Some Factors Affecting the Performance of a Class of Ammonium Perchlorate-Based Pyrotechnic Strobe Compositions

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Abstract: *Despite well over a century of research, which has seen the development of many effective pyrotechnic strobe compositions, there is as yet very little understanding of the strobe mechanism. In the past, theoretical models have been developed, but are here shown to be unable to explain many of the observed characteristics. Factors affecting the strobe frequency and the composition's thermal conductivity are re-evaluated, with the aim of producing a firm basis of fact for future advances in the understanding of the strobe mechanism.*

Keywords: *Pyrotechnic strobe, Ammonium perchlorate, Magnalium, Ignition*

Introduction

The characteristic feature of pyrotechnic strobe compositions is that they burn in an oscillatory manner. An ignited layer of composition starts burning with a relatively quiescent smolder reaction which eventually switches to a brief but highly energetic flash reaction, at which point the cycle begins again in the adjacent layer. The result is a regularly spaced sequence of bright flashes.

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. The only documentary evidence of the formulary's existence appears to be Wasmann's report[1] of a private communication from Ronald G. Hall who, at that time, was the technical director of Brocks Fireworks Ltd. According Harry W. Smee[2], who is a descendent of the Brock family, the formulary is not present in what remains of the company's papers and so it must be assumed to have subsequently been lost or destroyed. There is, however, additional indirect evidence of the formula's existence in a 1911 patent application by Frank Brock[3] for a very similar, but strontium nitrate-based, composition.

The uncertainties that now surround that early discovery could be viewed as being, in some sense, prophetic; despite more than a century of research, and the development of many other effective strobe compositions, there is still no clear understanding as to how any of them work.

The first studies that attempted to gain an understanding of the strobe mechanism were those of Krone[4] and Wasmann[5]. Although working with compositions of very different types, they both came to the conclusion that there were distinctly separate smolder and flash reactions, each using a different combination of the composition's ingredients.

That concept was further developed by Shimizu[6] who put forward the hypothesis that a strobe composition should be able to be described as a combination of two oxidizer/fuel mixtures, one responsible for the low temperature, smolder (or, in Shimizu's terms 'dark') reaction and the other for the higher temperature flash reaction. He investigated a number of different fuel/oxidizer pairings for their suitability to act in one or other of these roles. Although he found a number of effective compositions that fitted his hypothesis, they were based on a relatively small selection of the compositions he examined; many of his candidate dark and flash mixtures could not be combined to create samples that strobed effectively. It must be concluded that, regardless of the possibility that Shimizu's hypothesis may be a necessary condition, it cannot be a sufficient one, and has proved to have little or no predictive value.

A similar conclusion was reached by Jennings-White[7] who, in a survey of a wide range of known strobe compositions, attempted to show that they could plausibly be deconstructed into separate smolder and flash compositions. In the author's own words, there were cases where that attempt could be regarded as 'clutching at straws', possibly because

Article Details ***Article No:- 121***

Manuscript Received:- 21/05/2021 ***Final Revisions:- 14/06/2021***

Publication Date:- 15/06/2021 ***Archive Reference:- 1947***

the relevant chemistry was – and still is – insufficiently well understood.

Feng et al.[8] and Davies[9] have proposed thermokinetic models that are claimed to represent the strobe mechanism. Both models were based on theories of oscillating chemical reactions, where instabilities arise as the result of competing oxidation reactions between the three phases (solid, liquid and gas) of magnesium and an oxygen-rich gas produced by the decomposition of ammonium perchlorate. Although based on theoretically plausible reactions, both models suffer from the fact that they describe a situation where a given portion of the composition partakes in multiple cycles of the oscillation, which does not match the observed behavior.

Corbel[10] pointed out that the behavior of a strobe composition has much more in common with the variations in the speed of travel of the flame front that cause the spatial oscillations or "banded structures" that are sometimes observed in materials undergoing self-propagating high-temperature synthesis (SHS) than with any other form of chemical oscillator. Such instabilities tend to occur when an exothermic chemical reaction occurs on a much smaller timescale than the one associated with the transfer of heat from one layer of the composition to its neighbor. That suggests that the thermal conductivity of the composition is a significant factor that needs to be taken into account in any description of the strobe mechanism, and Corbel proposed a simple layered model that balanced the rate of heat being generated in one layer with the rate at which heat was conducted to neighboring layers.

Although the inclusion of the effect of heat transfer seems likely to be a significant advance in the understanding of the strobe mechanism, the precise model proposed by Corbel fails, as it can be shown that it does not describe an oscillation. Careful inspection reveals that the model's output, presented as a succession of peaks that Corbel claims to be evidence of a strobing behavior, is nothing other than a series of records of the change in temperature at a number of equally spaced points as the flame front moves past them at a constant rate.

Any viable theory of the strobe mechanism must be consistent with all the observed factors that affect the performance. But that raises the question of how well these factors are known, as the reliability of a theory can be no greater than that of the experimental data upon which it is based.

There have been very few experimental studies aimed at shedding light on the factors that affect the performance of strobes. Domanico[11] studied a composition consisting of ammonium perchlorate, magnesium, potassium dichromate and potassium sulfate, concentrating on a straightforward description of the dependence of the burn rate and the strobe frequency on the amount and particle size of the magnesium, without attempting to explain their significance. Corbel[10] made a much more extensive study of these factors on a range of compositions and found significantly more precise relationships.

The current study re-examines – and, where necessary, re-evaluates – the relationships between the strobe frequency and the amount and particle size of the composition's magnalium content. It also investigates the dependence of a composition's thermal conductivity on the magnalium content, which seems likely to be a significant factor in any future advance in the understanding of the strobe mechanism.

Experimental Section

The cylindrical samples that were used to investigate the dependence of the strobe frequency on both the magnalium content and the magnalium particle size were formed in thin-walled tubes with an internal diameter of 10 mm, formed from six lightly pasted turns of 70 gsm paper. Each composition was bound with an additional 2.5% (dry weight) of nitrocellulose dissolved in acetone. The damp composition was lightly pressed by hand into dry, pre-weighed tubes and left to dry for 24 hours at room temperature. Each assembly was then re-weighed and the length of the composition was measured with the aid of a digital micrometer. The calculated density of the samples was found to be somewhat variable, lying within the range of 50 to 60% of the theoretical maximum density (TMD).

The samples were ignited by the use of a hand-held blowtorch and each trial was recorded with the aid of a Panasonic HC-X900 video recorder, operating at 25 frames per second.

A hot wire technique was used to measure each unreacted composition's thermal conductivity. A tungsten wire of diameter 85 μm was used both as the heating element and temperature sensor, as described by Alvarado et al.[12]. The wire was mounted centrally in a test cell with internal dimensions 50x15x15 mm, which was then filled with a lightly pressed, approximately 13.5 g sample of the relevant composition, in this case with no added binder. The calculated density of all the samples was found to be 47 ± 1% of the TMD. Measurements of the variation of the potential difference across the wire with time were made with a series of currents in the range from 200 to 600 mA. The thermal conductivity, k, was calculated from the slope, m, of the linear portion of the plot of the change in voltage against the natural logarithm of the time, using the relation:

$$m = I^3 R_0^2 \sigma / 4\pi L k \qquad (1)$$

where I is the current, R_0 the initial resistance of the wire, σ the temperature coefficient of resistance of the wire's material and L is the wire's length.

The relatively small size of the cell means that the measurements are subject to a degree of error. However, the current study is concerned only with the general trend of the variation of thermal conductivity with magnalium content and so does not require particularly precise results.

Results and Discussion

The Effect of the Magnalium Particle Size

Although Domanico[11] noted a dependence of a strobe composition's overall burn rate with the metallic fuel's particle size, Corbel[10] was the first person to make a detailed investigation of the effect of the particle size on the strobe frequency, based on observations of compositions made with magnalium samples of six different average particle sizes.

She initially proposed a linear relationship between the mean time interval between flashes and the particle diameter by considering only the results for the four smallest particle sizes, claiming that the compositions containing particles of the two largest sizes burned too irregularly to be included. In a later paper, Corbel et al.[13] proposed a somewhat loose-fitting linear relationship across all six particle sizes. The two proposed relationships are reproduced in Figure 1.

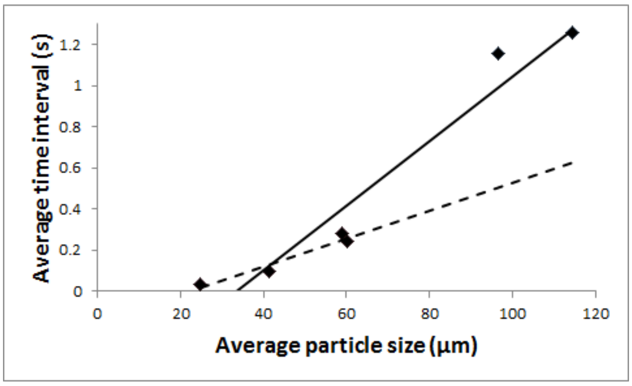


Figure 1. *The two linear relationships proposed by Corbel[10] (dotted line) and Corbel et al.[13] (solid line) between the strobe interval and the magnalium particle size.*

The test samples used in this part of the current study were made from the composition shown in Table 1, which is identical to that used by Corbel. Magnalium from a variety of sources was sieved into five separate grades, with average particle sizes ranging from 55 to 297 µm – a series that overlaps the range investigated by Corbel, but also extends to significanly larger mean diameters.

Table 1. *The composition used in the investigation of the dependence of the strobe frequency on the magnalium particle size.*

Material	%
NH_4ClO_4	57
$BaSO_4$	16
Magnalium	22
$K_2Cr_2O_7$	5

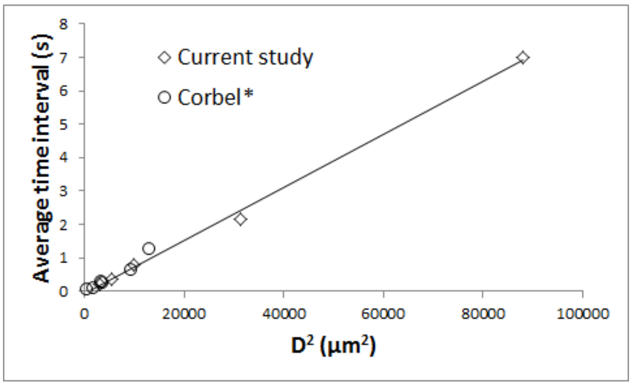
The results of the current study, together with those reported by Corbel[10], are given in Table 2, which shows that the time intervals steadily increase with increasing particle diameter, but the relationship appears to be far from linear.

Table 2. *The dependence of the flash interval on the magnalium particle size.*

Passes Mesh no.	Retained on Mesh no.	Mean Diameter (µm)	Interval (s)
-	-	25*	0.04*
-	-	41*	0.10*
250	-	55	0.22
-	-	59*	0.29*
-	-	60*	0.24*
200	-	74	0.37
-	-	97*	0.63*
100	200	100	0.79
-	-	115	1.25*
60	100	177	2.14
40	60	297	7.00

* Reproduced from Corbel[10].

In fact, as shown in Figure 2, plotting the average time interval, τ, against the square of the mean particle diameter, D, results in a linear relationship that appears to be very close to a direct proportionality.



* Using data reproduced from Corbel[10].

Figure 2. *The variation of the interval between flashes with the square of the mean magnalium particle diameter.*

It therefore seems reasonable to express the frequency, F, as:

$$F = 1/\tau \propto 1/D^2. \qquad (2)$$

With a few additional assumptions, this result is capable of being expressed in an alternative, and potentially more significant way. The surface area, a, and volume, v, of a particle are respecively proportional to the square and the cube of a typical dimension, D. If we make the simplifying assumptions that we are dealing with collections of particles of approximately similar shape and that in each sample the particles are approximately equal in size, their number, N, in a fixed quantity of the material is given by:

$$N \propto 1/v \propto 1/D^3 \qquad (3)$$

and the total surface area, A, can then be written as:

$$A = N.a \propto N.D^2 \propto D^2/D^3 = 1/D. \qquad (4)$$

Combining relationships (2) and (4) gives:

$$F \propto A^2 \qquad (5)$$

That the strobe frequency can be expressed as being directly proportional to the square of the total surface area of the magnalium may well prove to be a significant factor in understanding some aspects of the reaction.

The Effect of the Magnalium Content

The compositions used in this part of the study were chosen to match the range of compositions used by Corbel[10] in her original investigation of the dependence of the strobe frequency on magnalium content, and are listed in Table 3. The compositions vary in their magnalium content, while the relative proportions of the other ingredients to each other remains constant. In all cases, magnalium with a mean particle diameter of 100 µm was used. This is coarser than the sample used by Corbel, which had an average particle size of 41.3 µm, and was chosen so that the strobing action could be recorded without the need to use a high-speed camera.

Table 3. *The six compositions used in the investigations of the dependence of the strobe frequency and the thermal conductivity on the magnalium content.*

Material	A	B	C	D	E	F
NH_4ClO_4	65.0	61.4	57.7	54.0	50.4	46.8
$BaSO_4$	18.3	17.2	16.3	15.2	14.2	13.1
Magnalium	11.0	16.0	21.0	26.0	31.0	36.0
$K_2Cr_2O_7$	5.7	5.4	5.0	4.8	4.4	4.1

The results shown in Table 4 are averages of three trials with each composition. The burning rate and strobe frequency were directly observed quantities and the amount consumed in each flash cycle was calculated by dividing the rate by the frequency.

The very low strobe frequency and significant irregularities in the burning rate of the samples with the lowest magnalium content made it difficult to obtain reliable measurements in that case, which is likely to be an unwanted consequence of the decision to use a relatively coarsely grained magnalium. But in all but that case, all three properties were found to vary in a regular manner.

Table 4. *The dependence on the magnalium content of the burning rate, the strobe frequency and the thickness of the layer that is consumed in each flash cycle.*

Magnalium (%)	Rate (mm/s)	Frequency (Hz)	Per flash (mm)
11	0.57	0.38	1.50
16	0.68	0.37	1.84
21	0.86	0.60	1.43
26	0.95	0.87	1.09
31	0.98	1.02	0.96
36	1.18	1.46	0.81

For example, as illustrated in Figure 3, provided that the data point corresponding to the samples with the lowest magnalium content is excluded, the frequency showed a closely linear dependence on the amount of magnalium, which is consistent with Corbel's findings.

To be considered viable, any explanation of the strobe mechanism must show how all three dependencies arise. Corbel's strobe model[10,13] does predict, for a given metal particle size, appropriate relationships between metal content and both the burning rate and the strobe frequency but, being derived for layers of composition of arbitrary thickness, has nothing to say about the amount of material consumed in each flash cycle.

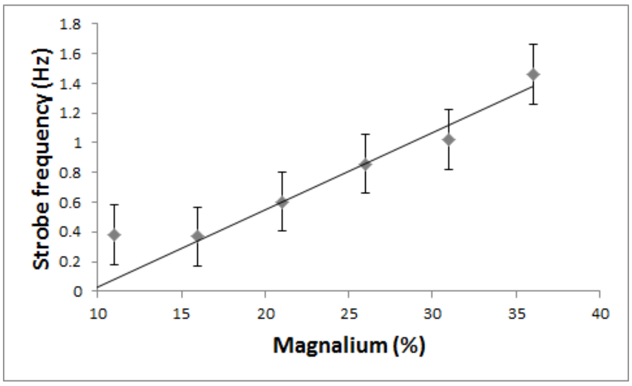


Figure 3. *The variation of the strobe frequency with magnalium content. The linear fit does not take into account the potentially problematic data point that corresponds to a magnalium content of 11%.*

There is no general theory that can accurately predict the thermal conductivity of an arbitrary mixture of two or more particulate materials. However, as pointed out by Tavman[14], there are two extreme cases, known as the series and parallel phase distribution models. The series model is one in which the component materials are considered to exist in separate layers, normal to the direction of heat flow, so that heat must flow through each layer in turn. Since, in a particulate mixture, any heat flow path must pass through particles of all types, the series model is likely to be the one that most closely approximates to the real situation.

For the series model, it can be shown that the overall effective thermal conductivity is dominated by materials with low conductivity. Indeed, applying the model to the compositions listed in Table 3 indicates that the effective thermal conductivity increases by about 40% as the magnalium content increases from 11 to 36%.

This raises a further potential issue with Corbel's strobe model[10,13], which indicates that an approximately sixfold increase in thermal conductivity is required in order to account for the observed variation in strobe frequency. However, it is not clear that the series model – which makes many assumptions, including that there is perfect thermal contact between the different layers – provides a reliable estimate. In consequence, it was decided that an experimental determination of the compositions' thermal conductivities would be the only way to be certain. The results are shown in Figure 4.

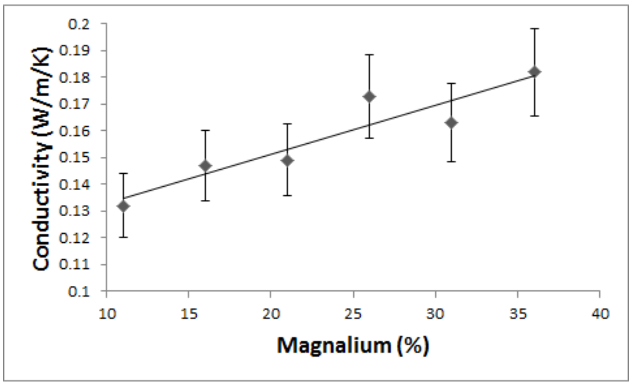


Figure 4. *The variation of the thermal conductivity with magnalium content.*

Comparing the experimental values with the results obtained from the series model showed that the model significantly overestimates the individual thermal conductivities, but correctly predicts the general trend. The measured values ranged from 0.132 to 0.182 W/m/K – a change of a little under 40% for a more than threefold increase in the magnalium content.

Conclusions

Following a brief discussion of the current state of the understanding of the pyrotechnic strobe mechanism, it was shown that existing theoretical models are incapable of accounting for all the experimentally observed features.

A series of measurements was made on a commonly used class of pyrotechnic strobe composition to re-evaluate the effects of changing either the amount or the particle size of its magnalium content.

The strobe frequency was shown to be inversely proportional to the square of the mean magnalium particle size and hence directly proportional to the square of the magnalium's total surface area – a result that may be a pointer to some aspect of the nature of the chemical reactions that occur in the smolder phase.

As was previously reported by Corbel[10], the strobe frequency and the rate of progress of the flame front were found to vary linearly with the magnalium content. In turn, those relationships imply that, for each composition, there is a definite and characteristic thickness to the layer of material that is consumed in each flash cycle.

Corbel's model is the only one to include the effect of the composition's thermal conductivity but, in addition to other issues with that model, it requires a variation with magnalium content that is more than a magnitude greater than that which has been observed.

These findings represent a relatively small, but essential first step along the path to the development of a better understanding of the strobe mechanism.

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