

Strobe Chemistry

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ABSTRACT

Pyrotechnic strobe compositions burn in an oscillatory manner such that there is a marked variation of emitted light intensity as a function of time. The most common theoretical explanation for the phenomenon is that such compositions contain within them sub-compositions that may be regarded as a smoulder composition and a flash composition. The smoulder reaction would have a lower activation energy and low heat output. The flash reaction would have a high activation energy and high heat output. The actual chemical components of strobe compositions are extremely diverse, confounding a unified chemistry of the phenomenon. Nevertheless the majority of strobe compositions can in fact be reasonably deconstructed into smoulder and flash compositions. However, there appear to be a few strobe compositions that defy such explanation; although it is possible that the author lacks the wit to comprehend the chemistry. It is also possible that the prevailing theory applies to some, but not to all, strobe compositions; and it is yet possible that a different theory will provide a more encompassing explanation with better predictive power.

Keywords: strobe, formulation, theory, flash, magnesium, smoulder, smolder

Introduction

The pyrotechnic strobe effect is produced by a light-emitting pyrobody, such as a star, wherein the light intensity is a cyclic variable function of time. The minimum light intensity may or may not be zero, but the frequency of the intensity peaks must be sufficiently slow such that the eye can distinguish between them. An example of a possible time course of light intensity is shown in Figure 1. To qualify as a strobe the composition must produce at least two flashes separated by a “dark” phase.

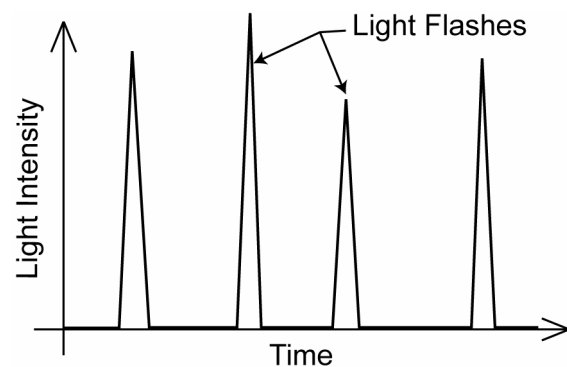


Figure 1. Representative time course of pyrotechnic strobe.

Shimizu has hypothesized that two different kinds of pyrochemistry are involved; one in the “light” or “flash” phase of a pyrotechnic strobe, and one in the “dark” or “smoulder” phase.^[1] These will be referred to as the “flash reaction” and the “dark reaction”. Shimizu suggests that a strobe composition may be thought of as a mixture of a flash composition and a smoulder composition. This is not the only possible hypothesis for the mechanism of strobe. For example, one could have postulated that a single pyrochemical reaction could occur at different rates for some reason (e.g., oscillatory thermal feedback or oxygen influx due to a pyrobody tumbling in air); or that a smoulder reaction gives rise to products capable of producing a flash reaction; or that a flash reaction gives rise to products capable of producing a smoulder reaction.

Shimizu’s hypothesis engenders very specific predictions regarding what type of composition could or could not function as a strobe. If Shimizu’s hypothesis is correct, then every composition that is capable of functioning as a strobe must contain ingredients that are capable of reacting as a flash composition, as well as ingredients that are capable of producing a dark reaction. Any exceptions to this would mean that

Shimizu's hypothesis is not universally applicable.

Genesis of the Shimizu Hypothesis

Firstly, Shimizu gives due credit to Wassmann^[2] and Krone^[3] for originating this line of thinking regarding the theoretical mechanism of pyrotechnic strobe. However, it will be referred to as the "Shimizu Hypothesis" here since he has made the largest contribution to our understanding of this phenomenon.

Shimizu had noticed in his studies on strobe compositions that, during the dark phase, "hot spots" develop in the smouldering slag layer which grow in size and temperature until a critical point is reached when the flash reaction commences. Thus it would appear that the dark reaction should have a small activation energy together with a relatively small heat output. By contrast the flash reaction should have a large activation energy (thereby allowing a delay before initiation) as well as a large heat output (thereby producing a relatively bright flash).

Testing the Shimizu Hypothesis

Various theories of glitter chemistry propose specific ingredients and/or intermediates and/or reactions.^[4] Such theories can be tested by, for example, manipulating the ingredients of the glitter composition and observing the resultant pyrotechnic effect. However, Shimizu has not proposed that any specific ingredients are necessary or that any specific reaction takes place, for the functioning of a pyrotechnic strobe.

Consequently, the testing of the flash composition, smoulder composition hypothesis will be more general. Indeed, one of the first testable predictions is that there should be not just one strobe chemistry but many strobe chemistries. Therefore stringent testing of Shimizu's strobe hypothesis would catalog as many widely different strobe compositions as possible, focusing on their predicted commonalities such as those listed below:

- 1) One should be able to write a plausible equation for the flash reaction.
- 2) One should be able to write a plausible equation for the dark reaction.

- 3) The strobe composition should be reconstitutable as a mixture of a flash composition and a smoulder composition.
- 4) Quenching a strobe composition shortly after a flash should yield a mixture depleted in the proposed flash components.
- 5) Quenching a strobe composition shortly before a flash should yield a mixture depleted in the proposed smoulder components.

Caveats:

- a) "Plausible" equations are ones that utilize ingredients of the composition and that are chemically reasonable.
- b) Shimizu's hypothesis does not predict that any mixture of a flash composition and a smoulder composition will be capable of strobing. It is proposed as a necessary condition, not a sufficient condition.
- c) There exists strobe composition consisting of only two components, neither of which is capable of independent functioning as either a flash composition or a smoulder composition. At first sight this would appear to contradict prediction No. 3. However, note that a mixture of 50A + 50B is also equivalent to a 1:1 mixture of 80A + 20B and 20A + 80B. These latter could be flash composition and smoulder composition.
- d) Atmospheric oxygen may be a plausible reactant in a smoulder composition (e.g., burning sulfur).
- e) It is possible that there may be more than one plausible flash reaction or dark reaction for a given strobe composition. Indeed, there may be more than one in actuality. A dictum of chemistry is that any reaction that can occur will occur. Consequently, the real chemistry involved in pyrotechnic strobes is necessarily more complex than can be depicted by a set of two equations. However, for the purpose of testing the Shimizu hypothesis, it is sufficient only to find one equation for each reaction type.
- f) Quenching experiments should be possible for long cycle strobes, but may be prohibitively difficult for fast strobes.

- g) Quenching experiments are left to those with more sophistication in the required techniques than has the author, and are therefore beyond the scope of this article.

Various Strobe Compositions

A set of diverse strobe formulations was chosen with the intent of maximizing the differences of ingredients between the formulations. Substitution of similar ingredients, such as one alkaline earth sulfate for another alkaline earth sulfate, was not considered as one may reasonably assume that these compositions function through an analogous sequence of reactions. Formulations are either previously published or devised by the author. For testing, compositions (6 g) were pressed into a short (1½-inch long) ½-inch i.d. tube glued to a metal base. “Hot” prime (1 g) was pressed on top of the composition and lit with a visco fuse. In certain cases no amount of priming would succeed in lighting the composition, but several seconds of direct blowtorch flame would eventually trigger the composition to start strobing by itself.

No consideration was given to the “usefulness” of the test composition. That is it may be hard to light, not reliably stay lit, strobe too fast, strobe too slow, have hygroscopic ingredients, not be stable on storage, be absurdly expensive, etc. None of these factors bear on the utility of the composition for testing theoretical principles. Thus the only inclusion criteria were (a) that the composition must fulfill the definition of “strobe” (i.e., at least two flashes separated by a dark phase), and (b) that the formulation must be significantly different from others under consideration.

Strobe formulations considered for their conformity with Shimizu’s theoretical predictions are listed in Table 1.

Table 1. Diverse Strobe Formulations.

| Ingredients | A | B | C | D | E | F | G | H | I | J | K | L | M |
|------------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Barium nitrate | 54 | 50 | | | | | | | | | | | |
| Sulfur | 23 | | | | | | | | | | | | |
| Magnalium (50:50) | 18 | 20 | 33 | 30 | 25 | 20 | | | | | | | 15 |
| Dextrin | 5 | | | | | | | | | | | | |
| Guanidine nitrate | | 30 | 33 | 42 | | | | | | 70 | 55 | | |
| Potassium perchlorate | | | 33 | | | | | | | | | | |
| Ammonium perchlorate | | | | 28 | 60 | 50 | 60 | | 50 | | 25 | 30 | |
| Barium sulfate | | | | | 15 | | | | | | | | |
| Hexamine | | | | | | 30 | 40 | 50 | | | | | |
| Lithium perchlorate | | | | | | | | 50 | | | | | |
| Magnesium | | | | | | | | | 50 | | | | |
| Mg ₂ Cu | | | | | | | | | | 30 | | | |
| Tetramethylammonium nitrate | | | | | | | | | | | | 40 | |
| Copper (atomized, -100 mesh) | | | | | | | | | | | 20 | 30 | |
| Copper(II) oxide | | | | | | | | | | | | | 10 |
| Bismuth(III) oxide | | | | | | | | | | | | | 75 |
| Reference | 5 | 6 | 7 | 7 | 8 | 7 | 7 | 7 | 1 | 7 | 7 | 7 | 9 |

“Dark” and “Flash” Binary Mixtures

There are a number of known binary (two-ingredient) compositions capable of a continuous smoulder reaction with little or no light output. More familiarly there are a number of known binary flash powers. A listing of such combinations, particularly those containing commonly used strobe ingredients, allows a shortcut to determining whether a strobe composition satisfies Shimizu’s proposed mechanism. That is to say, if the composition contains the ingredients of at least one binary mixture from each list then one need look no further.

Examples of known dark binary mixtures are listed in Table 2. Examples of known flash binary mixtures are listed in Table 3. Hypothetical strobe reaction equations for the strobe compositions under discussion are listed in Table 4.

Table 2. Known Binary Dark Mixtures.

| No. | Ingredient 1 | Ingredient 2 | Ref. |
|-----|------------------------|----------------------|------|
| 1 | Magnesium | Ammonium perchlorate | 1 |
| 2 | Magnalium | Ammonium perchlorate | 1 |
| 3 | Zinc | Ammonium perchlorate | 1 |
| 4 | Copper | Ammonium perchlorate | 1 |
| 5 | Cyanoguanidine | Ammonium perchlorate | 7 |
| 6 | Guanidine nitrate* | Ammonium perchlorate | 7 |
| 7 | Magnesium | Sulfur | 1 |
| 8 | Magnalium | Sulfur | 1 |
| 9 | Titanium | Sulfur | 1 |
| 10 | Copper | Sulfur | 1 |
| 11 | Air | Sulfur | 10 |
| 12 | Copper | Guanidine nitrate | 7 |
| 13 | Cupric oxide | Guanidine nitrate | 8 |
| 14 | Magnesium-copper alloy | Guanidine nitrate | 7 |

* Guanidine nitrate is a common informal name for the substance more properly called guanidinium nitrate.

Table 3. Known Binary Flash Mixtures.

| No. | Ingredient 1 | Ingredient 2 | Ref. |
|-----|-----------------------|--------------|------|
| 1 | Barium nitrate | Magnalium | 4 |
| 2 | Barium sulfate | Magnalium | 11 |
| 3 | Ammonium perchlorate | Magnalium | 11 |
| 4 | Potassium perchlorate | Magnalium | 12 |
| 5 | Barium nitrate | Magnesium | 1 |
| 6 | Barium sulfate | Magnesium | 1 |
| 7 | Ammonium perchlorate | Magnesium | 1 |
| 8 | Potassium perchlorate | Magnesium | 1 |

Discussion of the Strobe Formulations from Table 1

- A. The key components of this excellent classic white strobe star are barium nitrate, sulfur, and magnalium. This contains dark mixture No. 8 from Table 2, and flash powder No. 1 from Table 3. The Shimizu hypothesis is therefore satisfied by this formulation.
- B. Sulfur is by no means necessary, since here it is replaced by guanidine nitrate. The flash powder remains the same, but no combination appears in Table 2 as the dark mixture. In this case an experimental test of the Shimizu hypothesis is therefore necessary. The prediction is that some subset of materials present in formulation B is capable of producing a smoulder composition. Examination of Table 2 indicates that both magnalium and guanidine nitrate are components of known dark binary mixtures, and consequently constitute a candidate dark binary in admixture. Testing showed that the mixture 20% magnalium/80% guanidine nitrate will smoulder, though not reliably staying lit. An occasional flash also presented. This is sufficient to satisfy the Shimizu hypothesis.
- C. This is a similar composition to “B”, but the oxidizer is changed from barium nitrate to potassium perchlorate. Thus the flash powder is switched from No. 1 to No. 4 in Table 3. The Shimizu hypothesis is satisfied.
- D. The oxidizers are switched again, this time to ammonium perchlorate. The ammonium per-

chlorate/magnalium flash powder is No. 3 from Table 3. The Shimizu hypothesis is satisfied.

- E. This time the guanidine nitrate is replaced with barium sulfate, and our smoulder composition is gone. Barium sulfate and magnalium constitute a flash powder (No. 2 from Table 3), but it does not smoulder. However the ammonium perchlorate/magnalium mixture can function as a smoulder composition (No. 2, Table 2), as well as a flash powder, and so any composition containing both these components will automatically satisfy the Shimizu hypothesis regardless of other ingredients. Note, however, that in these sulfate type strobe compositions the sulfate is usually considered to act as the principal oxidizer in the flash reaction and the ammonium perchlorate acts as the principal oxidizer in the dark reaction.^[1] Specifically Shimizu has suggested that the magnesium content of the magnalium reacts with ammonium perchlorate in the dark reaction, leaving primarily barium sulfate and aluminum for the flash reaction.^[1] This is also consistent with the magnalium combustion mechanism proposed by Popov et al,^[13] involving preferential oxidation of the magnesium content.
- F. Hexamine is used here in place of barium sulfate. This does not further test the Shimizu hypothesis however because, as noted above, any composition containing both ammonium perchlorate and magnalium automatically qualifies.
- G. The simple omission of magnalium leaves a binary composition of ammonium perchlorate and hexamine that is still capable of strobing behavior. Now bereft of both known dark or flash binary mixtures, this composition would appear to pose a serious problem for the Shimizu hypothesis. Let us see if we can rescue the situation:

The sulfur strobes typified by "A" (Table 1) are hard to observe in the dark phase because the bright flash requires that one's eyes have some time to readjust, by which time another bright flash occurs. However, there is a closely related kind of composition for making "microstars" that in per-

formance essentially produce a single dark phase followed by a single flash phase.^[14] While this does not qualify as a strobe composition, which would require a minimum of two flashes, both the formulation and the effect are clearly related to strobe. The delay can be increased by increasing the sulfur content. So with a high-sulfur composition one may observe the dark reaction for some time before observing the flash. A typical formulation for such a composition would be: 40% barium nitrate, 30% sulfur, and 30% magnalium.^[14] The composition is made into microstars using a nitrocellulose binder. One may observe the microstars after being lit with a blowtorch. The appearance of the dark reaction is simply the typical dim blue flame of burning sulfur. This is followed by a single bright flash; so do not observe too closely.

Thus, although a reaction between magnalium and sulfur was postulated as the dark reaction for this kind of composition, it is also plausible that it could be a reaction between sulfur and air (No. 11 from Table 2) depleting the sulfur content until a suitable flash powder composition is reached. Hexamine is a fuel, like sulfur, that burns easily in air with a dim flame. So the burning of hexamine in air can be postulated as the dark reaction for strobes of type G.

Now we have an apparently even more intractable problem: No metal fuel, so where is the flash powder? An answer is perhaps found in the apparent capability of hexamine/potassium perchlorate mixtures (such as 30:70) of producing a sharp report when functioning as a flash powder.^[15] It is known that ammonium perchlorate can also function as the oxidizer in a flash powder.^[15] Thus one indeed might reasonably argue, based on literature precedent, that the ammonium perchlorate/hexamine mixture should be able to function as a flash powder after sufficient hexamine has burnt off, bringing the mixture closer to stoichiometric proportions (86% ammonium perchlorate, 14% hexamine). The proposed mechanism thus makes this composition analogous to various pyrotechnic compositions wetted with alcohol, wherein a portion

of the alcohol burns off the surface layer allowing the composition to flash; and the cycle repeats.

- H. If the explanation above suffices for this ammonium perchlorate/hexamine mixture (G), then it also suffices for the lithium perchlorate/hexamine mixture (H).
- I. Simple binary oxidizer/metal mixtures can also function as a strobe. In this case we have the known dark binary No. 1 from Table 2 and the known flash powder No. 7 from Table 3.
- J. Similarly to the case above, it is easy to make a dark binary composition by mixing magnesium-copper alloy with guanidine nitrate, No. 14 from Table 2. This is quite reasonable since the mixture of copper and guanidine nitrate, No. 12 from Table 2, will do the same. The flash powder might seem

a little odd since guanidine nitrate is a net fuel rather than a net oxidizer. Nevertheless guanidine nitrate does contain available oxygen and so might function in a flash powder in a similar way to barium sulfate in the presence of a highly energetic metal fuel.

- K. The dark binary composition is here fulfilled by either the copper/ammonium perchlorate combination or the copper/guanidine nitrate combination (Nos. 4 and 12 from Table 2). The fact that simple omission of ammonium perchlorate from this composition results in a smoothly burning smoulder composition perhaps favors the latter. No ammonia smell is produced, and the brown residue is insoluble in water. Unlike the previous guanidine nitrate strobes discussed, there is no active metal fuel present with which to form an obvious flash powder. However, the low melting point of guanidine

Table 4. Hypothetical Strobe Reaction Equations for Formulations in Table 1.

| Strobe | Flash Reaction | Smoulder Reaction |
|--------|---|---|
| A | $3 \text{ Ba}(\text{NO}_3)_2 + 10 \text{ Al} \rightarrow 3 \text{ BaO} + 3 \text{ N}_2 + 5 \text{ Al}_2\text{O}_3$ | $\text{Mg} + \text{S} \rightarrow \text{MgS}$ |
| B | $3 \text{ Ba}(\text{NO}_3)_2 + 10 \text{ Al} \rightarrow 3 \text{ BaO} + 3 \text{ N}_2 + 5 \text{ Al}_2\text{O}_3$ | $(\text{H}_2\text{N})_3\text{CNO}_3 + \text{Mg} \rightarrow (\text{H}_2\text{N})_2\text{CO} + \text{H}_2\text{O} + \text{N}_2 + \text{MgO}$ |
| C | $3 \text{ KClO}_4 + 8 \text{ Al} \rightarrow 3 \text{ KCl} + 4 \text{ Al}_2\text{O}_3$ | $(\text{H}_2\text{N})_3\text{CNO}_3 + \text{Mg} \rightarrow (\text{H}_2\text{N})_2\text{CO} + \text{H}_2\text{O} + \text{N}_2 + \text{MgO}$ |
| D | $6 \text{ NH}_4\text{ClO}_4 + 10 \text{ Al} \rightarrow 3 \text{ N}_2 + 12 \text{ H}_2\text{O} + 2 \text{ Al}_2\text{O}_3 + 6 \text{ AlOCl}$ | $(\text{H}_2\text{N})_3\text{CNO}_3 + \text{Mg} \rightarrow (\text{H}_2\text{N})_2\text{CO} + \text{H}_2\text{O} + \text{N}_2 + \text{MgO}$ |
| E | $3 \text{ BaSO}_4 + 8 \text{ Al} \rightarrow 3 \text{ BaS} + 4 \text{ Al}_2\text{O}_3$ | $2 \text{ NH}_4\text{ClO}_4 + \text{Mg} \rightarrow 2 \text{ NH}_3 + \text{H}_2 + \text{Mg}(\text{ClO}_4)_2$ |
| F | $6 \text{ NH}_4\text{ClO}_4 + 10 \text{ Al} \rightarrow 3 \text{ N}_2 + 12 \text{ H}_2\text{O} + 2 \text{ Al}_2\text{O}_3 + 6 \text{ AlOCl}$ | $2 \text{ NH}_4\text{ClO}_4 + \text{Mg} \rightarrow 2 \text{ NH}_3 + \text{H}_2 + \text{Mg}(\text{ClO}_4)_2$ |
| G | $5 \text{ C}_6\text{H}_{12}\text{N}_4 + 36 \text{ NH}_4\text{ClO}_4 \rightarrow 30 \text{ CO}_2 + 84 \text{ H}_2\text{O} + 36 \text{ HCl} + 28 \text{ N}_2$ | $\text{C}_6\text{H}_{12}\text{N}_4 + 9 \text{ O}_2 \rightarrow 6 \text{ CO}_2 + 6 \text{ H}_2\text{O} + 2 \text{ N}_2$ |
| H | $2 \text{ C}_6\text{H}_{12}\text{N}_4 + 9 \text{ LiClO}_4 \rightarrow 9 \text{ LiCl} + 12 \text{ CO}_2 + 12 \text{ H}_2\text{O} + 4 \text{ N}_2$ | $\text{C}_6\text{H}_{12}\text{N}_4 + 9 \text{ O}_2 \rightarrow 6 \text{ CO}_2 + 6 \text{ H}_2\text{O} + 2 \text{ N}_2$ |
| I | $2 \text{ NH}_4\text{ClO}_4 + 5 \text{ Mg} \rightarrow \text{N}_2 + 3 \text{ H}_2\text{O} + 3 \text{ MgO} + 2 \text{ Mg}(\text{OH})\text{Cl}$ | $2 \text{ NH}_4\text{ClO}_4 + \text{Mg} \rightarrow 2 \text{ NH}_3 + \text{H}_2 + \text{Mg}(\text{ClO}_4)_2$ |
| J | $(\text{H}_2\text{N})_3\text{CNO}_3 + 2 \text{ Mg} \rightarrow 2 \text{ NH}_3 + \text{N}_2 + \text{CO} + 2 \text{ MgO}$ | $(\text{H}_2\text{N})_3\text{CNO}_3 + 2 \text{ Cu} \rightarrow (\text{H}_2\text{N})_2\text{CO} + \text{H}_2\text{O} + \text{N}_2 + \text{Cu}_2\text{O}$ |
| K | $4 \text{ NH}_4\text{ClO}_4 + 5 (\text{H}_2\text{N})_3\text{CNO}_3 \rightarrow 21 \text{ H}_2\text{O} + 5 \text{ CO}_2 + 12 \text{ N}_2 + 4 \text{ HCl}$ | $(\text{H}_2\text{N})_3\text{CNO}_3 + 2 \text{ Cu} \rightarrow (\text{H}_2\text{N})_2\text{CO} + \text{H}_2\text{O} + \text{N}_2 + \text{Cu}_2\text{O}$ |
| L | ? | ? |
| M | $\text{Bi}_2\text{O}_3 + 2 \text{ Al} \rightarrow 2 \text{ Bi} + \text{Al}_2\text{O}_3$ | $\text{Bi}_2\text{O}_3 + 3 \text{ Mg} \rightarrow 2 \text{ Bi} + 3 \text{ MgO}$ |

nitrate (217 °C) could facilitate the production of a molten mixture with oxidizer, such mixtures having the potential for almost explosive decomposition.^[7]

- L. The very idea of a black strobe, such as this, does not really fulfill the definition given earlier since no visible light is produced at any stage in the combustion. However, it is very closely related to some blue strobe compositions.^[7] Moreover, the combustion gases produced during the “flash” phase may be ignited to produce a blue flame. This flame does not stay lit in the absence of an external ignition source.

The combustion alternates between a slow smoulder and a fast smoulder accompanied by a loud sizzling sound; an acoustic strobe perhaps? The point here is that the composition can be altered by fine gradations (increasing the ammonium perchlorate to 40%) wherein the combustion gases produced during the flash phase reliably ignite in air of their own accord to produce the blue flame. Therefore the flash phase of this kind of blue strobe actually consists of two separate reactions: the pyrochemical reaction that is essentially the same as that operating in this black strobe (L, producing no light), and the combustion of the resulting gases in air to produce a blue flame. Thus, regardless of whether we address the black strobe or the related blue strobe, we would still need to postulate a flash reaction that produces no light. The triangle diagram for the similar system, K, with guanidine nitrate in place of tetramethylammonium nitrate (TMAN) did not show any areas of black strobe.^[7] Consequently one may not assume that the mechanisms are necessarily analogous. However, the peculiarity of the black strobe phenomenon is not limited to compositions containing TMAN. Investigations of various potential blue strobe systems also revealed a black strobe in combinations of ammonium perchlorate, cupric salicylate, and hexamine.^[7] It would appear that the explanatory power of the Shimizu hypothesis breaks down here. These compositions have a flash phase consisting of a fast smoulder, and contain nothing like the ingredients expected of a flash powder.

What of the “dark” reaction, or should we say “slow” reaction in these cases? TMAN is a net fuel that has very similar burning properties to hexamine: easy to ignite, burning at a low temperature, with small light output. The author postulated the burning of hexamine in air as the dark reaction for cases G and H.^[7] One might thus similarly postulate the burning in the air of TMAN as the dark reaction for strobes containing this material. However, the ammonium perchlorate/cupric salicylate/hexamine system mentioned above has been found NOT to produce a visible flame during the dark phase, and this was also observed to be the case for some TMAN compositions. The dark reaction for TMAN strobes is therefore just as non-obvious as the flash reaction.

- M. The acoustic strobe effect was referred to in the section above. Certain crackling microstar compositions, such as this one, have a propensity for multiple reports along with flashes and so also fit in the acoustic strobe category.^[9] Shimizu has proposed a mechanism for the lead based crackling microstars that is analogous to his strobe suggestions.^[16] One may note that most crackling microstars contain magnalium, just as do the most common kinds of strobes. Thus Shimizu proposes that the magnesium primarily takes part in the dark reaction, and the aluminum primarily takes part in the explosive flash reaction. It would not seem unreasonable that a similar mechanism could operate in the bismuth based microstars.

Conclusions

The principal mechanism that has been proposed to explain the chemistry of pyrotechnic strobe compositions is based on alternating reactions corresponding to the “dark” and “flash” phases of the strobe.^[1-3] The dark reaction should have a low activation energy, together with a low heat of reaction. The flash reaction should have a high activation energy, together with a high heat of reaction. These qualities are characteristic of a smoulder composition and a flash composition respectively. Thus the hypothesis predicts that a pyrotechnic strobe composition is capable of deconstruction into a

smoulder composition and a flash composition. It is not necessary for the components of these compositions to be different, since certain binary mixtures are capable of each reaction mode at different compositional ratios.

Theoretical analysis of the diverse strobe formulations above indicates that, for the most part, pyrotechnic strobe compositions can indeed be plausibly deconstructed into a smoulder composition and a flash composition. By and large this is supportive of the prevailing hypothesis. However, there nevertheless exist some strobe compositions for which an opponent of this hypothesis could reasonably claim that such deconstruction is “clutching at straws”. There is room for doubt. There are several possibilities. It could be that the prevailing hypothesis is correct and general, but we do not have sufficient understanding of some strobe compositions to see the applicability. It could be that the prevailing hypothesis is applicable to most strobe compositions, but not to all. It could be that the prevailing hypothesis is not really the most appropriate description of strobe mechanism, and that there may yet be a hypothesis of more general validity and predictive value. The hypothesis that a strobe composition can be thought of as a mixture of a smoulder composition and a flash composition may have value as a post facto explanation. Nevertheless, it does not have much predictive value since mixtures of a smoulder composition and a flash composition will not generally produce a strobe composition. Perhaps it is a necessary, but not sufficient condition. Our understanding of the pyrotechnic strobe would be furthered by a theoretical analysis of the thermodynamics and kinetics involved. Quenching experiments should provide valuable evidence regarding the chemical changes that have occurred in different phases of the cycle.

Strobe Frequency

While we do not yet have a good theory to enable discovery of new strobe compositions, it is nevertheless possible to tailor the properties of existing compositions in order better to serve our needs. In particular there are some reliable methods for fine tuning the strobe frequency to suit one’s purpose. The majority, but by no means all,^[17] of practical strobe compositions

contain a metal powder. It seems that in these cases the frequency may be increased by increasing the available surface area of the metal. Most commonly this is achieved either by increasing the percentage of metal in the formulation or by decreasing the particle size of the metal powder. In order to decrease the frequency, the opposite is done.

In addition, altering the physical form of a strobe composition can affect the frequency. Increasing the thermal feedback will usually increase the frequency. Thus, a composition in a tube will exhibit a greater frequency than the same composition as a naked star flying through the air.

Safety Considerations

Firework composition safety considerations most commonly fall into the categories of accidental ignition hazard or toxicity hazard. Many strobe compositions contain ingredients that are also found in flash powders. Moreover, the hypothetical mechanism proposes that strobe compositions could be regarded as being partly comprised of flash powder. Thus one might reasonably assert that strobe compositions should be treated with the same respect that one would afford flash powder. Practical experience of many pyrotechnists has borne this out. Strobe compositions have been known to explode catastrophically when subjected to impact. Strobe mines have been known to shred metal mortars. Nor should one assume that strobe compositions devoid of active metal fuel are free from such considerations.

A wide variety of firework chemicals are used in the preparation of strobe compositions, and it is necessary to be aware of particular combinations that engender a greater than normal predisposition for spontaneous combustion. Most notable in this context is the combination of magnesium and ammonium perchlorate. As stated by Lancaster, “Magnesium is particularly liable to heat up in the presence of ammonium salts”.^[18] Unfortunately this happens to be a combination that otherwise has been shown to be especially effective for the production of variously colored strobe compositions.^[1] The usual expedient for accommodating this situation is to pacify the magnesium surface with potassium dichromate or ammonium dichro-

mate. The techniques have been mostly developed by Shimizu, and nicely summarized by Lancaster.^[18] The use of dichromates, however, introduces a toxicity hazard significantly greater than typically associated with pyrotechnic compositions.^[19] Dichromates are known to be carcinogenic, with potential long latencies after exposure. For use in fireworks, therefore, it is necessary to take greater than normal precautions to prevent access to lungs and skin during manufacture. There have been some efforts to solve the magnesium/ammonium perchlorate incompatibility problem in a way that avoids undue toxic hazard.^[20]

The use of magnesium aluminum alloy (magnalium) instead of magnesium, in combination with ammonium perchlorate, goes a long way in reducing the probability of an unintended exothermic reaction. However, magnalium and ammonium perchlorate, in combination with some other materials, have also been known to heat up in the presence of water.^[21] Non-aqueous binding generally solves the problem, nitrocellulose being popular for strobe stars.

Crackling microstars may be classified as a pyrotechnic strobe. The use of lead oxide in these compositions presents significant toxic hazard.^[22] The neurotoxicity for the developing brain is of particular concern. While infants may not be engaged in fireworks manufacture, they can nevertheless still smell the smoke.

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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.