A Study of a Set of Nitrate-Based Pyrotechnic Strobe Compositions

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Abstract: *The subject of this study is a set of simple pyrotechnic strobe compositions, containing only barium nitrate, a magnesium-aluminum alloy and sulfur, together with a small amount of nitrocellulose to act as a binder. Despite the fact that compositions of this type have been known for well over one hundred years, thare is still no consensus about how they work.*

Observations of the compositions' behavior by means of a variety of techniques were used to gain information regarding the chemical mechanisms that are most likely to be occurring during the dfferent reaction phases. While the findings support earlier suggestions for the nature of the flash reaction, they indicate that the mechanism during the more quiescent phase is different from that which has previously been proposed.

Keywords: *Pyrotechnic strobe, Sulfur, Magnalium, Reaction mechanisms*

Introduction

Pyrotechnic strobe compositions are ones that, when ignited, burn in an oscillatory manner, producing a series of bright flashes, separated by 'smolder' phases that emit little or no light. The first known examples of this type of composition, containing mixtures of barium nitrate, sulfur, magnesium and aluminum, are said to have appeared under the name 'Orion Flashing Guns' in a Brocks Fireworks formulary, dated 1898. That formulary has subsequently been lost and the only documentary evidence of its existence appears to be Wasmann's report[1] of a private communication from Ronald G. Hall who, in the mid to late 1970s, was the technical director of Brocks Fireworks Ltd.

The discovery of those first strobes occurred not long after magnesium and aluminum first became available in commercially viable quantities, and it seems likely that they were the result of investigations into the effect of including these new materials in previously known compositions.

So, as is the case with most other types of pyrotechnic composition, it appears that the first strobes were discovered by accident, and subsequent discoveries of new variants – including those that use new and/or more environmentally friendly ingredients – were all the result of trial and error.

One of the earliest studies that attempted to gain an understanding of the strobe mechanism was that of Krone[2] who reported his findings regarding compositions whose principal components were barium or strontium nitrate and a 50:50 alloy of magnesium and aluminum (magnalium). From the results of a chemical analysis of cooled residue from samples that failed to produce flashes, he concluded that magnesium was preferentially consumed in the smolder phase, leaving aluminum to react to produce the flash. He also noted that the separation of the smolder and flash phases was significantly enhanced by the inclusion of compounds, such as ammonium perchlorate or nitroguanidine, that release large amounts of gaseous reaction products which, he suggested, might serve to inhibit the flash reaction during the smolder phase.

At about the same time, Wasmann[3] published a study of compositions containing strontium or barium perchlorate as oxidizer and a mixture of complex organic polymers as the fuel. In that paper and a later publication[1] he pointed out that, in addition to the possible chemical reactions, physical processes such as evaporation and heat transfer must play a significant role in any explanation of the mechanism.

In his study of strobes, Shimizu[4] proposed a generalization of the mechanism suggested by Krone. He put forward the hypothesis that the strobing behavior is the result of the presence of two fuel-oxidizer pairs. One pair is involved in the smolder phase and so should have a relatively low activation energy and be only moderately exothermic. The flash phase is produced by the second pair, which needs to be more exothermic and have a significantly greater activation energy. He experimented with a range of candidate compositions of each type but found that relatively few of them could be combined to produce a successful strobe. It therefore appears that his hypothesis may define a necessary, but not sufficient, condition for the nature of the constituents of a strobe composition.

Jennings-White[5] looked at this issue from a different direction – taking a range of known strobe compositions and looking for the potential existence in each of them of two appropriate fuel-oxidizer pairs. In every case it was asserted that this was possible, although as the author freely admitted, in some cases the identification involved "clutching at straws". It should also be pointed out that some of the identified pairs may not exhibit the reaction characteristics that would be required for their proposed roles.

It is worth mentioning at this stage that the preferential oxidation of magnesium that was proposed by Krone[2] may not actually occur. As pointed out by Dreizin and Schoenitz[6], samples of residue from a high temperature reaction can continue to react during cooling, so such analyses as those performed by Krone are unlikely to represent the actual state of the reaction at elevated temperatures. In addition to these concerns regarding the likelihood that Krone's interpretation is correct, Nie et. al.[7]

showed that the two-stage process observed during the controlled oxidation of an alloy of magnesium and aluminum is the result of a change in the reaction mechanism that involves both metals at all stages and not, as others had previously concluded in studies of the same type, evidence of the preferential oxidation of either metal. Further evidence of the involvement of both aluminum and magnesium at all stages, this time in a freely reacting mixture of copper (II) oxide, magnalium and aluminum is provided by Harrison[8]. However, regardless of the truth or falsehood of Krone's conclusion, Shimizu's two component hypothesis remains valid – although it may mean that some of the previously proposed reaction candidates may need to be reconsidered.

As reported in a review article by Verbovytskyy and Harrison[9], there have been many studies of a wide variety of strobe compositions. However, apart from those that have already been cited here, very few of them make any significant attempt to shed light on the relevant chemical mechanisms.

A notable exception is the small number of reports that have proposed theoretical models of the strobe mechanism. Feng et. al.[10] and Davies[11] produced thermokinetic models that are based on the oxidation of solid, liquid and gaseous magnesium in atmospheres with varying oxygen concentrations, and Corbel[12] created a model in which the oscillation is claimed to be the result of an imbalance between the heat generated from a chemical reaction and that conducted to neighboring regions of the composition. Unfortunately, as is argued in the above-mentioned review[9], all three models fail, in one way or another, to reproduce the characteristic behavior of actual strobes.

It therefore remains the case that the strobe mechanism is still, at best, only poorly understood. The aim of the current paper is to examine a group of relatively simple strobe compositions and to report a series of observations that provide insights into the nature of the various reaction mechanisms.

Experimental

	A	B	C	D	E	F	G	H
Barium nitrate	71	68	64	61	57	53	50	0
Magnalium, -60 mesh	29	27	26	24	23	22	20	40
Sulfur	0	5	10	15	20	25	30	60

The eight compositions used in this study are listed in Table 1. Composition A is an approximately stoichiometric mixture of barium nitrate and magnalium, and compositions B to G are effectively mixtures of composition A with varying proportions of sulfur. Composition H is an approximately stoichiometric mixture of magnalium and sulfur. To each sample was added a further 3 % (dry weight) of nitrocellulose dissolved in acetone, included to act as a binder. The materials come from a range of different suppliers and, while they appear to be reasonably pure, the precise degree of purity of any of them is not known.

Two samples of each of the compositions were made by lightly pressing the moist mixture into thin-walled (two thicknesses of 80 grams per square meter paper) casings, 20 mm in length and 6.35 mm in diameter. Once fully dry, measurements of each sample's length and mass showed that, regardless of which composition was present, the density was close to 60 % of the relevant theoretical maximum.
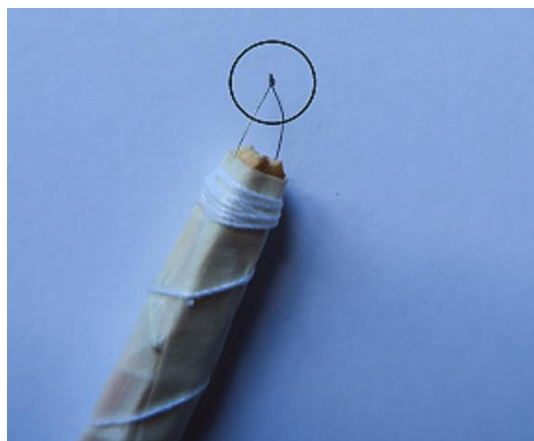

Figure 1. A thermocouple assembly. The imposed circle indicates the thermocouple's positioning within a 6.35 mm sample. The exposed sections of wire outside the sample were coated in an insulating material to protect them from any stray flame.

Five additional samples of composition E were made and fitted with a type G thermocouple, inserted at a known position, about halfway along the sample's length, to record the temperature changes at one millisecond intervals as the flame front passed by. Each thermocouple was constructed as a 5-turn twisted pair from 0.1 mm diameter tungsten (+ve) and tungsten-rhenium alloy (26 wt% Re) wires, as shown in Figure 1. Further details of the thermocouples' construction and the nature of the apparatus used to record the temperature profiles are given elsewhere[8, 13].

In all cases the samples were ignited with a hand-held blowtorch and the progress of the reaction was recorded with the aid of a Panasonic HC-X900 video recorder operating at 50 frames per second.

Results and Discussion

The preferred behavior of a strobe composition is that it should produce uniform, sharply defined flashes at evenly spaced intervals. However, as can be seen from the example in Figure 2, which is typical of the behavior of all the compositions from B to G in Table 1, this is not the case for any of the chosen compositions. They all produce flashes that differ significantly in both their intensity and duration. There are also large variations in the lengths of the intervening smolder phases – including cases where flashes are so close together that they are effectively not distinguishable.
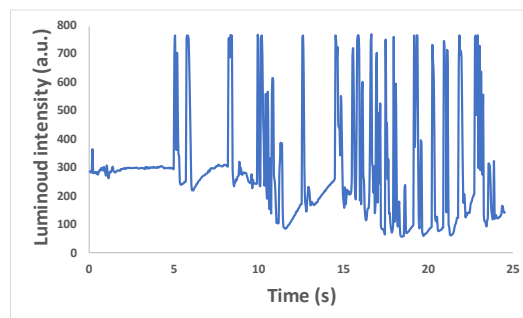

Figure 2. Variation of luminous intensity with time for an example of composition E.

To check whether the lack of regularity was the result of using a moderately coarse grade (60 mesh, < 250 micron) of magnalium, samples of composition F were made with a 275 mesh (< 53 micron) alloy. The result was that the flashes were more closely spaced, but there was no visible improvement in their regularity. Compositions of a similar nature, such as those reported by Shimizu[14], contain significant amounts of other ingredients, which may well act to regularize the flashes. For the present study it was decided to keep the number of ingredients as small as possible, to limit the number of potential reactions, despite the observational difficulties resulting from the irregular behavior.

That irregularity means, for example, that it was not possible to determine a meaningful value for the flash frequency for any of the tested samples – and, in consequence, even less possible to draw any conclusion about how the frequency depended on the samples' compositions.

A further consequence is that interference between the effects of multiple closely spaced flashes disrupted many of the measured temperature profiles, greatly reducing their usefulness in providing information about the reaction mechanisms in either the smolder or the flash phases. One of the clearer examples is shown in Figure 3, but such cases provide only limited clues to the chemical processes that are taking place.
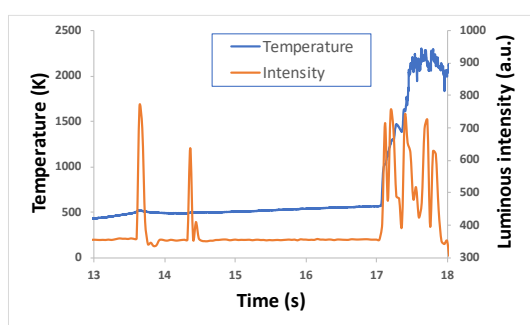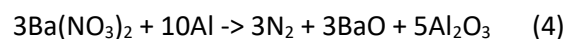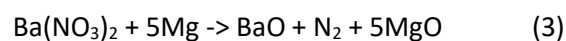

Figure 3. Variation of temperature and luminous intensity with time for an example of composition E.

One feature that is consistently shown is that the transition to the flash phase is very abrupt and occurs at a relatively low temperature – certainly not more than 1000 K and, as illustrated in Figure 3, possibly as low as 750 K. At such a transition, the rate of increase of temperature rises from around 100 K/s to over 8000 K/s, which suggests that the flash reaction is much more exothermic than any of the processes that may be occurring in the smolder phase.

For compositions of this type, Jennings-White suggested that the Shimizu hypothesis would be satisfied if the smolder reaction was between magnalium and sulfur and that the flash reaction involved barium nitrate and magnalium. If that is the case, the smolder reaction should be a combination of reactions such as those shown in equations (1) and (2), and the flash reaction should involve reactions of the type shown in equations (3) and (4).

$$Mg + S \rightarrow MgS \tag{1}$$

$$2Al + 3S \rightarrow Al_2S_3 \tag{2}$$

$$Ba(NO_3)_2 + 5Mg \rightarrow BaO + N_2 + 5MgO \tag{3}$$

$$3Ba(NO_3)_2 + 10Al \rightarrow 3N_2 + 3BaO + 5Al_2O_3 \tag{4}$$

These reactions were the basis for the specification of the approximately stoichiometric compositions A and H, listed in Table 1.

Samples of composition A proved somewhat difficult to ignite, requiring several seconds of exposure to the blowtorch flame. However, once ignited the reaction proceeded with almost explosive vigor until it self-extinguished, leaving a significant portion of unreacted material. This behavior is highly consistent with a strobe's flash phase, so reactions (3) and (4) appear to be viable candidates for that phase.

Composition G was found to be almost as hard to ignite and burned almost as vigorously as composition A, with the output of light, but without the tendency to self-extinguish. These features are not compatible with the observed behavior during a strobe's smolder phase, so it seems unlikely that reactions (1) and (2) represent the relevant mechanism.

Based on widely available values of the enthalpies of formation of the relevant materials, the heat released by reaction between barium nitrate and magnalium was calculated to be 7.8 kJ/g, and that released when magnalium reacts with sulfur is 7.1 kJ/g – a difference of no more than about 10 %. The

fact that the ignition of both compositions was somewhat difficult also suggests that both have at least moderately high activation energies. There does not appear to be a sufficiently large difference between the two mechanisms to meet the requirements of Shimizu's hypothesis, so it seems that – at least for the smolder phase – a more likely alternative needs to be found.

Some of the samples formed a residue that was mostly composed of a mixture of the oxides of barium, aluminum and magnesium, but a qualitative chemical analysis showed it to contain small amounts of sulfate $[SO_4]^{2-}$ and sulfide $[S]^{2-}$ radicals. This does indicate that reactions involving sulfur and one or more of the other components must have occurred at some stage, but only to a limited extent. The presence of sulfates was unexpected but, as mentioned earlier, analysis of such materials is unlikely to represent the actual state of the reaction at elevated temperatures; it is possible that sulfates may have been formed by atmospheric oxidation of one or more sulfides as the material cooled to the ambient temperature.
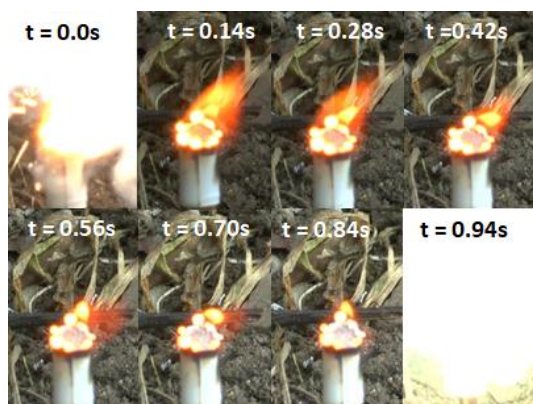

Figure 4. The progress of a single smolder phase, for an example of composition E.

Some clues to the nature of the smolder mechanism were found by examination of the video records of the behavior of the samples during this phase. As shown in Figure 4, each such phase produced a semi-transparent flame which steadily decreased in size until it almost completely disappeared immediately before the next flash occurred. The flame's appearance and the presence of sulfur dioxide in the released gas suggest that the principal reaction during this phase is the combustion of

sulfur in atmospheric oxygen, according to equation (5).

$$S + O_2 \rightarrow SO_2 \tag{5}$$

The heat released by this reaction is 4.7 kJ per gram of the reactants. This is significantly less than that produced by any of reactions shown in equations (1) to (4) and so is a better fit to the requirements of the Shimizu hypothesis. Furthermore, it should be noted that only a proportion of that heat will be available to raise the temperature of the as yet unreacted material, as significant amounts of heat will be lost to the surroundings, principally from the flame and the associated escape of hot gas. Some additional heat is likely to be absorbed to vaporize the remaining sulfur, which boils at a temperature of 718 K. Interestingly, this temperature is quite close to the lowest temperature (about 750 K) at which the transition to the flash reaction was observed to occur.

A further piece of evidence that supports this interpretation of the smolder mechanism is
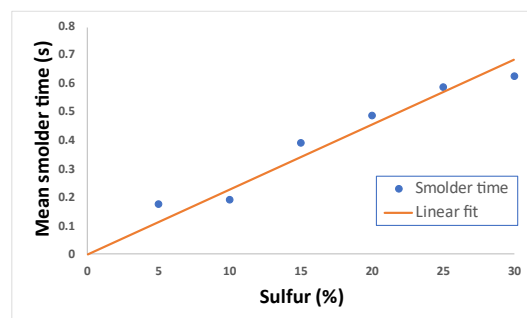

Figure 5. The variation of the mean smolder duration with sulfur content. The linear fit is one that is constrained to pass through the origin.

the variation of the length of the smolder phase with the composition's sulfur content. Although the irregular behavior, with flashes that sometimes overlap, makes it impossible to determine reliable values of the frequency, the durations of the individual smolder phases between distinct flashes can be measured with good precision. For any given sample, these durations showed great variation – by a factor of 10 or more – but their average value proved to be remarkably consistent, which indicates that it is likely to be a physically significant quantity. Furthermore, as shown in Figure 5, the variation of the mean duration with the composition's sulfur content is closely linear,

and the relationship is consistent with a direct proportionality.

A further check was made by immersing an ignited sample of composition E in a container filled with carbon dioxide. One additional flash was observed as the sample entered the gas, but the sample was then immediately extinguished.

This and all the other aspects of the observed behavior are consistent with the proposed interpretation, that the smolder mechanism is principally the result of the combustion of sulfur in atmospheric oxygen, with heat losses moderating the temperature increase, until the local concentration of sulfur falls to a sufficiently low value. Only then can the temperature rise sufficiently to trigger the flash reaction, which is most likely to be principally between barium nitrate and magnalium. That reaction is sufficiently energetic to disperse the reactants, thereby exposing a new surface in which the cycle can recommence.

Conclusions

The behavior of a series of pyrotechnic strobe compositions containing varying proportions of barium nitrate, magnalium and sulfur, together with a small quantity of an NC binder was observed, using a combination of simple techniques. These included the measurement of temperature profiles and the examination of various aspects of the video recordings.

It was argued that the reaction between magnalium and sulfur, proposed by Jennings-White[5] as a candidate for the smolder reaction, was, on energetic grounds, not likely to be involved to any great extent – a conclusion that was supported by the chemical analysis of residue from the reactions which revealed that only small amounts of compounds of sulfur were present. Instead, it was suggested that the combustion of sulfur in atmospheric oxygen was both energetically more appropriate and the only reaction that is consistent with the observational evidence presented in this study.

In contrast, it was concluded that the reaction between magnalium and barium nitrate is, as proposed by Jennings-White, likely to be the one that is responsible for producing the flashes.

While there was some evidence of the involvement of reactions between sulfur and the metal fuel in either or both phases, the amounts of material that were involved was found to be relatively small. It was therefore concluded that these reactions were unlikely to have a significant effect on the progress during either stage.

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