erroneous.

The theories of both Shimizu and Swisher require, and predict, that there must be an increase in spritzel temperature prior to the flash in order to trigger the flash reaction. The other theories rely on an increase in potassium sulfate concentration to trigger the flash reaction. Experimental studies indeed suggest that the light intensity of the spritzel, and thus its temperature, rapidly increases just prior to the flash.^[27] This result is as predicted by Shimizu and Swisher. However, it does not count against the other theories for, while not being a requirement, the observation is nonetheless consistent with them.

Discussion

There is as yet no universally agreed upon chemical mechanism that explains the pyrotechnic phenomenon of glitter. However, the five theories discussed here all agree upon a certain basic sequence of events. "On board" reactions produce some chemical intermediates. These chemical intermediates are modified as the spritzels fall through the air. Finally, there is a flash reaction involving the oxidation of an energetic fuel.

The experimental evidence is not yet sufficient to reach a definitive verdict regarding the validity of the various theories of glitter. However, the evidence so far would appear to be strongly supportive of Oglesby's theory. The aluminum carbide and aluminum sulfide theories are less consistent with the experimental observations.

No doubt further experiments will gradually shed more light on the chemistry of glitter. However, the practical control of glitter delay is already well understood.

Regardless of the theoretical considerations, the basis of glitter may be considered to be the combination of green powder (or equivalents), aluminum (including certain alloys), and delay agents. The practical mastery of glitter centers around the choice of delay agent, which falls into one of three categories: firstly, antimony sulfide as the sole delay agent; secondly, the combination of sulfur with another delay agent, most commonly a carbonate, an oxalate, barium nitrate, or ferric oxide; finally, the combination of antimony sulfide with any other delay agent(s). Only the theories of Fish and Shimizu unambiguously predict that the simple mixture of green powder and aluminum will not produce glitter. Moreover they specifically require the presence of either additional sulfur or antimony sulfide, allowing for the possibility that Swisher's thermitic flash reaction with antimony sulfide could be an "on board" reaction in the Fish scheme. Besides these chemical delay agents, one can also make use of the minor contribution of physical delays. These are primarily poor incorporation, by use of green powder in place of commercial meal powder, and increased metal particle size.

Colored Glitter

An exciting prospect for the future is the production of various colored glitters, a feat which, with the sole exception of yellow, remains tantalizingly out of reach. Shimizu has tested the combination of Parlon® with barium carbonate and copper carbonate glitter additives without success.^[17] The author has tested the addition of chlorine donors to glitter compositions containing barium nitrate or strontium nitrate, as well as the use of a number of glitter additives that may be thought to have the potential of imparting color (Table 3). None of these experiments led to a clearly colored glitter flash.

Table 3. Materials Not Yet Found To Produce Colored Glitter.

Name	Formula
Lithium carbonate	Li ₂ CO ₃
Lithium oxalate	Li ₂ C ₂ O ₄
Rubidium nitrate	RbNO ₃
Cesium nitrate	CsNO ₃
Calcium carbonate	CaCO ₃
Strontium nitrate	Sr(NO ₃) ₂
Barium nitrate	Ba(NO ₃) ₂
Boron	B
Indium metal	In
Indium carbonate	In ₂ CO ₃
Indium sulfide	In ₂ S ₃
Thallium nitrate	TlNO ₃

If the perchlorate glitters of von Baum do indeed proceed via the intermediacy of potassium sulfide, then there must necessarily be some available chlorine and they are thus potential candidates for producing colored glitter.^[20] However, von Baum notes that the use of strontium carbonate in such formulations does not produce colored glitter flashes.^[20] The author has found that the substitution of lithium oxalate for sodium bicarbonate in this system does not produce a glitter.

Both Winokur and Oglesby claim to have made pink glitter, using strontium salts or lithium salts, respectively.^[2,19] The author has tested such compositions in front of audiences psychologically prepared in two different ways. One group was specifically asked ahead of time to look for the pink glitter flashes. The other group was told nothing about the purpose of the experiment. After the glitters had performed (in roman candles), some, but not all, of the first group reported that they had seen that the glitter flashes were pink. Members of the second group were asked what was the color of the glitter flashes. None reported that they were pink and were by no means easily convinced by the suggestion that perhaps they might have been pink. Clearly the subjective experience of the pink color is influenced by the pre-bias of the observer (a well known psychological phenomenon). In other words, it is not beyond possibility for the eager experimenter to delude themselves as to the success of their experi-

ment. A colored glitter should not count as a colored glitter unless it is clearly recognized as such by an unbiased audience.

The most successful colored glitter is the yellow produced by the combination of magnalium with sodium bicarbonate as in formulation 13 adapted from Winokur.^[19] If one proceeds from analogy with this, then the most likely candidate for the production of a different color is the combination of magnalium with lithium carbonate. However, so far such compositions produce only white.^[21] Perhaps the problem is simply the quantity of lithium, which constitutes only 19% of lithium carbonate. One solution may be to load up the lithium content of the composition, in the form of lithium-aluminum alloy suggested by Winokur: "It is possible that alloys containing lithium or strontium could be used to produce pink or red glitter. The high cost of such alloys makes it doubtful that such material could ever become commonly used in commercial items."^[19] On the other hand, Partington states "Lithium burns when heated in air above its melting point, with a *white* flame..." (Author's italics).^[4]

The author was able to obtain some lithium-aluminum alloy (20:80, LiAl, 40 to 200 mesh) for testing in glitter compositions. The first test of water compatibility resulted in an extremely violent reaction, although not resulting in ignition. Consequently no attempt was made to prepare glitter stars with this material and only fountains were tested. Mixtures (20 g) with various glitter additives and 5 or 10% of lithium-aluminum alloy were prepared and pressed into a 5/8" tube with a clay choke of a type that works well in standard glitter fountains. One exception to this was for the composition that contained a combination of 10% bismuth subnitrate and 10% antimony sulfide as the glitter additives. In this case, when the lithium-aluminum alloy was added to the other premixed dry components, a substantial exotherm ensued with concomitant emission of hydrogen sulfide. Although ignition did not occur, the author was not comfortable with the safety aspects of pressing this composition in a tube, and the test was performed by ignition of the loose powder. This large exotherm did not occur with the compositions containing the combination of bismuth

subnitrate and sulfur or the combination of lithium carbonate and antimony sulfide.

In all cases the result of the test was the production of white sparks with no delayed glitter flashes and no observable pink coloration. In one case, when the glitter additive combination of lithium carbonate and sulfur was used, there appeared to be a slight increase in brightness of the sparks towards the end of their trajectories. The compositions containing 10% each of lithium carbonate and lithium-aluminum alloy have a total lithium content of 4%, apparently insufficient for coloration if insufficiency is the problem. However, it would appear unwise to increase further the lithium content of the lithium-aluminum alloy as the 20% material reported here is already dangerously reactive and disabling of the glitter mechanism.

Safety Considerations

Two kinds of safety considerations pertain to fireworks in general: toxicity and accidental ignition. The most commonly cited toxicity issue for glitter compositions concerns the use of antimony sulfide. For example, Troy Fish asks "Is this poison necessary?"^[12] However, Fish provides no data in support of his hypothesis that antimony sulfide may be unduly toxic, and the toxicological literature suggests to the contrary: "The fact that two men, one employed for one year, where the air concentrations at their highest were 52 mg/m³ showed no ill-effects, suggested that the trisulfide has a low toxicity".^[30] Such low toxicity is entirely in accord with its low solubility of 0.000175 g/100 cm³.^[31] The assertion that antimony sulfide is particularly toxic would appear to have no basis in fact, and perhaps came about due to erroneous comparison with other more soluble antimony compounds that are indeed very poisonous. Oglesby correctly points out that other antimony compounds tested for use in glitter compositions are much more poisonous than the sulfide. Of more concern might be acute poisoning by ingestion of sodium oxalate.

Besides the safety considerations common to dealing with any pyrotechnic composition, glitter compositions are renowned for their potential for an exothermic reaction upon dampening

with water. This is reasonable since all glitter compositions contain an active metal, in the form of aluminum or an alloy of aluminum.

The most common problem stems from the use of fine flake aluminum which can undergo an alkaline decomposition with a nitrate in the presence of water. This may be avoided by the addition of a boric acid buffer, or simply by the use of atomized aluminum. In addition, certain combinations of glitter additives with aluminum or magnalium must be avoided. These are listed in Table 4. The pattern of unwanted reactivity is in accord with chemical expectations; note that the pH of saturated lithium carbonate solution is 11 (strongly alkaline), whereas that of saturated lithium oxalate is 7 (neutral). Thus, aluminum, which is sensitive to alkaline conditions, can not be used with lithium carbonate, and lithium oxalate should be used instead. It is interesting that Troy Fish has stated that lithium carbonate is not effective in glitter.^[12] This is certainly not the case when magnalium is being used in combination with lithium carbonate.^[21] Presumably, the problem with aluminum is the decomposition upon dampening, rather than any inherent deficiency of lithium carbonate. Shimizu has reported that magnalium is actively attacked by wet sodium oxalate,^[32] and this is also true for lithium oxalate^[21] and antimony oxalate (the latter suggested for use with aluminum by Kosanke^[33]). In these cases it is safer to use as alternatives more alkaline materials such as lithium carbonate or sodium bicarbonate, which do not cause such decomposition with magnalium.^[32]

Table 4. Adverse Reactivities of Metals with Glitter Additives in an Aqueous Environment.

Ingredient	Aluminum	Magnalium
Lithium carbonate	x	
Sodium carbonate	x	
Lithium oxalate		x
Sodium oxalate		x
Antimony oxalate		x

x = unwanted reaction upon dampening.

Curiously, Lancaster has stated “One last point on glitter mixes: when using finely-powdered magnalium be very careful to add boric acid, or else the mix can heat up (on damping)...”^[10] Such advice flies in the face of both theory and experiment. Magnalium (unlike aluminum) is more reactive under acidic conditions than under alkaline conditions, and thus theoretically should have such reactivity exacerbated rather than alleviated by the addition of boric acid. The relevant published experiments support this theoretical prediction.^[32,34] The combination of boric acid with magnalium should be considered hazardous and best avoided. Indeed, Lancaster may have changed his opinion on this issue for recently he has stated: “Magnalium is attacked by weak acids (e.g., boric acid)”^[35]

This controversy, like the glitter flash discussion, highlights an important principle of science, stated here in the words of two great scientists: Richard Feynman (Nobel laureate in Physics) “Science is the belief in the ignorance of experts”^[36] and Carl Sagan (Astronomer extraordinary) “One of the great commandments of science is mistrust arguments from authority”^[37] The author hopes that the arguments presented in this article will also be treated with the skepticism they deserve.

Acknowledgments

The author would like to acknowledge Troy Fish, Lloyd Scott Oglesby, Takeo Shimizu, Myke Stanbridge, and Michael Swisher for their contributions to the theory of glitter chemistry. Particular thanks go to Lloyd Scott Oglesby and Michael Swisher for their time and energy discussing their theories with the author. Of necessity some theories fared better than others under the light of experimental scrutiny. It should be remembered that in science there are no “losers”; the invention of erroneous hypotheses is an essential feature of the scientific method.

Some of the glitter theories are not explicit in every detail. Consequently the author may have made errors of interpretation and, in taking responsibility for these, remains open for correction. In addition to the pyrotechnists men-

tioned above, the experimental contributions of Robert Winokur are particularly noteworthy.

Thanks go to Ken Kosanke, Robert Winokur and Dan Dolata for their helpful suggestions in the preparation of this article.

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(2/98)

Events Calendar

(Continued from page 18)

Pyrotechnics (cont.)

26th International Pyrotechnics Seminar

Oct. 1–4, 1999, Nanjing, China

Contact: Allan J. Tulis, Seminar Chairman

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Phone: 410-532-3260

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Nov. 16–19, 1998, San Diego, CA USA

Contact: ADPA/NSIA

Phone: 703-247-2582

FAX: 703-522-1885

e-mail: slevin@ndia.org

Web site: www.adpansia.org/events

ISEE 25th Annual Conference on Explosives & Blasting Technique

Feb. 7–10, 1999, Nashville, TN, USA

Contact: Int'l Soc. Explosive Engineers

Phone: 440-349-4004

17th Symposium on Explosives & Pyrotechnics

Apr. 27–29, 1999, Essington, PA, USA

Contact: Franklin Applied Physics, Inc.

Phone: 640-666-6645

FAX: 640-666-0173

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January 20–21, 1999, Helidon, 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

10th Western Winter Blast

Feb. 12–14, 1999, Lake Havasu, AZ USA

Contact: Steve Rhodes

Phone: 906-685-2968

e-mail: remains4u@aol.com

Web site: wpa.pyrotechnics.org

Pyrotechnics Guild International Conv.

Aug. 8–13, 1999, Fargo, ND USA

Contact: Erv Haman, Chairman

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Becker, MN 55308

Phone: (612) 261-2793

FAX: (612) 261-2795

e-mail: (not available yet)

Web site: www.pgi.org

High Power Rocketry

LDRS XVIII

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e-mail: johnb@southwind.net

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Name of Event

Dates and Place of Event

Contact information — including, if possible, name of contact person, address, telephone and fax numbers, e-mail address and web site information.

Communications

Brief technical articles, comments on prior articles and book reviews

Review of "Pollution Caused by Fireworks"

by Doris Gnauck White,
American Environmental Laboratory,
Int'l Scientific Communications, Shelton, CT, USA,
Oct. 1996, pp 22-26.

C. P. Weeth

122 S. 17th St., La Crosse, WI 54601-4208, USA

"Pollution Caused by Fireworks" appeared as the feature article for the October 1996 issue of *American Environmental Laboratory*. Given the importance of the topic to the pyrotechnic community, the article certainly deserves some mention in the literature.

There is no question that fireworks, like every other human endeavor, cause some pollution. The issue though is not whether fireworks cause pollution but: "How much pollution?" "How serious is that pollution?" and "Is this pollution over a short-term, long-term or both?" Once these questions are answered the next step is to determine what can be done about the pollution.

There are also significant differences in looking at the pollution issues from the production of the raw materials, the actual manufacturing and assembly processes, where workers are regularly exposed to dusts and vapors, and the ultimate use. Each of these in turn must be analyzed, based on the environmental conditions in which these activities take place as well.

The author of this article, Doris G. White, is a Professor of Curriculum and Instruction, Science Education at William Patterson College in Wayne, New Jersey, USA. One expects it to meet the minimum standards for a scientific or academic report and hopefully provide some useful information that helps answer the perennial questions above. Instead, the paper starts out with sweeping generalizations such as "Fireworks constitute a serious international

environmental problem that needs to be confronted" and "a major cause of worldwide pollution is fireworks". Prof. White provides no comparisons to "industry and/or agriculture", which she believes "are routinely blamed for the pollution", and fails to even estimate the type, the amount, much less the seriousness of pollution she alleges is caused by fireworks.

According to Prof. White, "Pollution is caused by light, sound, heat, and chemicals", a declaration that is so all encompassing, it is absurd. To classify fireworks effects and their sources as "pollution" totally misses the point why people use them in the first place. It is also a general condemnation of every living endeavor and natural phenomenon.

Prof. White believes that "Since many theme parks explode fireworks nightly, and since fireworks are used for celebrations throughout the world, the public should be informed of their hazards and of the precautions that can be taken to prevent harm". She does not provide any precautions that could be taken or describe how the public could be informed.

This paper is essentially a list of 53 chemicals and substances used, as she says to "concoct" fireworks, and covers aluminum to gunpowder to starch to zinc. Curiously clay is included on the list but paper and cardboard, two of the most common and voluminous components of fireworks are not. She notes in short, choppy sentences some of the appearance, solubility, and history of many of these chemicals while in others she has bits on how the chemicals are made or their places of origin. Some explain the problems of certain combinations, or the handling or processing risks, but not much else. Only a few explain why or how they are (or were used) in fireworks, and none provide any description of the resulting "pollution" once these chemicals are consumed when the fireworks function.

Many of the chemicals on the list are not commonly used in modern fireworks, such as Paris green. Others were rarely, if ever, used

such as Nitroglycerin. Her list is little more than a random collection of notes of unknown origin that do little to support the main premise of the essay.

Prof. White makes no attempt to verify her feeling that "It is distressing to learn that PVC is used in fireworks, because of the fear of dioxins resulting from the burning of PVC". There is nothing in this article that compares the quantities of these chemicals used in fireworks to the same chemicals used by individuals, agriculture or industry, so the scope of the pollution is in any perspective.

Her assertion that "pollution caused by fireworks should not be blamed on industry or agriculture" falls far short of reality. The total quantity of fireworks used in the USA in 1996, which includes a substantial amount of inert organic material such as paper, cardboard, clay, rice hulls, and so forth, was about 118 million pounds.^[1, 2] This is in comparison to individuals, agriculture and industry using billions and billions of *tons* of the same materials, meaning fireworks constitutes only a very tiny part of the overall pollution problem.

There has been little scientific research into the issue of pollution caused by fireworks, something that most certainly needs to be addressed. This is especially important for workers in manufacturing facilities that are routinely exposed to the chemicals that go into fireworks, even though these chemicals generally have low toxicity levels.

One specific study of fireworks use analyzed water samples collected over a 10-year period from a virtually fixed lake at a theme park. The lake had nearly 3,000 displays fired over it in 8 of the 10-years; so there were substantially more fireworks used over this one location than most others. The study concluded, "Fireworks activity does not appear to contribute substantially to the eutrophication of water bodies."^[3]

While this study is encouraging, it is hardly a comprehensive answer to the overall question of the extent of pollution caused by fireworks. If the fireworks pollution problem is to be addressed, it must first be assessed carefully from the beginning of the manufacturing process to the end use. The extent and seriousness of the

pollution need to be determined and solutions on how to reduce or eliminate them need to be detailed. And all of this needs to be done using the scientific method, not value judgements.

Given the academic institution Prof. White represents and the publication's status, one expected an in depth paper that reported on research conducted according to the scientific method. However the 5,000 word article not only does not meet those expectations, it leaves one totally disappointed and seriously questioning the author's true purpose.

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Review of "Pollution Caused by Fireworks"

by Doris Gnauck White,
American Environmental Laboratory,
Int'l Scientific Communications, Shelton, CT, USA,
Oct. 1996, pp 22-26.

Monona Rossol

181 Thompson St. #23, New York, NY 10012, USA

The basic problem with Professor White's paper is that she is preaching to the converted. Most subscribers to the *American Environmental Laboratory* understand that igniting any substance pollutes the air. These readers know that burning autumn leaves, having barbecues, or putting a log in the fireplace is outlawed in many areas of the country because it significantly impacts air quality.

For this reason, Professor White only felt it necessary to list 53 chemicals that might be found in fireworks and let readers imagine their breakdown products drifting off in a cloud of smoke. If she really wanted to worry her readers, she would have included lead azide "bombs" set off on movie sets, or discussed theatrical pyrotechnics where the audience and performers are trapped in an enclosed space with pyrotechnic emissions.

The author also made no attempt to quantify the pollution except to point out that fireworks are used all over the world and that many theme parks that set off effects daily. I have no doubt that, at least locally, these fireworks can be a significant source of pollution. However, it would be nice to know more about the actual volumes of various chemicals used in the U.S. and worldwide in fireworks.

I would fault Professor White for omitting quantity data in the article if it were not that the fireworks industry is not making this data easily accessible. I have never seen a professionally prefabricated effect that was labeled with all its ingredients and their amounts. Even the material safety data sheets (MSDSs) that I see usually withhold pyrotechnic ingredients and their amounts as trade secrets. Such is the case at the Palace Theater on Broadway where Beauty and

the Beast technicians set off "pyro" daily and twice on Wednesdays. The American Federation of Musicians has been unable to find out what is in the effects whose emissions their workers have been breathing for over two years.

Even worse, the chemicals released after ignition are not well known. Assuming you could identify all the ingredients in the effect, you then could use theories about the reactions to predict emissions. But actual emissions often vary from the theoretical. Air and residue sampling is needed and I don't see much of this data being compiled.

The MSDSs on pyrotechnic products also do not list the break down products after the effect is set off. Instead, the section on "decomposition products" on the MSDSs usually lists only the decomposition products of single chemicals if they were subjected to controlled toxic waste incineration. These individual chemical incineration emissions are very different from those given off when the two or more components are mixed and ignited.

Unfortunately, Professor White demonstrates her ignorance of this fact in her conclusions where she writes:

The author sent the New Jersey Board of Health, Right to Know Division (Trenton, NJ), an outline of this paper. In return, the author received seven boxes of technical information on the breakdown products and how they can harm humans, animals, plants and the environment in general.

She is almost certainly referring to the New Jersey Department of Health's "Hazardous Substances Fact Sheets". They are excellent sources of information, but they only list decomposition products of the individual chemicals. These data sheets will not be very helpful in assessing the breakdown products of fireworks made with these chemicals.

The Professor's concern about "heat pollution, which can result from being burned by fireworks" is spurious. Being burned is not pollution, it is an accident. But I found Professor White's statements about noise and light pollution valid. The author pointed out that children

and pets can be startled by bright lights and loud sounds.

Professor White could have strengthened her argument by including the impact of noise on people with weak hearts, nervous system defects, and other physical problems. A friend of mine, an ICU nurse, was deeply concerned for her patients during the Fourth of July when each loud blast caused heart monitors all over the unit to jump. This startle response is well-known and responsible managers of theaters and theme parks now post warnings when fireworks, lights, lasers, and smoke are being used.

Instead of looking at the shortcomings of Professor White's article, I would suggest that the fireworks and pyrotechnic industries look to themselves. They should not wait for some pro-

fessor to write a technically shaky article on fireworks. They should be compiling data on the chemicals they use.

While the total amounts of chemicals used in the fireworks industry is far smaller than many other air-polluting industries, the fireworks industry has no anti-pollution control mechanisms. Essentially the entire output of the fireworks industry is thrown into the air and ignited. And it is almost always done in highly populated areas.

The fireworks and pyrotechnics industries also should study the emissions from pyrotechnic reactions. If they believe they are not a significant source of pollution, they should compile the data to prove it.

Editorial Policy

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

Table of Contents from Prior Issues

Issue 1, Summer 1995:

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

Issue 2, Winter 1995:

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

Issue 3, Summer 1996:

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

Issue 4, Winter 1996:

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

Issue 5, Summer 1997:

Model Rocket Motors, Theory and Design	1
Flow Agents in Pyrotechnics	8
Hazard Analysis for the Manufacture of a UN Gas Generant	11

Techniques for the Quantitative Analysis of Sulfur and Chlorate in Fireworks Compositions	25
A Survey of Concussion Powders	33
The Nitrous Oxide Hybrid Rocket Motor	47
Correspondence: Comments on "Flash Powder Output Testing: Weak Confinement" from Issue No. 4	60

Issue 6, Winter 1997:

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

Issue 7, Summer 1998:

Production of Music with Pyrotechnic Whistles ..	1
High-Nitrogen Pyrotechnic Compositions	11
An Oxygen-Exchange Approach to Pyrotechnic Formulations	15
Artificial Meteor Fireworks	26
Studies on the Use of Epoxy Resin Binder in Small Rockets	33
Development of a Video Spectrometer	37
Studies of Thermal Stability & Sensitiveness of Sulfur/Chlorate Mixtures	51
Part 2. Stoichiometric Mixtures	51
Novel Powder Fuel for Firework Display Rocket Motors	59

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