# **Glitter Chemistry**

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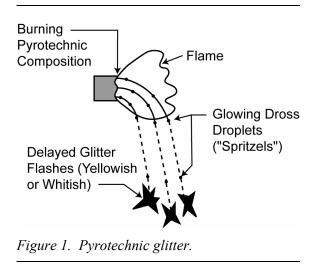
#### ABSTRACT

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



#### 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,<sup>[1]</sup> 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".  $\space{[2]}{}^{[2]}$ 

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.

| 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                               |    |    |    | 10   |  | ~      |       |        | 7       | 10     |        |         |    |
| (atomized, 120–140 mesh)               |    |    |    | 10   |  | 9      |       |        | 7       | 10     |        |         |    |
| Aluminum                               |    |    |    |  |  |        |       |        |         |        | 7      |         |    |
| (atomized, 325 mesh)                   |    |    |    |  |  |        |       |        |         |        | 7      |         |    |
| Magnalium                              |    | 10 | 2  |  |  |        |       |        |         |        |        |         |    |
| (20:80, 200 mesh)                      |    | 10 | 2  |  |  |        |       |        |         |        |        |         |    |
| Magnalium                              |    | 35 | 7  |  | 10   |        | 10    | 10     |         |        |        | 10      | 10 |
| (50:50, –60 mesh)                      |    | 35 | '  |  | 10   |        | 10    | 10     |         |        |        | 10      | 10 |
| Titanium (20–40 mesh)                  |    |    |    |  |  | 3      |       |        |         |        |        |         |    |
| Antimony sulfide                       |    |    |    | 10   | 10   | 14     | 8     | 10     |         | 10     |        |         | 10 |
| (fine powder)                          |    |    |    | 10   | 10   | 14     | 0     | 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:                   |    |    |    |  | 7.   | Sodiu  | m Nit | rate ( | Glitter | (not v | erv us | eful ir | ı  |
| 1. Golden Streamer                     |    |    |    |  |  | practi |       |        |         | (      | 5      |         |    |
| 2. Flash Powder compatible with Golden |    |    |    | 8. Potassium-free Bright Silver Glitter (excellent |  |        |       |        |         |        |        |         |    |
| Streamer (better to use $-200$ mesh    |    |    |    | but expensive)                                     |  |        |       |        |         |        |        |         |    |
| magnalium for flash powder)            |    |    |    |  | 9. Perchlorate Glitter                           |        |       |        |         |        |        |         |    |
| 3. Pearl Glitter (short delay)         |    |    |    |  | 10. Silver Glitter (good)                        |        |       |        |         |        |        |         |    |
| 4. Silver Glitter                      |    |    |    |  | 11. Glitter Fountain (off-white color of glitter |        |       |        |         |        |        |         |    |
| 5. Bright Silver Glitter (long delay)  |    |    |    |  | flashes is aesthetically displeasing)            |        |       |        |         |        |        |         |    |
|  |    |    |    | 12. Bright Silver Glitter (very expensive)         |  |        |       |        |         |        |        |         |    |
| 6. Silver Glitter Fountain             |    |    |    |  |  | Vivid  |       |        | · ·     | cry cx | pensiv | (0)     |    |
|  |    |    |    |  | 13.  | vivid  | relic | W G    | itter   |        |        |         |    |

#### Table 1. Formulations.

# Lloyd Scott Oglesby: Potassium Sulfide Theory<sup>[2,3]</sup>

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,<sup>[4]</sup> "The proportions of the constituents and the main products of combustion correspond roughly with the following equation:

$$2 \text{ KNO}_3 + \text{ S} + 3 \text{ C} \rightarrow \text{ K}_2\text{S} + \text{ N}_2 + 3 \text{ CO}_2$$

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:

 $2 \text{ KNO}_3 + 2 \text{ S} + 3 \text{ C} \rightarrow \\ \text{K}_2\text{S}_2 + \text{N}_2 + 3 \text{ CO}_2$ 

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 "spritzels". Accordingly, the subsequent set of reactions, occurring in these glitter droplets, can be called "spritzel reactions". Oglesby suggests a two stage oxidation of the spritzels 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".<sup>[5]</sup> In such compositions the liquid potassium 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 spritzels. Then as the potassium sulfate concentration increases, a critical point is reached when the glitter flash reaction occurs:

 $2 \ K_2 SO_4 \ + \ 8 \ Al \ \rightarrow \ 3 \ K_2 S \ + \ 4 \ Al_2 O_3$ 

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

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:

$$Ba(NO_3)_2 + S + 3 C \rightarrow BaS + N_2 + 3 CO_2 \text{ (on board reaction)}$$

 $BaS + 2O_2 \rightarrow BaSO_4$  (spritzel reaction)

$$3 \text{ BaSO}_4 + 8 \text{ Al} \rightarrow 3 \text{ BaS} + 4 \text{ Al}_2\text{O}_3$$

(flash reaction)

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 spritzel 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*-

$$\begin{array}{l} 2 \text{ KNO}_3 + \text{ S} + 3 \text{ C} \rightarrow \text{ K}_2 \text{ S} + \text{ N}_2 + 3 \text{ CO}_2 \\ 3 \text{ K}_2 \text{ S} + \text{ Sb}_2 \text{ S}_3 \rightarrow 2 \text{ K}_3 \text{ SbS}_3 \end{array} \qquad (\text{on board reactions}) \\ \\ \hline 4 \text{ K}_3 \text{SbS}_3 + 3 \text{ O}_2 \rightarrow 6 \text{ K}_2 \text{ S}_2 + 2 \text{ Sb}_2 \text{ O}_3 \\ \text{ K}_2 \text{ S}_2 + \text{ O}_2 \rightarrow \text{ K}_2 \text{ S} + \text{ SO}_2 \\ \text{ K}_2 \text{ S} + 2 \text{ O}_2 \rightarrow \text{ K}_2 \text{ SO}_4 \end{array} \qquad (\text{spritzel reactions}) \\ \hline 3 \text{ K}_2 \text{ SO}_4 + 8 \text{ Al} \rightarrow 3 \text{ K}_2 \text{ S} + 4 \text{ Al}_2 \text{ O}_3 \end{array}$$

*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.<sup>[8]</sup> 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<sub>3</sub>SbS<sub>3</sub>). Secondly, the oxidative decomposition of this in the spritzel to produce potassium disulfide and antimony oxide (Sb<sub>2</sub>O<sub>3</sub>). 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<sub>3</sub>SbS<sub>4</sub>). 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:

$$2 K_2 S_2 + K_2 S + S b_2 S_3 \rightarrow 2 K_3 S b S_4$$

(on board reaction)

$$K_3SbS_4 + O_2 \rightarrow K_3SbS_3 + SO_2$$

(first spritzel reaction)

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,<sup>[9]</sup> introduces yet another glitter additive, strontium oxalate. Oglesby suggests that such materials function in a way described by the following equations:

 $\begin{array}{l} \mathrm{SrC_2O_4} \rightarrow \mathrm{SrCO_3} + \mathrm{CO} \mbox{ (on board reaction)} \\ \mathrm{SrCO_3} \rightarrow \mathrm{SrO} + \mathrm{CO_2} \mbox{ (on board reaction)} \\ 2 \ \mathrm{SrO} + 3 \ \mathrm{K_2S_2} \rightarrow 2 \ \mathrm{SrS} + 3 \ \mathrm{K_2S} + \ \mathrm{SO_2} \\ \mbox{ (spritzel reaction)} \\ \mathrm{SrS} + 2 \ \mathrm{O_2} \rightarrow \ \mathrm{SrSO_4} \mbox{ (spritzel reaction)} \end{array}$ 

 $3 SrSO_4 + 8 Al \rightarrow 3 SrS + 4 Al_2O_3$ 

(flash reaction)

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               | ×       | ×         |             |  |  |  |
| Strontium            | ×       | ×         |             |  |  |  |
| Calcium              | ×       | ×         |             |  |  |  |
| Magnesium            | ×       | ×         |             |  |  |  |
| Lithium              | ×       | ×         |             |  |  |  |
| Sodium               | ×       |           | ×           |  |  |  |
| Potassium            | ×       |           | ×           |  |  |  |
| Antimony             | ×       |           |             |  |  |  |
| 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'".<sup>[10]</sup>

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<sup>[11]</sup>

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:

| $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$   |
|--|
| $4 \text{ Al} + 3 \text{ C} \rightarrow \text{Al}_4\text{C}_3$ (on board reaction)   |
| $K_2S_2 + O_2 \rightarrow K_2S + SO_2$ (spritzel reaction)   |
| $K_2S + 2 O_2 \rightarrow K_2SO_4$ (spritzel reaction)   |
| $3  \text{K}_2 \text{SO}_4 + 8  \text{Al} \rightarrow 3  \text{K}_2 \text{S} + 4  \text{Al}_2 \text{O}_3 $ (spritzel reaction) $- \text{ not flash}$ |
| $3 \text{ K}_{2} \text{SO}_{4} + A \text{ L}_{2} \text{ C}_{2} \rightarrow$  |

$$3 \text{ K}_2 \text{SO}_4 + \text{Al}_4 \text{C}_3 \rightarrow$$
  
 $3 \text{ K}_2 \text{S} + 2 \text{ Al}_2 \text{O}_3 + 3 \text{ CO}_2$   
(flash reaction)

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<sup>[12]</sup>

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".<sup>[13]</sup> Under certain conditions the reaction can be quite violent.<sup>[14]</sup> 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:

 $\begin{array}{l} 2 \ KNO_3 \,+\, S \,+\, 3 \ C \,\rightarrow\, K_2S \,+\, N_2 \,+\, 3 \ CO_2 \\ (on \ board \ reaction) \end{array} \\ \begin{array}{l} 2 \ Al \,+\, 3 \ S \,\rightarrow\, Al_2S_3 \\ K_2S \,+\, 2 \ O_2 \,\rightarrow\, K_2SO_4 \end{array} \quad (on \ board \ reaction) \\ \begin{array}{l} 3 \ K_2SO_4 \,+\, 2 \ Al_2S_3 \rightarrow \\ & 3 \ K_2SO_4 \,+\, 2 \ Al_2S_3 \rightarrow \\ & 3 \ K_2SO_4 \,+\, 2 \ Al_2S_3 \rightarrow \\ & (flash \ reaction) \end{array} \end{array}$ 

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 sulfurcontaining 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:

 $2 \hspace{0.1cm} Sb_2S_3 \hspace{0.1cm} + \hspace{0.1cm} 9 \hspace{0.1cm} O_2 \hspace{0.1cm} \rightarrow \hspace{0.1cm} 2 \hspace{0.1cm} Sb_2O_3 \hspace{0.1cm} + \hspace{0.1cm} 6 \hspace{0.1cm} SO_2$ 

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

# Michael Swisher: Thermitic Theory<sup>[15]</sup>

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 thermite reaction:

$$Fe_2O_3 + 2 Al \rightarrow Al_2O_3 + 2 Fe$$

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.<sup>[16]</sup>

 $Sb_2S_3 + 3 Fe \rightarrow 3 FeS + 2 Sb$ 

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

 $Sb_2S_3 + 2 Al \rightarrow Al_2S_3 + 2 Sb$ 

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:

 $Sb_2O_3 + 2 Al \rightarrow Al_2O_3 + 2 Sb$ 

### Takeo Shimizu: Polysulfide Reduction Theory<sup>[17]</sup>

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  $K_2S_x$ ."

 $3 K_2 S_2 + 2 Al \rightarrow 3 K_2 S + Al_2 S_3$  (flash reaction)

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 observations 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".<sup>[2]</sup> 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.<sup>[18]</sup> 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<sup>[19]</sup>).

#### 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,<sup>[19]</sup> 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 surrounding 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.<sup>[19]</sup>

The use of selenium in a glitter composition has also been tested by Winokur and found to be ineffective.<sup>[19]</sup> 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,<sup>[20]</sup> 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.<sup>[20]</sup> 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.<sup>[21]</sup> 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.<sup>[22]</sup>

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.<sup>[23]</sup> 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<sub>2</sub>C. 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 favorable thermodynamic properties of manganese carbide.<sup>[11]</sup> 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.<sup>[19,24,25]</sup> By contrast certain other alloys of aluminum, for example with zinc or zirconium, have not been found to function in glitter compositions.<sup>[2,22]</sup> Alloys with copper and nickel appear to be marginal cases of little use for glitter.<sup>[19]</sup> 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 cooxidizer 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:

 $K_2S_2 + MoS_2 = K_2MoS_4$ 

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.<sup>[19]</sup> 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 Thermitic Theory

In order for a thermitic 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 thermitic theory is not a candidate for the explanation of all kinds of glitter compositions. However, the thermitic 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 thermitic 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 thermitic 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 thermitic reaction with aluminum and Swisher reports making excellent glitters using it.<sup>[15]</sup> The author has found that bismuth subnitrate is a useful glitter additive, and this too can engender a thermitic reaction after initial decomposition to bismuth oxide  $(Bi_2O_3)$ . The effectiveness of molybdenum sulfide is also consistent with the thermitic theory.

In contrast with these experiments, Winokur has reported using manganese dioxide  $(MnO_2)$  and lead oxide  $(Pb_3O_4)$ ,<sup>[19]</sup> both known to undergo thermite reaction with aluminum,<sup>[13]</sup> and found them to be useless. Thus the evidence regarding the thermitic 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), cobaltaluminum (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 Winokur.<sup>[19]</sup>

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  $(2\mu)$ , 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.<sup>[26]</sup> 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.<sup>[27]</sup> The compositions used were made according to a standard gold glitter formulation,<sup>[28]</sup> 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...".<sup>[11]</sup> 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.<sup>[27]</sup> 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.<sup>[27]</sup> 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.<sup>[17]</sup> 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.

| Name              | Formula                           |
|-------------------|-----------------------------------|
| Lithium carbonate | Li <sub>2</sub> CO <sub>3</sub>   |
| Lithium oxalate   | $Li_2C_2O_4$                      |
| Rubidium nitrate  | RbNO <sub>3</sub>                 |
| Cesium nitrate    | CsNO <sub>3</sub>                 |
| Calcium carbonate | CaCO <sub>3</sub>                 |
| Strontium nitrate | Sr(NO <sub>3</sub> ) <sub>2</sub> |
| Barium nitrate    | Ba(NO <sub>3</sub> ) <sub>2</sub> |
| Boron             | В                                 |
| Indium metal      | In                                |
| Indium carbonate  | In <sub>2</sub> CO <sub>3</sub>   |
| Indium sulfide    | $In_2S_3$                         |
| Thallium nitrate  | TINO <sub>3</sub>                 |

Table 3. Materials Not Yet Found ToProduce Colored Glitter.

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.<sup>[20]</sup> However, von Baum notes that the use of strontium carbonate in such formulations does not produce colored glitter flashes.<sup>[20]</sup> 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.<sup>[2,19]</sup> 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 experiment. 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.<sup>[19]</sup> 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.<sup>[21]</sup> 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 lithiumaluminum 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."<sup>[19]</sup> On the other hand, Partington states "Lithium burns when heated in air above its melting point, with a *white* flame..." (Author's italics).<sup>[4]</sup>

The author was able to obtain some lithiumaluminum 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 lithiumaluminum 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?"<sup>[12]</sup> 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/m<sup>3</sup> showed no ill-effects, suggested that the trisulfide has a low toxicity".<sup>[30]</sup> Such low toxicity is entirely in accord with its low solubility of 0.000175 g/100 cm<sup>3.[31]</sup> 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.<sup>[12]</sup> This is certainly not the case when magnalium is being used in combination with lithium carbonate.<sup>[21]</sup> 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,<sup>[32]</sup> and this is also true for lithium oxalate<sup>[21]</sup> and antimony oxalate (the latter suggested for use with aluminum by Kosanke<sup>[33]</sup>). 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.<sup>[32]</sup>

# Table 4. Adverse Reactivities of Metalswith Glitter Additives in an AqueousEnvironment.

| Ingredient        | Aluminum | Magnalium |
|-------------------|----------|-----------|
| Lithium carbonate | ×        |           |
| Sodium carbonate  | ×        |           |
| Lithium oxalate   |          | ×         |
| Sodium oxalate    |          | ×         |
| Antimony oxalate  |          | ×         |

 $\mathbf{x}$  = unwanted reaction upon dampening.

Curiously, Lancaster has stated "One last point on glitter mixes: when using finelypowdered magnalium be very careful to add boric acid, or else the mix can heat up (on damping)...".<sup>[10]</sup> 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.<sup>[32,34]</sup> 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)".<sup>[35]</sup>

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"<sup>[36]</sup> and Carl Sagan (Astronomer extraordinary) "One of the great commandments of science is mistrust arguments from authority".<sup>[37]</sup> The author hopes that the arguments presented in this article will also be treated with the skepticism they deserve.

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

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