

A Study of a Set of Pyrotechnic Strobe Compositions Based on Ammonium Perchlorate

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Abstract: *The subject of this study is a set pyrotechnic strobe compositions, containing ammonium perchlorate, a magnesium-aluminum alloy, barium sulfate and potassium dichromate, together with a small amount of nitrocellulose to act as a binder. Despite the fact that compositions of this type have been previously studied in some detail, there is still no consensus about the reaction mechanisms that are likely to be involved.*

An examination of temperature profiles obtained from freely reacting samples provides support for earlier ideas about the nature of the flash reaction, but indicates that the principal reaction in the smolder phase is likely to be different from those that have previously been proposed.

Keywords: *Pyrotechnic strobe, Ammonium perchlorate, 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.

As reported by Wasmann [1], 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. A further vibrational composition, known as 'Golden Shimmeron', was reported by Stanbridge [2] to have been developed by Arthur Brock in the early years of the 20th century, and Smee [3] (great grandson of Arthur Brock and at one time a board member of Brocks Fireworks Ltd.) points out that Arthur Brock himself mentioned an effect that he called 'Shimmer Light' in a speech made to the press in 1911.

Those compositions were, at the time, proprietary to Brocks Fireworks and therefore not known outside the company. There appears to be no evidence of the development of similar effects by other contemporary

firework manufacturers and, in fact, there is little or no evidence of any other significant studies of compositions that burned in such an oscillatory manner throughout most of the following half century.

A revival of interest from the 1960s onwards resulted in the development of strobe compositions by workers in Japan, Russia and Germany. Shimizu [4] reported that at least one Japanese manufacturer was producing "Twinklers" as early as 1961 and that, in 1967, Y. Kinsei, of the Hosoya Firework Co., discovered that compositions based on ammonium perchlorate could also exhibit vibrational burning. In Russia, Madyakin and a group of co-workers made extensive studies of colored flame compositions, including ones that burned vibrationally. That research resulted in a series of patents, including one that describes a "Pyrotechnic composition of white flame with periodical flame flares" [5]. In Germany, studies by Krone [6] and Wasmann [7] were some of the first to propose potential mechanisms for the smolder and flash reactions. Krone's analysis of a cooled, partially reacted strobe composition that originally contained a 50:50 by weight alloy of magnesium and aluminum (magnalium) found

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it to contain about 30 to 35 % of the original aluminum content, but only traces of magnesium, which led him to conclude that magnesium was preferentially oxidized during the smolder phase and that the remaining aluminum was involved in the flash reaction. However, as pointed out by Dreizin and Schoenitz [8], samples of residue from a high temperature reaction can continue to react during cooling, so analyses such as that performed by Krone are unlikely to represent the actual state of the reaction at elevated temperatures. Nevertheless, it remains possible that magnesium may be – at least to some degree – preferentially consumed in the smolder phase.

Contemporaneously with Krone's study, Wasmann [7] investigated the behavior of a different range of compositions, leading him to similar conclusions regarding the two-stage nature of the reaction. However, he also pointed out that, in addition to the chemistry, physical processes such as changes of state and heat transfer must also be considered when attempting to understand a strobe's behavior.

Partially based on the conclusions arrived at by Krone and Wasmann, Shimizu [9] proposed the more general hypothesis that every strobe composition could be considered to contain two fuel and oxidizer pairs, one responsible for the smolder reaction and the other to create the flash. He examined a range of candidate compositions of each type and found that only some combinations produced an effective strobing action. It must therefore be concluded that, while his hypothesis may be a necessary condition, it is not a sufficient one. There must be other significant factors that need to be considered when attempting to understand a strobe's behavior.

One technique that has received little attention in the past is the measurement of the temperature evolution in a freely burning sample. Although Shimizu [9] used thermocouples to measure the ignition temperature in slowly heated mixtures of each

of a set of oxidizers mixed with an equal weight of magnesium powder, he made no further use of the information, other than to classify the oxidizers into two groups according to their ignition temperatures. Corbel's extensive study [10] of strobe compositions included spectrographic measurements of the variation of the temperature of ignited samples of five variant compositions. Unfortunately, with each measurement being subject to an estimated uncertainty of about ten percent, the results gave little or no information on the progress of the evolution from smolder to flash, and Corbel could only report the minimum and maximum temperature values attained during a reaction cycle. However, by repeating the measurements in atmospheres of argon, nitrogen, air and oxygen, she was able to conclude that the reactions were mainly dependent on oxygen provided by the strobe composition itself, with no observable reliance on the presence of atmospheric oxygen.

Embedding a thermocouple at a given point in a pyrotechnic composition is a more accurate and reliable method of obtaining a record of how the temperature changes as the flame front passes that point. Examples of the use of this technique include studies by Boddington et al. [11], Tribelhorn et al. [12], Brown [13] and Harrison [14]. Although it provides only indirect evidence of the physical and chemical processes that occur, it is one of the few techniques that can create a real-time record of changes that occur in a freely reacting pyrotechnic composition.

Experimental

The six strobe compositions used in this study, which approximately match the range of compositions previously studied by Corbel [10], are listed in Table 1. One difference is that Corbel used magnalium samples with average particle sizes ranging from 25 to 100 μm ; in this study, to keep the strobe frequency relatively low, the magnalium that was used had an average particle size of about 200 μm .

Table 1. The strobe compositions used in this study.

	A	B	C	D	E	F
Ammonium perchlorate	65.0	61.4	57.7	54.0	50.4	46.8
Magnalium, -60+100 mesh	11.0	16.0	21.0	26.0	31.0	36.0
Barium sulfate	18.3	17.2	16.3	15.2	14.2	13.1
Potassium dichromate	5.7	5.4	5.0	4.8	4.4	4.1

Table 2. Three further compositions.

	G	H	J
Ammonium perchlorate	73.0	0.0	57.7
Magnalium	0.0	26.0	0.0
Aluminum	0.0	0.0	21.0
Barium sulfate	20.6	74.0	16.3
Potassium dichromate	6.4	0.0	5.0

Three further compositions are listed in Table 2. The first of these (G) is effectively a base composition that, with the addition of appropriate amounts of magnalium, forms compositions A to F; composition H is an approximately stoichiometric mixture of its two constituents and composition J is the same as composition C, except that the magnalium is replaced by atomized aluminum that passes 100 mesh. 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.

Five samples of each of the compositions were made by adding a further 3 % (dry weight) of nitrocellulose dissolved in acetone, included to act as a binder, and then lightly pressing the moist mixture into thin-walled casings, 20 mm in length and 10 mm in diameter. The filling was done in two stages, with a type G thermocouple being inserted through the side wall of the casing after the first stage had fully dried. The column length and the sample's mass were measured at each stage and showed that, regardless of which composition was present, the density was close to 60 % of the relevant theoretical maximum.

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 and was used to measure the temperature in an ignited sample at one millisecond intervals. Further details of the thermocouples' construction and the nature of the apparatus used to record the temperature profiles are given elsewhere [14, 15].

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

Although five samples of each composition were made and tested, not all of them produced usable temperature profiles. In a few cases, particularly for the compositions containing higher proportions of magnalium, the profiles were disrupted by interference from the heat released from a preceding flash

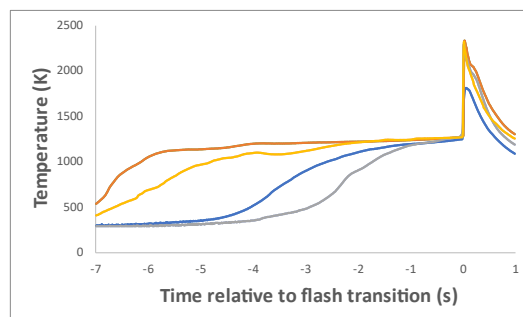


Figure 1. Temperature profiles for four samples of composition A, aligned by the onset of the flash reaction.

cycle, and in a few other cases the thermocouple failed part-way through the recording.

Four successfully measured temperature profiles for composition A are shown in Figure 1, where the records are arranged so that the starts of the flash phases are aligned. In all four cases the temperature at which the initiation of the flash phase occurs is very similar, being close to 1270 K, but the evolutionary paths taken during the smolder phases appear to be very different.

However, as is shown in Figure 2, if the records are aligned to give the closest match of the temperature profiles during the smolder

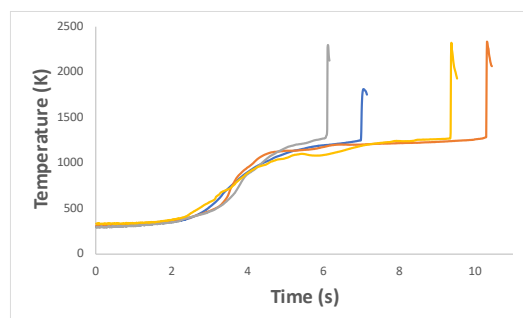


Figure 2. The same four examples of composition A as shown in Figure 1, but aligned by their smolder temperature profiles.

phase, a different picture emerges. The temperature profiles during the smolder phase are seen to follow very similar paths and the most significant difference is the length of the delay to the start of the flash. There is some indication that the variation in the delay may be the result of small differences in the relatively slow rate of rise in temperature as the critical value is approached.

A similar picture emerged when the same analysis was applied to compositions B to F. In each case it was found that there was a good match of the measured temperature profiles in the smolder phase, resulting in the same kind of agreement as that shown in Figure 2.

A more unexpected result was found when the temperature profiles of compositions A to F were compared. As shown in Figure 3, the profiles match sufficiently closely that, ignoring the inevitable noisiness of the data, they may be deemed to be virtually identical.

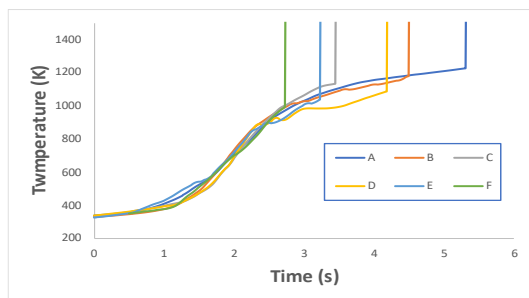


Figure 3. Averaged temperature records for up to five examples of each of the compositions A to F, aligned by their smolder temperature profiles.

The only significant difference in the behavior of these six compositions appears to be the temperature at which the transition to the flash phase occurs. As with the length of the delay, it was found that, for any given composition, there was a noticeable variation in the transition temperature from sample to sample. This may be an intrinsic feature of these compositions, but it could also be the result of the inevitable variations in the alignment of the thermocouple with the relevant portion of the sample. However, as shown in Figure 4, there was a regular and closely linear decrease in the mean value of the transition temperature for each composition with increasing magnalium content.

As shown in Figure 5, the rise in temperature for composition G – which contains no magnalium – is quite similar to that for

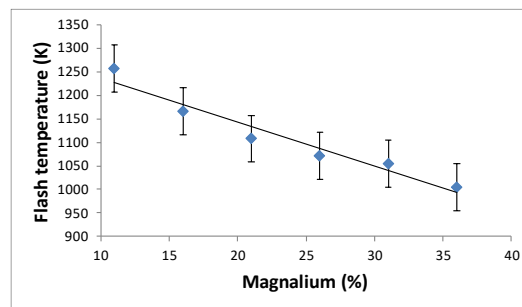


Figure 4. The variation of the temperature of the transition to the flash phase with magnalium content.

composition A, indicating that the exothermic decomposition of ammonium perchlorate is a significant contributor to heating during the smolder phase. The fact that the presence of magnalium results in a relatively small additional increase in temperature suggests that only a small amount of the metal fuel is oxidized during this phase.

Some idea of the amount that is consumed can

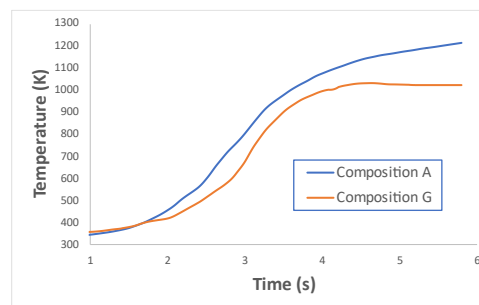


Figure 5. A comparison of the temperature profiles for compositions A and G.

be obtained by considering how the strobe frequency varies with a composition's magnalium content. The earlier studies by Corbel [10] and Harrison [16] on compositions of the type discussed here both show that the frequency increases linearly with the percentage of magnalium and, in both cases, extrapolating the observed relationship indicates that the frequency falls to zero for a magnalium content of about 7%. If it is assumed that this happens because the remaining metal content is insufficient to initiate the flash reaction, this figure represents an upper bound to the amount consumed during the smolder phase.

However, an alternative estimate can be made, based on the release of energy during both the decomposition of ammonium perchlorate and the oxidation of the metal fuel. A simple calculation, ignoring effects such as heat loss to

the surroundings and the changes in a sample's physical properties as the reaction progresses, indicates that the oxidation of less than 2 out of the 11 % of metal fuel in composition A is sufficient to account for the additional increase in temperature shown in Figure 5.

Although neither of these two values is likely to be entirely accurate, they both indicate that there is a limit to the amount of metal fuel that is oxidized during the smolder phase. Furthermore, the similarity shown in Figure 3 between the temperature profiles of all the samples, irrespective of their magnalium content, indicates that approximately the same amount of metal is oxidized in every case during this phase. In all cases it is the exothermic decomposition of ammonium perchlorate that causes the majority of the rise in temperature.

Given Corbel's finding [10] that the reaction's progress is unaffected by the presence or absence of atmospheric oxygen, a possible explanation may be that the degree of oxidation of the metal fuel is limited by the amount of oxygen-rich gas released during the decomposition of the ammonium perchlorate; the effect of an increasing proportion of magnalium is largely counterbalanced by a corresponding decrease in the amount of oxidizer. However, there is no obvious explanation of why these two effects appear to balance so exactly as to result in the closely similar smolder phase temperature profiles for all six strobe compositions.

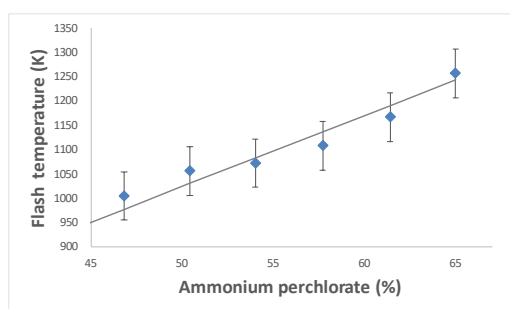


Figure 6. The variation of the temperature of the transition to the flash phase with ammonium perchlorate content. The linear plot is a least squares fit of a direct proportionality between the rise in temperature and the amount of ammonium perchlorate in each composition.

A further indication of the significance of ammonium perchlorate during the smolder phase is given by a plot of the flash transition temperature against the amount of the

oxidizer, instead of the magnalium content. As shown in Figure 6, the variation is not only closely linear, but is consistent with the rise in temperature from ambient being directly proportional to the composition's ammonium perchlorate content.

That relationship, in turn, gives rise to the further speculation that the trigger for the start of the flash reaction may simply be the local exhaustion of the ammonium perchlorate content. At present, the mechanism that causes the transition is unclear but, if this supposition is correct, it would imply that the flash reaction can only involve the oxidation of the remaining magnalium by the barium sulfate.

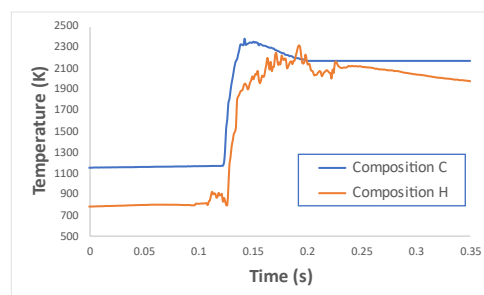


Figure 7. A detailed comparison of the temperature profile of the transition to the flash phase for composition C and a corresponding profile for an ignited sample of composition H.

A further aspect that is worthy of discussion is the nature of the transition from the smolder phase. Figure 7 shows a more detailed view of the temperature profile across such a transition for a sample of composition C, together with a corresponding profile for composition H. In the case of composition C, it can be seen that the transition to the flash phase is abrupt. The rate of change of temperature during the smolder phase is typically in the region of 500 K/s, but at the start of the flash reaction there is an almost instantaneous change in the rate, which rises by a factor of about a hundred, to a value in the region of 50,000 K/s. In the case of composition H, the initial slow rise in temperature is most likely to be the result of the transfer of heat from previous burning segments. But when the flame front reaches the position of the thermocouple, the change in the rate of increase in temperature is also sudden, and – at least in the early stages – attains a value similar to that observed for composition C. Despite the differences in the profiles in the later stages of the combustion,

both samples reach similar peak temperatures, in excess of 2000 K.

Despite not containing any magnesium, composition J demonstrated a definite, although somewhat irregular, strobing behavior. The frequency is approximately 0.1 Hz – compared with a frequency of about 0.7 Hz for composition C. Also, in contrast with the compositions containing magnesium, each ‘flash’ phase has a long duration – typically about 3 seconds, compared with one or two tenths of a second for compositions A to F – and exhibits rapid fluctuations in intensity. It also reaches a much higher temperature, resulting in the destruction of the thermocouple as the wires pass their melting point, a little above 3000 K.

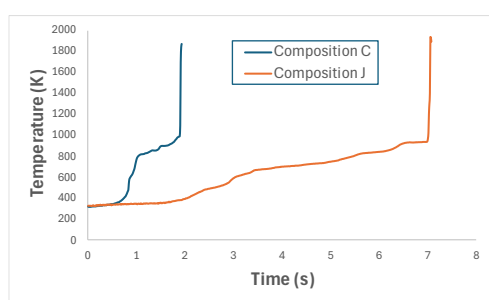


Figure 8. Typical temperature profiles for individual samples of compositions C and J.

As shown in Figure 8, the duration of the smolder phase for composition J is three to four times longer than that for composition C, but the flash transition occurs at a similar temperature in both cases. Bearing in mind that a longer smolder phase means that a greater amount of heat will be lost to the surroundings, it can be concluded that, as in the case of compositions that contain magnesium, a portion of the metal must be involved in the reaction during this phase.

These results show that aluminum alone can participate in both the smolder and flash reactions, but that it is significantly less effective in either role than when alloyed with magnesium. The greater effectiveness of the alloy could be the result of its lower melting point, the absence of a protective surface oxide layer, and/or some degree of preferential oxidation of the alloy's magnesium content.

None of the results reported here provide any direct evidence either for or against the

preferential oxidation of magnesium in the smolder phase. However, the evidence does indicate that only a small portion of the metal fuel is consumed in that phase, and that sufficient magnesium must still be present to significantly influence the progress of the flash reaction. It can therefore be concluded that any such preferential oxidation must occur to a significantly smaller extent than was reported by Krone, based on his analysis of a cooled, partially reacted sample.

Conclusions

An examination of the observed temperature profiles of ignited samples of a series of strobe compositions that are based on ammonium perchlorate and have previously been the subject of studies by Corbel [10] and Harrison [16] has led to the following set of hypotheses:

1. The rise in temperature during the smolder phase is principally the result of the exothermic decomposition of ammonium perchlorate.
2. A secondary source of heat during this phase is the oxidation of a relatively small proportion of the magnesium, the amount being likely to be limited by the steadily diminishing local supply of oxidizing gas resulting from the decomposition of the remaining ammonium perchlorate.
3. The flash reaction is not triggered until the local supply of ammonium perchlorate is virtually exhausted and, in consequence, that reaction principally involves only magnesium and barium sulfate.

A comparison of the performance of a composition containing aluminum with one containing a similar amount of magnesium indicated that magnesium plays a significant role in both the smolder and flash phases. The evidence presented here neither confirms nor denies the preferential oxidation of magnesium in the smolder phase. It does, however, show that only a relatively small portion of the metal fuel is consumed in that phase. It must therefore be concluded that, if such a process occurs, it cannot consume more than a modest fraction of the magnesium, leaving a significant amount to take part in the flash reaction.

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