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A major effort has been undertaken to review all articles for correctness. However, it is possible that errors remain. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

Table of Contents

Issue Number 4 Winter 1996

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SEM Studies on a Strobe Star Composition

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ABSTRACT

Data obtained from an analysis of an extinguished strobe star using the technique of scanning electron microscopy (SEM) is used to provide additional evidence for a previous model for the cyclic burning process seen in a white strobe star composition. The model relies on the generation of hot liquid on the surface of the star to initiate the burning process.

Keywords: strobe star, scanning electron microscopy (SEM), hot liquid model

Introduction

The phenomenon of repeated cyclic flashing of a star is well documented.[1-4] It is thought to consist of alternate dark and light reactions, with the formation of localised "hotspots" resulting in an ignition of the gas evolved from the composition. The star then appears to self extinguish, and the cycle repeats.

This model was proposed by Shimizu[1] as a result of detailed and comprehensive experimental studies. The burning of the star is thought to start with a so-called "dark" reaction in which the combustion reaction appears to proceed without the generation of significant amounts of light. After a delay which can range from a few tens of milliseconds to several seconds depending on the composition, the semi-reacted zone undergoes a rapid reaction, producing a strong flash of light accompanied by a burst of noise. This is the "light" reaction. It is thought that a thin layer of semi-reacted material remains on the surface of the composition, and results in another "dark" reaction. The combustion process then cycles between "dark" and "light" reactions, thus producing the attractive stroboscopic effect.

The chemical nature of the "dark" and "light" reactions or the proposed thin layer of semi-reacted material have yet to be fully elucidated. This is not particularly surprising, since the examination of fleeting chemical phenomena on an extremely hot surface is not a trivial matter. In this paper, an extinguished white strobe star was examined using SEM and X-ray fluorescence techniques, these being two methods which have not been applied to the investigation of pyrotechnic strobe effects. Evidence obtained from these studies has been examined in the light of previous postulates for the strobe effect mechanism.

Composition Details

A relatively complex white strobe composition has been used for the studies presented in this paper. The base composition used is given in Table 1.

A star was used instead of powder in order to simplify the SEM work. This necessitated the use of a binder. Binders for strobe compositions need to be carefully selected so that they do not interfere with the strobing process.[1,2] Several binders were assessed for their suitability and rejected, including dextrin paste, epoxy resin, resorcinol resin, xanthan gum, accaroid resin, beeswax and polyvinylpyrrolidone. Locust bean gum was found to be the best binder of those tested, since it did not interfere too much with the strobe process. Further work is in progress on several binders in order to find a suitable one for use in simple pumped stars.

Table 1. Components of White Strobe Star Composition.

Material	Grade	Parts
Barium nitrate	140 mesh	7.0
Magnalium alloy (50:50)	60 mesh	2.0
Ammonium perchlorate	140 mesh	0.25
Antimony trisulphide		0.25
Sodium oxalate		0.25
Potassium benzoate	140 mesh	0.25
Binder (locust bean gum)		0.50

The solid components outlined in Table 1 (except the binder) were sieved separately, then mixed by repeated tumbling on paper. This was then added to a thick paste made from the binder and water, and the resulting composition was thoroughly mixed until homogeneity had been achieved. The composition was pressed into stars using a small handpress. The stars were dried in an oven for 2 hours at 60 °C.

The pellet was ignited using a silicon/red lead primer. A Black Powder based priming composition was tried, but was found to be unreliable.

Experimental

The SEM photograph taken from a star which had initiated but failed to function fully is reproduced in Figure 1. Table 2 represents an elemental analysis produced by the X-ray fluorescence method of the marked zones in Figure 1. No complex sample preparation was required. The star was fixed to a metallic probe, and placed in the instrument sample chamber. The machine used was a Jeol JSM840.

Area **a** has the appearance of a cooled liquid. Areas **c** and **d** appear to contain the flash ignition site (**c** being a charred zone, **d** being the actual flash site). Areas **b** and **f** appear to be unreacted composition. Area **e** appears to be a localised charred area.

Discussion

When combined with visual observations, this evidence immediately suggests that ignition of the star involves the liquefaction of one (or more) of the components of the star. This is based on the presence of zone **a**, which appears to be a cooled liquid.

The fact that area **a** does not cover the whole of the surface of the star suggests that the whole of the material does not liquefy during the combustion process. It is possible that liquefied areas correspond to the “hotspots” described by Shimizu.[1]

Area **a** has a relatively large amount of barium present. It is therefore possible that ignition of the star involves the melting of a barium compound. The only barium compound present in the initial composition is barium nitrate, which melts at a relatively high temperature (about 860 K), but it is possible that the barium nitrate could form a solid solution with at least one other component.

Table 2. Elemental Analysis of Zones in Strobe Star.

Zone	C	O	Na	Mg	Al	S	Cl	K	Sb	Ba
a	L	L	L	L	L	L		L	L	H
b	L	L	M	M	M	M	L	L	L	H
c	H		M	M	M		M	H	M	M
d	L						M	H	M	H
e	H									
f	L	L	M	M	M	M	L	L	L	M

Key : L = low, M = medium, H = high, blank = not present.

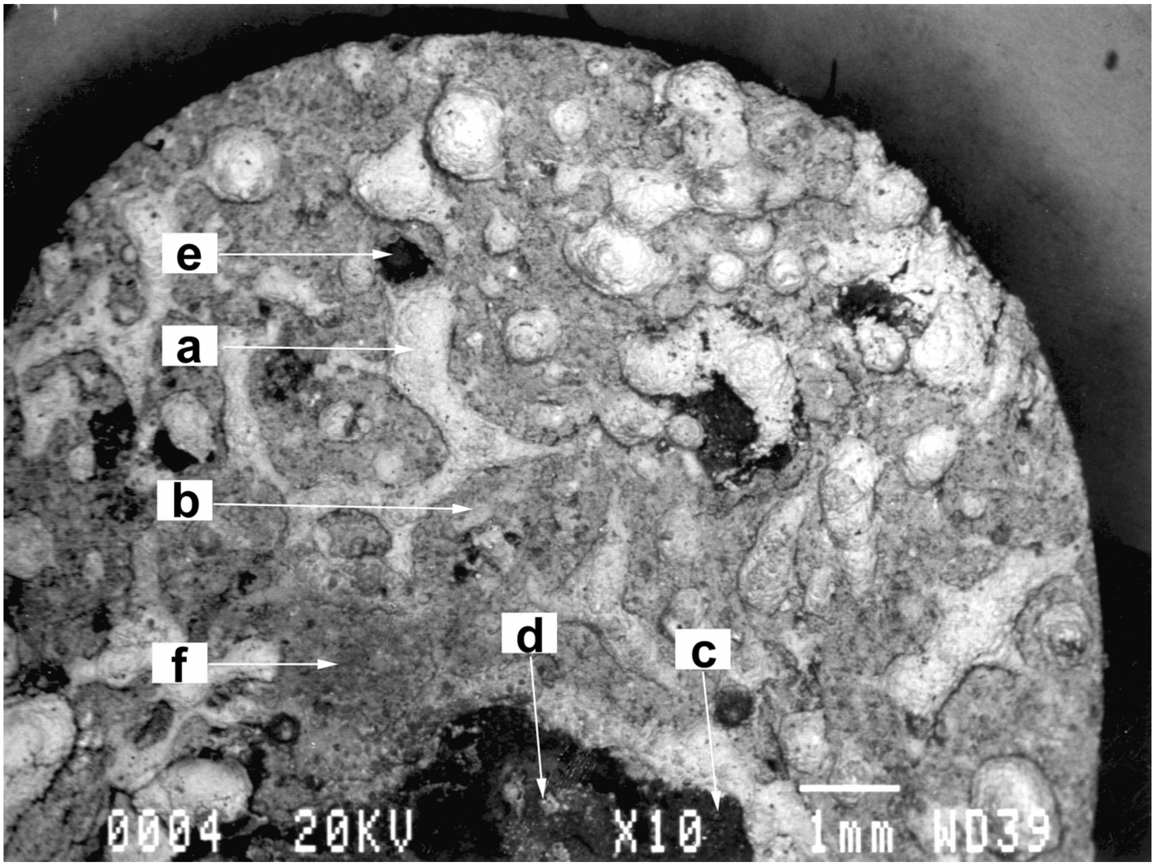

Figure 1. SEM photograph of surface of strobe star.

This would result in a eutectic mixture with a significantly lower melting point than barium nitrate. Thermal analysis studies are currently in progress to examine possible eutectic mixtures involving barium nitrate.

The star is difficult to ignite. This ties in with the above proposal that ignition requires the melting of an inorganic solid or solid solution. The high temperature required for this process may be responsible for the charring zones (**c** and **e**) in the vicinity of the unreacted cooled liquid (area **a**) and the flash site (area **d**). The charred zones contain a relatively large amount of carbon, which indicates the rapid burning of organic material such as the potassium benzoate or the organic binder.

The production of gaseous products from the light-producing reaction will probably blow some of the unreacted hot liquid off the surface of the star. It is possible that subsequent ignitions will take place at other points on the surface of the star, where enough hot liquid remains. If, however, too much of the liquid is blown off the surface of the star, then the reaction will cease and the star will go out.

The presence of ammonium perchlorate appears to facilitate the strobing process. Chlorine is present in areas **b**, **c** and **d**. Area **b** is unreacted and unmelted composition, so the presence of chlorine is not entirely unexpected. It is possible that the presence of ammonium perchlorate speeds the production of the hot liquid phase, but its presence is not critical since strobing will occur without ammonium perchlorate being present.[5]

Conclusion

The work presented in this paper suggests that the mechanism of operation of the strobe star relies on the generation of a hot liquid on the surface of the star. The liquid may contain barium nitrate, and its melting is possibly accelerated by the presence of ammonium perchlorate. The presence of the hot liquid results in a light generating reaction at points on the surface of the star (i.e., the strobing process). This was first put forward by Shimizu in the early 1980's.[1]

After the light-generating reaction has occurred, the gases produced during this reaction blow any localised hot liquid off the surface of the star. The process will then repeat the above cycle. If, however, too much of the hot liquid is removed from the surface of the star, then the reaction will stop and the strobing will cease.

Ternary strobe systems are currently being examined using the techniques used in this work, and it is intended to use gas analysis methods to provide additional data on which a more descriptive model can be constructed. Work on finding a suitable binder is also in progress. We hope to be able to report on this work in the not too distant future.

Acknowledgments

The author wishes to thank Mr. Rob Kimber (RMCS) for the SEM analyses.

References

1) T. Shimizu, "Studies on Strobe Light Pyrotechnic Compositions", *Pyrotechnica VIII*, 1982, p 5–28.

2) R.G. Cardwell, "Strobe Light Pyrotechnic Compositions : A Review of their Development and Use", *Pyrotechnica V*, 1979, p 6–24.

3) U. Krone, "Strahlungsemission in Intervallen - oscillierende Verbrennung pyrotechnischer Satze", *Pyrotechnik : Grundlagen, Technologie und Anwendung* (International Conference of ICT, 1975, Karlsruhe, BRD), 1975, p 225–238.

4) C. Jennings-White, "Blue Strobe Light Pyrotechnic Compositions", *Pyrotechnica XIV*, 1992, p 33–45.

5) R.I. Grose, unpublished data.

Errata — Issue No. 3

Page 39, Equation 6 A_e should be A_b. The equation should read:

$$P = B\left(\frac{A_b}{A_t}\right)^{\frac{1}{1-n}}$$

Flash Powder Output Testing: Weak Confinement

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ABSTRACT

A variety of flash powders were tested under weak confinement to determine the sound pressure levels and tonal characteristics produced. In these tests it was found that: the sound output from mixtures prepared with potassium perchlorate from four manufacturers are essentially equivalent; there are significant differences in the level of sound output as a result of using six different common aluminum powders; the addition of either of two common flow or bulking agents have essentially no effect on the sound produced; the substitution of potassium chlorate for potassium perchlorate in a common flash powder has essentially no effect on the sound produced; and the addition of antimony sulfide or sulfur reduces the duration of positive phase without increasing the level of the sound produced. In short, it was found that nothing surpassed the level of sound produced by a 70:30 mixture of reasonably high-quality potassium perchlorate and a high quality flake aluminum powder. This is significant because the use of potassium chlorate, antimony sulfide, and sulfur, can seriously increase the sensitiveness of flash powders to accidental ignition.

Keywords: flash powder, sound pressure level, blast pressure, weak confinement, positive phase

Introduction

The science of pyrotechnics as applied to fireworks frequently suffers from a lack of basic scientific data. Too often, conjecture serves as the basis for what eventually becomes "common knowledge". The sound output from flash salutes is one area in which there is much common knowledge but little quantitative data reported in the literature. This study of the sound output from a collection of flash powders under weak confinement is an attempt to provide some of the needed measurements.

For most of this study, only flash powders using 70% potassium perchlorate and 30% aluminum were examined. With these flash powders, the relative effectiveness of four types of potassium perchlorate, six types of aluminum, and two bulking agents were examined. Following this, a series of seven flash powders using one or a combination of potassium chlorate, barium nitrate, antimony trisulfide and sulfur were tested for sound output under the same conditions.

Background

All blast waves, even those produced by radically different explosives have much the same basic shape,[1a] illustrated in Figure 1. The blast wave is a shock wave, traveling greater than the speed of sound in air. Prior to the arrival of the shock front, ambient (atmospheric) pressure is unaffected. With the arrival of the shock front, there is a near instantaneous rise in pressure (overpressure) to some peak value.

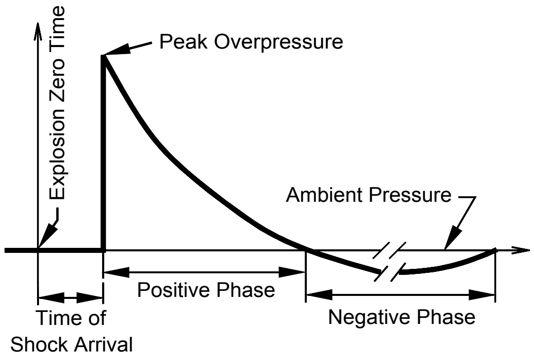

Figure 1. Sketch of a typical blast overpressure wave showing pressure as a function of time.

Thereafter, overpressure falls, returning to ambient level. This excursion is termed the "positive phase" of the blast wave. The peak overpressure attained is a function of the magnitude of the explosion and, to a lesser extent, on ambient pressure. Except for distances very close to the explosive, there is a "negative phase" of the blast wave.[1b] This negative phase is much less extreme than the positive phase, although it lasts somewhat longer. Figure 2 is the blast wave recorded for one test salute used in this study. At increasing distances from the explosion, the peak overpressure becomes less, and the duration of the positive phase becomes longer; this effect is illustrated in Figure 3.

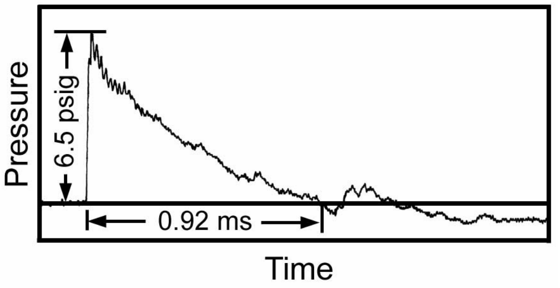

Figure 2. Blast wave from a test salute using 70:30 potassium perchlorate and German dark aluminum.

For the most part, it is only peak overpressure and the duration of the positive phase that are needed to characterize a blast wave. In terms of the sound produced, peak overpressure determines the loudness of an explosion, and the duration of positive phase presumably determines its tonal quality. That is to say the higher the overpressure, the louder the sound of the explosion. Also a short positive phase is expected to correspond to an explosion with a sharp crack sound, and a long positive phase, to a more mellow boom. Thus, from what is seen in Figure 3, all explosions sound louder and sharper at close range, and become softer and more mellow at greater distances. (For a more complete discussion of the sound levels and their measurement, see reference 2.)

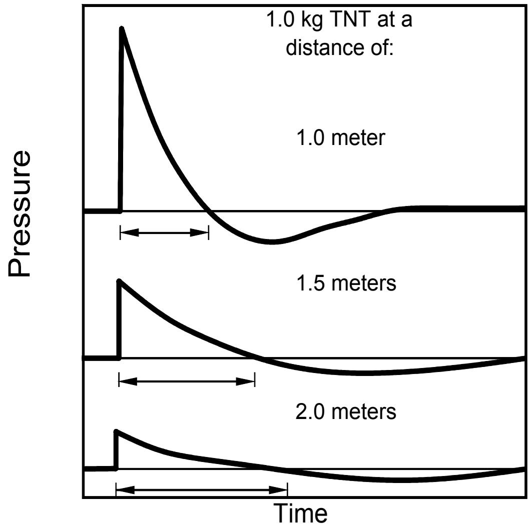

Figure 3. Sketch of the decay of a typical blast wave with distance from the explosion; based on data from Kinney & Graham.[1c]

Experimental Method[a]

The flash powders for these tests were each prepared by pre-screening the ingredients, rough mixing until there was uniformity in color, then tumbling at a rate of approximately 60 revolutions per minute in closed containers for one hour. This degree of mixing far exceeds that generally employed by the fireworks industry, but was chosen to eliminate any inconsistencies in test results that are caused by incomplete mixing.

For each flash powder type, three test salutes were prepared and fired. The test salutes were made using 3 ounce (90 mL) polyethylene bottles with metal screw caps. The containers were chosen to provide an easily reproducible configuration with fairly consistent confinement. Each container was loaded with 50 g (1.8 ounce) of flash powder. A Daveyfire[3] hooded electric match (SA–2001) was used for ignition. The match was installed in the cap of each container using a thermal setting adhesive, see Figure 4. Each test salute container was mounted capside down, such that flash powder filled the space between the electric match and its hood. This was done to provide a minor degree of confinement for that small amount of flash powder, thus perhaps providing a more powerful ignition stimulus. It was anticipated that this would tend to compensate for the relatively weak confinement provided by the polyethylene bottle.

Figure 4. An electric match installed in the cap of a test salute casing (polyethylene bottle).

For test firing, the salutes were suspended 3.5 feet (1.2 m) above the ground. A pair of free-field blast gauges (PCB Piezotronics[4] 137A11) were positioned in line at the same height and at a distance of 4.0 feet (1.9 m) from the center of the test salute, see Figure 5. Upon firing the salute, blast overpressure data was collected using amplifying power supplies and a digital oscilloscope (50 MHz), for subsequent plotting, see Figure 6.

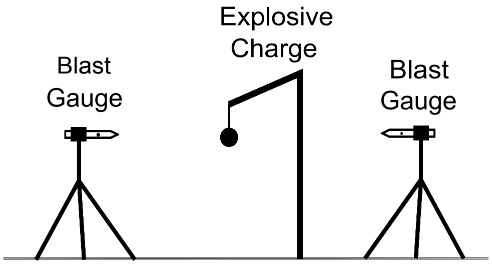

Figure 5. Sketch of the physical arrangement of test salute and blast gauges.

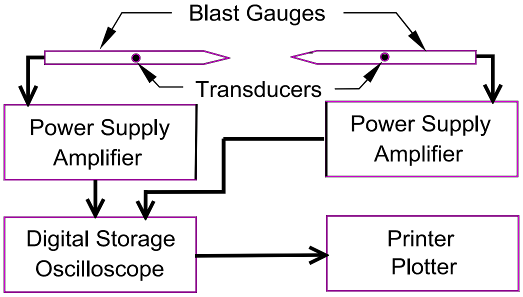

Figure 6. Block drawing for the data collection of blast overpressure data.

Test Results

In this section, the characteristics of the flash powders and the raw output data are presented. Discussion of the results is deferred to a later section.

Potassium Perchlorate Types

The four types of potassium perchlorate used in this study are described in Table 1.

As determined by microscopic analysis, only the Swedish material has fairly sharp angular particles, such as might be expected from grinding. The other three materials have particles with a more generally rounded appearance, such as might be expected from milling. The screen analysis for these materials is presented in Table 2. Small samples of potassium perchlorate, as received from the supplier, were sieved for three minutes using a vibrating sieve shaker. It is likely that the material contained some moisture and that drying may have produced slightly different sieve analyses. This not withstanding,

Table 1. Types of Potassium Perchlorate Investigated.

Source	Manufacturer	Product Information
Swedish	EKA Nobel(a)	S140, –140 mesh
US	Western Electro Chemical[5]	60 micron
Chinese	Senochem(a)	Hunan China(b)
Italian	Societa Elettrochimico(a)	Borgo Franco(b)

(a) Supplied by Service Chemical, USA.[6]

(b) No other product information available.

the samples were not dried for use in the flash powders because it was believed that their condition, as received, is more typical of how they are used in manufacturing fireworks.

Table 2. Sieve Analysis of the Types of Potassium Perchlorate.

Source	Mesh Fraction (%)			
	+100	100–200	200–400	–400
Swedish	0.0	51.1	39.5	9.4
US	0.3	47.2	44.2	8.3
Chinese	0.1	32.3	50.7	16.9
Italian	0.0	3.0	73.0	23.9

The flash powders used for comparison of the potassium perchlorate types were all 70:30 ratios with Obron[7] 5413 (commonly called German dark aluminum). The results from the four sets of sound pressure output tests are presented in Table 3. The data from the two blast gauges were always very nearly the same, and have been averaged for presentation in the Table.

Aluminum Types

The six types of aluminum used in this study are described in Table 4. In addition to these six aluminum powder types, a mixture of 67% (by weight) Reynolds 400 and 33% Alcan 2000 was also investigated. This was done because it had previously been suggested that a mixture of atomized and flake aluminum provided additional reactivity over either type aluminum alone.[12]

Table 3. Sound Pressure Output for Potassium Perchlorate Types.

Potassium Perchlorate	Peak Over-Pressure (psi)	Positive Phase (ms)
Swedish	6.08	0.82
	6.16	1.00
	6.30	1.10
US	5.90	0.90
	6.20	0.95
	6.44	1.01
Chinese	5.69	0.90
	5.98	1.08
	6.02	1.15
Italian	6.21	0.90
	6.32	0.88
	6.24	0.88

For conversion to SI units, 1 psi = 6.89 kPa.

Table 4. Aluminum Powder Types.

Manufacturer	Product No.	Description(a) *[Morphology]*(b)
Obron	5413	German Dark *[Flake 8μ(c)]*
Obron	10890	American Dark *[Flake 15μ(c)]*
Alcan[9]	7100	American Dark *[Flake 13μ]*
Reynolds[10]	400	Atomized *[Spheroidal 6μ]*
US Aluminum[11]	809	American Dark *[Flake 30μ(c)]*
Alcan	2000	Bright *[Flake 36μ]*

(a) The descriptions German Dark, American Dark and Bright are used in the context generally adopted and understood by the American pyrotechnics industry. For more information on aluminum metal powder types, see reference 8.

(b) Basic particle shape and average particle size in microns. Note that 1 micron (μ) = 10^{-6} meter = 3.9×10^{-5} inch.

(c) Average particle size was estimated by the authors using microscopy.

The flash powders were all made with 70:30 ratios using Swedish potassium perchlorate and the various aluminums. The sound output data from the seven sets of tests are presented in Table 5. The data from each of the two blast gauges were always very nearly the same and have been averaged for presentation in the Table.

Table 5. Sound Output Results for Aluminum Types.

Type of Aluminum	Peak Over-Pressure (psi)	Positive Phase(ms)
Obron 5413	6.08	0.82
	6.16	1.00
	6.30	1.10
Obron 10890	5.76	1.00
	6.11	0.96
	5.47	1.03
Alcan 7100	5.61	1.02
	5.61	1.08
	5.12	0.86
Reynolds 400	2.58	1.25(a)
	2.58	1.62(a)
	3.22	1.19(a)
US Aluminum 809	2.30	0.98
	2.54	1.15
	2.72	0.88
Alcan 2000	1.28	1.00
	1.52	1.12
	1.58	0.90
Reynolds 400 + Alcan 2000	2.28	1.15(b)
	2.80	1.18(b)
	1.83	1.07(b)

For conversion to SI units, 1 psi = 6.89 kPa.

(a) In each case, the Reynolds 400 flash powder produced a double blast wave, as shown in Figure 7, resulting in a longer positive phase.

(b) In each case, the use of the Reynolds 400 and Alcan 2000 mixture produced flash powder that also exhibited a weak double blast wave structure.

Flow and Bulking Agents

The two flow and bulking agents used in this study were Cab-O-Sil[13] (M-5, colloidal silica) and red wheat bran. In the first tests, flash powders were based on 70:30 mixtures of Swedish potassium perchlorate and Obron 5413 aluminum. In one test, three percent Cab-O-Sil was added to the base flash powder. In a second test, ten-percent red wheat bran was added. Another 70:30 flash powder was made using US Aluminum 809; to this base, 10% red wheat bran was added. In all tests, the net amount of flash powder, not including the flow or bulking agent, was 50 grams. These results are presented in Table 6.

Table 6. Sound Output Results Using Flow or Bulking Agents.

Aluminum Type *[Additive]*	Peak Over-Pressure (psi)	Positive Phase (ms)
Obron 5413 *[None]*	6.08	0.82
	6.16	1.00
	6.30	1.10
Obron 5413 *[3% Cab-O-Sil]*	6.32	0.98
	6.18	0.85
	6.12	0.93
Obron 5413 *[10% Red Bran]*	5.61	0.93
	6.36	1.05
	6.02	0.90
US Alum. 809 *[None]*	2.30	0.98
	2.54	1.15
	2.72	0.88
US Alum. 809 *[10% Red Bran]*	1.73	1.00
	1.92	0.95
	2.12	1.05

For conversion to SI units, 1 psi = 6.89 kPa.

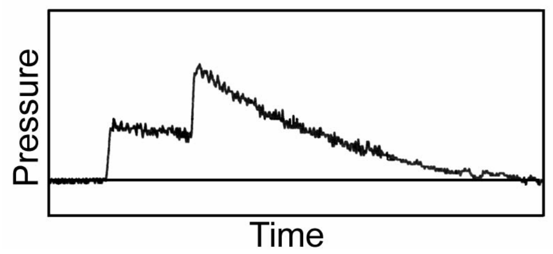

Figure 7. Typical double peaking blast wave recorded for flash powders made using Reynolds 400 aluminum.

Table 7. Flash Powder Formulations Used in Test Salutes.

Ingredient	Flash Formulations (weight percent)						
	1	2	3	4	5	6	7
Potassium perchlorate ($KClO_4$)	70	64	62	70	—	—	—
Potassium chlorate ($KClO_3$)	—	—	—	—	70	64	—
Barium nitrate ($Ba(NO_3)_2$)	—	—	—	—	—	—	68
Aluminum, Obron 5413 (G.D.)	30	—	—	—	—	—	—
Aluminum, Obron 10890 (A.D.)	—	27	23	30	30	9	—
Aluminum, Alcan 2000 (Bright)	—	—	—	—	—	—	23
Antimony trisulfide (Sb_2S_3)	—	—	15	—	—	9	—
Sulfur (S)	—	9	—	—	—	18	9
Reference	(a)	14	14	(a)	(a)	15	16

(a) This is a common formulation with no specific reference.

Formulations

Many different flash powders are used in fireworks. However, only seven flash powder formulations were used in this study. They are listed in Table 7, along with literature references. These formulations were chosen to provide information on the effect of the choice of oxidizer and the use of sulfur and antimony sulfide. However, beyond that criterion, the choice was somewhat arbitrary. Table 8 lists the sound output results from the test salutes using these formulations.

Discussion of Results

It is important to note that the results and conclusions reported in this article are only valid within the context of this study. For example, only three tests were conducted for each flash powder; the average variation about the mean peak overpressures was about 4% and the average deviation in the duration of positive phase was about 6%. Accordingly, any small differences reported for these parameters may be merely statistical in origin. Further, these results are only valid for the conditions examined, specifically, weak confinement with a moderately powerful ignition stimulus.

Table 9 presents the averages of the sound output data from the tests using potassium perchlorate from different sources. Also in the table are sound pressure levels in dB and relative loudness (N). Decibel and loudness values were calculated using the following equations:[17]

$$\text{dB} = 170.8 + 20 \log P \quad (1)$$

$$\log N = 0.03 \text{ dB} - 1.2 \quad (2)$$

where P is peak overpressure in psi.

Table 8. Sound Output Results for Test Formulations. (Also, see Table 7.)

Formulation No. and Description	Peak Over-Pressure (psi)	Positive Phase (ms)
1) $KClO_4$ + G.D.	6.08	0.82
	6.16	1.00
	6.30	1.10
2) $KClO_4$ + A.D. + S	5.90	0.82
	5.88	0.92
	5.76	0.88
3) $KClO_4$ + A.D. + Sb_2S_3	5.85	0.78
	5.90	0.92
	5.75	0.84
4) $KClO_4$ + A.D.	5.76	1.00
	6.11	0.98
	5.47	1.03
5) $KClO_3$ + A.D.	6.31	0.88
	5.94	1.15
	5.10	0.78
6) $KClO_3$ + A.D. + S + Sb_2S_3	3.50	0.72
	3.77	0.78
	3.64	0.63
7) $Ba(NO_3)_2$ + Bright + S	0.22	1.00
	0.17	1.20
	0.11	1.00

For conversion to SI units, 1 psi = 6.89 kPa.

Table 9. Average Results from Different Potassium Perchlorates.

Potassium Perchlorate Type	Positive Phase (ms)	Peak Overpressure (psi)	Sound Pressure Level (dB)	Relative Loudness
Swedish	1.01	6.18	186.5	≡1.00
US	0.95	6.18	186.6	1.00
Chinese	1.04	5.90	186.2	0.97
Italian	0.89	6.26	186.7	1.01

For conversion to SI units, 1 psi = 6.89 kPa.

It must be noted that the reported dB levels were calculated using peak overpressures measured with an instrument with an extremely fast rise time. Thus, these values will be somewhat greater than would have been found using conventional sound measuring equipment, even when using their peak-linear mode setting. (For a more complete discussion of sound pressure levels, loudness, and the effect of instrument parameters, see reference 18.) While it is possible that the peak overpressures observed for the Chinese potassium perchlorate are slightly less than for the other materials, it is within the limits of statistical precision of these measurements. Furthermore, it is doubtful that a typical observer would be able to detect such a small loudness difference, even if it were real. Similar comments are appropriate for the slightly larger value for the Italian potassium perchlorate.

Those materials with roundish particle shape (US, Chinese and Italian), rather than sharp angular particles (Swedish), are likely to mix more thoroughly when using procedures typical of fireworks manufacturing. Accordingly, under more typical mixing conditions than used in this study, it is possible these materials would produce slightly louder flash powder salutes.

Differences in particle size and shape can play a role in determining burn rate, which in turn would influence the sound levels produced by salutes. However, generally it is the size and shape of the fuel that is of primary importance. Typically, this is because the melting point of the oxidizer is lower than the ignition temperature of the mixture. (See reference 19 for a more complete discussion of the factors affecting burn rate.) Based on the above results, for those potassium perchlorate samples examined, it seems that oxidizer particle size and shape only play a minor role in the sound levels produced.

The average durations of positive phase are also essentially within the limits of statistical precision of the measurements. Accordingly, a significant difference in the tonal quality of the sounds produced by the test salutes would not be expected, except possibly for the Italian material that may produce a slightly sharper sound.

Table 10 presents the average sound output data from the tests using different aluminum powders. For the test salutes used in this study, the sound outputs fall roughly into three groups. The first group consists of the two Obron products and Alcan 7100; these produced the greatest output, with the Alcan material possibly producing slightly lower sound levels. The Reynolds, US Aluminum, and mixture of flake and atomized aluminums produced significantly lower sound levels. The Alcan 2000 produced the least sound output.

In all cases, except when Reynolds 400 was used, the durations of positive phase were equivalent. Accordingly, it would be expected that the tonal quality of all the test salutes would be the same. With the Reynolds 400, there was some degree of double peaking of the blast wave (see Figure 7). The authors do not have a satisfactory explanation for this; however, it has never been observed in any other tests and is always observed for Reynolds 400. Thus, it seems that it must be a manifestation of the aluminum powder and not an artifact of the measurement. (It has been suggested that the second peak may be a result of a secondary aluminum dust explosion following the rupture of the test salute casing.) For whatever reason the double peak is produced, it would seem that

Table 10. Average Results from Different Aluminums.

Aluminum Types	Positive Phase (ms)	Peak Overpressure (psi)	Sound Pressure Level (dB)	Relative Loudness
Obron 5413	1.01	6.18	186.6	≡1.00
Obron 10890	1.00	5.78	186.0	0.96
Alcan 7100	0.99	5.45	185.5	0.93
Reynolds 400	1.35(a)	2.79	179.7	0.62
US Aluminum 809	1.00	2.52	178.9	0.59
R. 400 + A. 2000	1.13(a)	2.30	178.0	0.54
Alcan 2000	1.01	1.46	174.1	0.42

For conversion to SI Units, 1 psi = 6.89 kPa.

(a) The Reynolds 400 aluminum produced double explosions, see Figure 7.

this aluminum would produce a more mellow sound than the others.

Table 11 presents the average sound output data from the tests of flash powders with a flow or bulking agent. Recall that in all cases, the net amount of flash powder was 50 g (1.8 ounce), exclusive of the added flow or bulking agent. With the 70:30 Swedish potassium perchlorate and Obron 5413 aluminum flash powder, the agents had essentially no effect on relative loudness. However, for the flash powder using US Aluminum 809, there was a minor, but noticeable, reduction in relative loudness. It is unlikely there was a significant affect on the duration of positive phase (tonal quality). The addition of flow and bulking agents is expected to facilitate mixing and help keep flash powders from compacting over time. Thus, it is possible that their addition would produce greater relative sound output under other conditions than in this study

Table 12 presents the average sound output from the seven flash powder formulations listed in Table 7. In terms of loudness, no formulation out performed the Obron 5413 (German dark aluminum) and potassium perchlorate.

Of the formulations using Obron 10890 (sometimes referred to as American dark aluminum), the addition of sulfur or antimony sulfide, or the substitution of potassium chlorate for potassium perchlorate (formulations 2, 3 and 5) made no difference in loudness. However, there was a shortening of the positive phase duration with the addition of either sulfur or antimony sulfide, which should produce a sound perceived as being less mellow. That the addition of antimony sulfide produced a more brisant explosion was expected, based on common knowledge in the fireworks trade. However, it was not expected that the addition of sulfur would have the same effect. Common experience is that sulfur produces a more mellow sound. At the present, the authors have no satisfactory explanation for this. However, work is continuing to study this. Use of antimony sulfide or sulfur decreased the duration of the posi-

Table 11. Average Results from Flow or Bulking Agent.

Aluminum Type	Flow / Bulking Agent Type	Positive Phase (ms)	Peak Over-Pressure (psi)	Sound Pressure Level (dB)	Relative Loudness
Obron 5413	None	1.01	6.18	186.6	≡1.00
	Cab-O-Sil (3%)	0.92	6.21	186.6	1.00
	Red Bran (10%)	0.96	6.00	186.4	0.98
US Aluminum 809	None	1.00	2.52	179.1	≡1.00
	Red Bran (10%)	1.00	1.92	176.5	0.85

For conversion to SI units, 1 psi = 6.89 kPa.

Table 12. Average Results from Various Formulations.

Formulation Number and Description	Positive Phase (ms)	Peak Over-Pressure (psi)	Sound Pressure Level (dB)	Relative Loudness
1) $KClO_4$ + Obron 5413	1.01	6.18	187.6	≡1.00
2) $KClO_4$ + Obron 10890 + S	0.87	5.85	186.1	0.97
3) $KClO_4$ + Obron 10890 + Sb_2S_3	0.85	5.83	186.0	0.96
4) $KClO_4$ + Obron 10890	1.00	5.78	186.0	0.96
5) $KClO_3$ + Obron 10890	0.94	5.78	186.0	0.96
6) $KClO_3$ + Obron 10890 + S + Sb_2S_3	0.71	3.64	182.0	0.73
7) $Ba(NO_3)_2$ + Alcan 2000 + S	1.07	0.17	155.4	0.11

For conversion to SI units, 1 psi = 6.89 kPa.

tive phase without increasing peak overpressure. This combination of effects means that the pressure impulse produced is less for these flash powders. In turn, that may mean that the blast effect perceived by the audience, the so-called "chest thump", will be less for salutes using these flash powders.

When both sulfur and antimony sulfide were added and potassium chlorate was used as the oxidizer (formulation 6), the duration of positive phase was reduced further. However, there was also a significant reduction in loudness of the test salutes (presumably a result of its rather low percentage of aluminum). The use of potassium chlorate, sulfur or antimony sulfide in flash powders can increase the sensitiveness to accidental ignition from one or more factors: impact, friction, electrostatic discharge or temperature.[20] The use of a combination of potassium chlorate and sulfur or antimony sulfide is expected to result in a substantial increase in sensitiveness. While a discussion of these effects would be interesting and important, they are beyond the scope of this article.

Under these test conditions, the test salutes made using formulation 7, with barium nitrate and Alcan 2000 (bright) aluminum, resulted in reports of considerably reduced loudness, but with a positive phase duration perhaps a little longer than typical of the other flash powders.

Conclusion

There are a number of inferences that can be drawn from the above data sets; however, these must only be made within the context of these measurements. It is possible that other conclusions would be reached for other experimental conditions. Nonetheless, these data imply:

- The sound output from mixtures prepared with common sources of potassium perchlorate from four manufacturers is essentially equivalent.
- There are significant differences in the level of sound output as a result of using six different common aluminum powders.
- The addition of either of two common flow or bulking agents have essentially no effect on the sound produced (for freshly prepared items).
- The substitution of potassium chlorate for potassium perchlorate in a common flash powder has essentially no effect on the sound produced.
- The addition of antimony sulfide or sulfur reduces the duration of positive phase without increasing the level of the sound produced.

In short, nothing surpassed the level of sound produced by a 70:30 mixture of reasonably high-quality potassium perchlorate and a high quality flake aluminum powder. This is significant because the use of potassium chlorate, antimony sulfide, and sulfur can seriously increase the sensitiveness of flash powders to accidental ignition.

It had been anticipated that, as a follow-on to this study, there would be a study of the sensitiveness of these flash powders. This was posed on the assumption that there was a performance benefit to the use of potassium chlorate and antimony sulfide or sulfur. It was thought that information would allow manufacturers to decide whether the performance gain was worth the added risk of using such formulations. However, since there is no performance advantage, there is no potential benefit and no reason to use formulations that are more hazardous. Accordingly, there is little point in measuring the sensitiveness of those formulations, and plans for that study have been abandoned.

Acknowledgments

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Note

[a] In this article, for accuracy of reporting, the actual units of measurement are given first, followed by either their SI or English equivalent.

References

1) G. F. Kinney and K. J. Graham, *Explosive Shocks in Air*, 1985; [a] p 88; [b] p 90; [c] p 254.
2) K. L. and B. J. Kosanke, and R. K. Wharton, “Impulse Sounds, Their Measurement and Effects on Hearing”, in Preparation.
3) Daveyfire, Sacramento, CA 95831, USA.
4) PCB Piezotronics, Depew, NY, USA.
5) Western Electrochem, Cedar City, UT 84721, USA.
6) Service Chemical, Hatfield, PA 19440, USA.
7) Obron Atlantic, Painesville, OH 44077, USA.
8) K. L. and B. J. Kosanke, “Aluminum Metal Powders Used in Pyrotechnics”, *Pyrotechnics Guild International Bulletin*, No. 85, 1993, pp 24–34. Also in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke Part 3 (1993 and 1994)*, Journal of Pyrotechnics, 1995.
9) Alcan-Toyo America, Naperville, IL 60563, USA.
10) Reynolds Metal, Richmond, VA 23261, USA.
11) US Aluminum, Flemington, NJ 08822, USA.
12) E. Raszkowski, “In Search of Flash Powder Brisance”, *Pyrotechnics Guild International Bulletin*, No. 31, 1982, p 5.
13) Cabot, Tuscola, IL 61953, USA.
14) C. L. Hill, “Sound in Fireworks”, *American Fireworks News*, No. 122, 1991, p 2.
15) T. L. Davis, *The Chemistry of Powder and Explosives*, Angriff Press (reprint), 1943, p 117.
16) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing, 1968, p 370.
17) *Van Nostrand’s Scientific Encyclopedia*, 5th ed., Van Nostrand Reinhold, 1976, p 25.
18) K. L. and B. J. Kosanke, “A Survey of Concussion Powders”, *Journal of Pyrotechnics*, No. 5, 1997. Also in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke Part 4 (1995 through 1997)*, Journal of Pyrotechnics, 1999.
19) B. J. and K. L. Kosanke, “Control of Pyrotechnic Burn Rate”, *Proceedings of the 2nd International Symposium on Fireworks,* Vancouver, Canada, 1994, p 243. Also in *Selected Pyrotechnic Publications of K.L. and B.J. Kosanke Part 3 (1993 and 1994)*, Journal of Pyrotechnics, 1995.
20) C. Jennings-White, and K. L. & B. J. Kosanke, “Hazardous Chemical Combinations”, *Journal of Pyrotechnics*, No. 2, 1995, p 22. Also in *Selected Pyrotechnic Publications of K.L. and B.J. Kosanke Part 4 (1995 through 1997)*, Journal of Pyrotechnics, 1999.

Evaluation of Fire and Explosion Hazards for a Non-Azide Gas Generant

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ABSTRACT

A hazard evaluation has been carried out for the safety assessment of a new non-azide gas generant for automotive airbag inflators. The gas generant (UN) is composed of urazole (U) and a metal nitrate (MNO_3;N) with other additives included to provide the required performance. The impact, shock, friction, electric spark, hot object and heat sensitivities were determined by the appropriate tests. Propagations of detonation, deflagration and combustion were examined using the United Nations gap test and VP 30 tube test. A mixture of urazole with $KClO_4$ in a stoichiometric ratio propagated detonation as measured by the gap test and self-sustaining combustion as measured by the tube test. The mixture of urazole with KNO_3 propagated combustion, but no detonation.

Keywords: airbag, gas generant, urazole, hazard evaluation, test methods

1. Introduction

A non-azide gas generant (AK) containing azodicarbonamide (ADCA;A) and potassium perchlorate ($KClO_4$;K) as basic ingredients was developed by our group.[1] Recently, a new composition (UN) containing urazole (1,2,4-triazolidine-3,5-dione;U) and a metal nitrate (MNO_3;N) as basic ingredients has been developed as a gas generant for airbag inflators. The new composition (UN) has higher thermal stability and lower combustion temperature than AK.

To assess the safety of manufacturing the UN gas generant, the Yoshida Hazard Analysis (YHA)[2] has been carried out for the two compositions typical of the UN gas generant. One composition is UKS, a mixture of urazole (U), $KClO_4$ (K) and soluble starch (S) in a mass ratio of 37:61:2, respectively. The second is UNSSi, a mixture of urazole (U), potassium nitrate (KNO_3;N), starch (S) and silicon dioxide (SiO_2;Si) in a mass ratio of 27:55:2:16, respectively. Both compositions are two extremes of our intended composition. The test methods used are sensitivity, burning and explosion propagation tests. The results of these tests are used in the YHA for the manufacturing process of the UN gas generant.

2. Experimental

2.1 Materials

Materials used are listed in Table 1.

Table 1. Materials Used.

Name	Symbol	Size (µm)	Supplier
Urazole	U	19	Otsuka Chemical Co., Ltd.
$KClO_4$	K	21.9	Japan Carlit Co., Ltd.
KNO_3	N	60	Otsuka Chemical Co., Ltd.
Starch	S	—	Wako Pure Chemical Industries Co., Ltd.
SiO_2	Si	7.5	Tokuyama Soda Co., Ltd.

Samples used in the experiments are listed in Table 2. KNO_3 and $KClO_4$ are practical oxidizers because they are not hygroscopic and have low toxicity. $KClO_4$ is more reactive than KNO_3 in this case.

Table 2. Composition of Sample.

	Symbol	Urazole	$KClO_4$	KNO_3	Starch	SiO_2
A	UKS	37	61	—	2	—
B	UNSSi	27	—	55	2	16
C	Urazole	100	—	—	—	—
D	KNO_3	—	—	100	—	—

2.2 Test Procedures

2.2.1 Drop Hammer Test

The drop hammer test is a method for determining the sensitivity of energetic materials to a mechanical impact. A drop hammer test in accordance with Japanese Standard JIS K4810–1979 was used in this work. The mass of the hammer is 5 kg. About 30 mg of sample in tin foil is sandwiched between two cylinders placed on the anvil as shown in Figure 1. The cover is then placed on the anvil. The iron hammer is dropped on the cylinder, and any explosion is noted.

If an explosion occurs (test positive), the height of the hammer is reduced. If none occurs, the height is increased. In either case, the height is varied in 0.1 log intervals in height. Twenty tests are carried out. The data are analyzed by the Bruceton up-and-down method.[3] If materials react with the tin foil, the test is carried out without the foil.

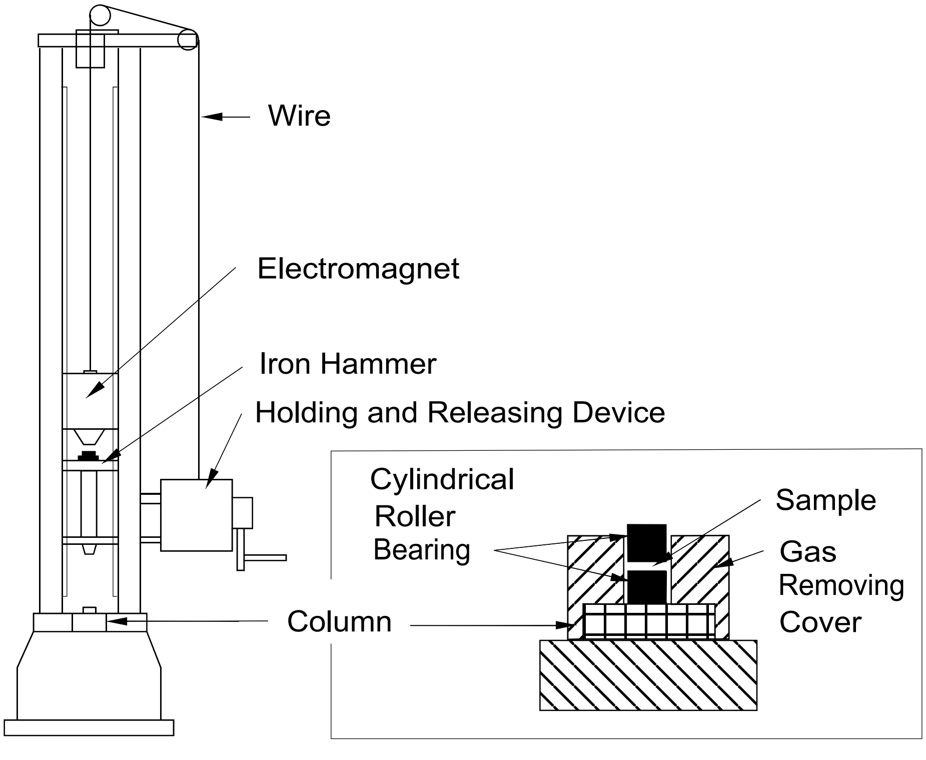

Figure 1. Assembly and the lower part of the JIS drop hammer test.

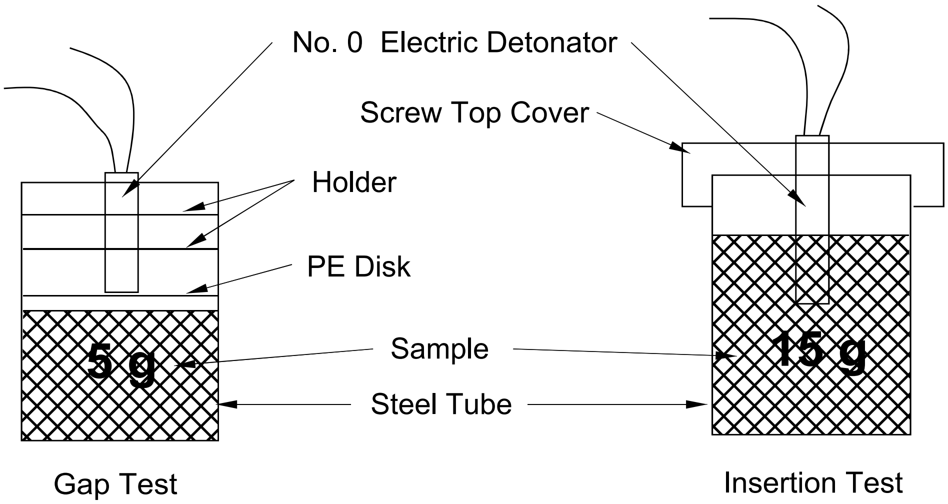

Figure 2. Sample assemblies for the shock ignitability test.

2.2.2 Shock Ignitability Test[4]

The shock ignitability test is a method for determining the shock sensitivity of medium-sensitive energetic materials, especially pyrotechnic compositions. The sample container has an inner diameter of 31 mm, an outer diameter of 34 mm, and a depth of 35 mm with the bottom cover in place. There are two types of containers: one with and one without the screw top cover as shown in Figure 2. Polyethylene (PE) gap disks with a diameter of 30 mm and a thickness of 1–4 mm are used for the gap test in the shock ignitability test. The sample in the container is initiated by a No. 0 detonator containing 18 mg of diazodinitrophenol (DDNP) inserted through the gap disks or directly into the sample.

2.2.3 VP 30 PVC Tube Initiation Test[5,6]

The VP 30 PVC tube initiation test is suitable for examining the ability of commercial explosives and pyrotechnic compositions to propagate explosions. A VP 30 polyvinyl chloride (PVC) tube with an inner diameter of 31 mm and a length of 150 mm (JIS K6742–1971) is filled with 100 g of sample. Both sides of the tube are covered with adhesive paper tape. A No. 6 detonator containing 18 mg DDNP and 40 mg pentaerythrytol tetranitrate (PETN) is inserted into the sample at one side of the tube. The sample assembly is placed horizontally 0.2 m deep in sand. The general arrangement is shown in Figure 3. Propagation of an explosion

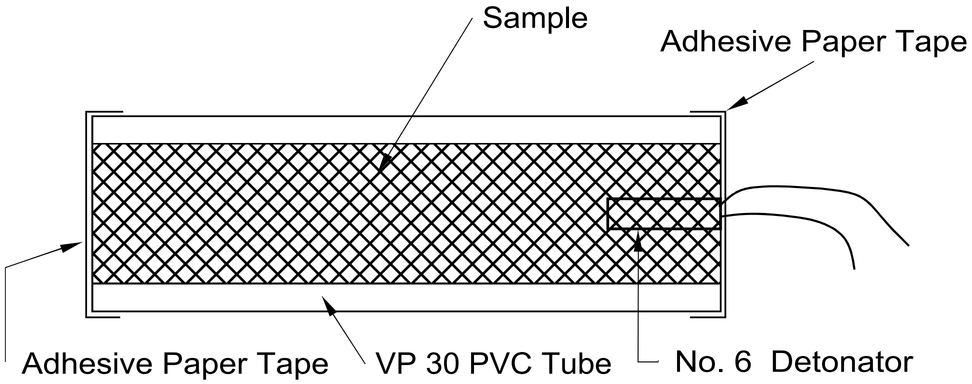

Figure 3. Setup for the VP30 PVC tube initiation test.

by the sample is judged from the size of the crater formed, the amount of unreacted sample remaining and/or the fragmentation of the PVC tube.

2.2.4 United Nations Gap Test[7]

The United Nations gap test is a method for examining the ability of low-sensitive energetic materials to propagate explosions and especially to propagate detonations. Figure 4 shows the setup of the United Nations gap test. Approximately 500 mL of sample is placed in a carbon steel tube with an outside diameter of 48 mm, a thickness of 4.0 mm, and a length of 0.4 m. A booster charge of 160 g cast pentrite (a 50:50 mixture of PETN/TNT) is used. The witness plate is a soft steel square plate 0.15 m × 0.15 m × 3.2 mm. A ring-shaped aluminum plate 50 mm (o.d.) × 40 mm (i.d.) × 1.6 mm is used as a spacer and sandwiched between the witness plate and sample. A No.6 electric detonator holder is fixed to the booster charge. The booster charge, the spacer and the witness plate are combined and fixed to the steel tube filled with the sample. The sample assembly is buried horizontally 0.5 m deep in sand to prevent scattering of any fragments.

2.2.5 Friction Sensitivity Test

The friction sensitivity test is used to examine the ease of ignition when an energetic material is subjected to mechanical friction. Bailey et al.[8] showed that incidents involving energetic materials caused by friction are the most frequent among those caused by external stimuli. The BAM friction tester[9] was used for evaluating the friction sensitivity of urazole, UKS and UNSSi. Figure 5 shows the BAM (Bundesanstalt für Mäterialforchung und prüfung) friction tester and the sample holder. A sample weighing several mg is placed on the rough surface of a porcelain plate and pressed by the rough surface of a porcelain peg with a known force. When the start button is pushed, the porcelain plate moves back and forth with a fixed speed through a distance of 10 mm. Ignition is judged by noise, a flash or smoke. The force exerted by the peg is selected by changing the weight and position of the hanging weight.

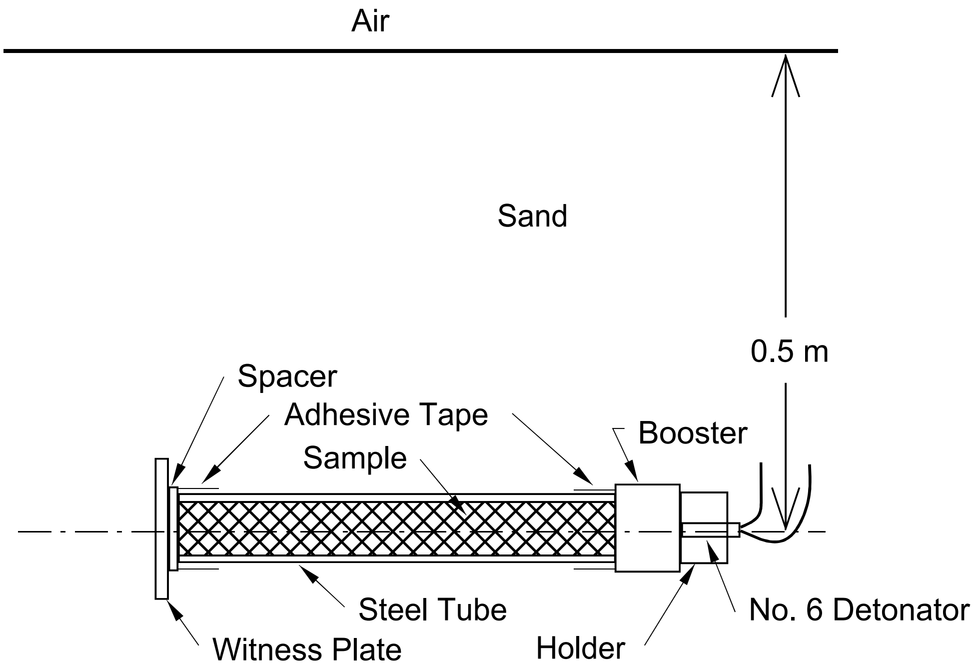

Figure 4. Setup for the United Nations gap test.

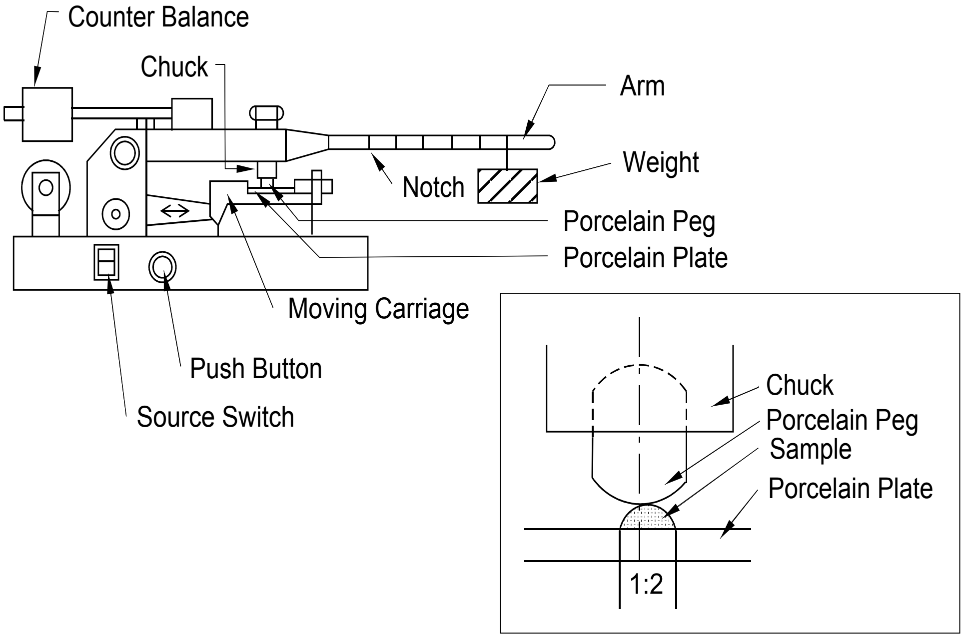

Figure 5. BAM friction sensitivity tester.

These experiments were carried out twenty times using the Bruceton up-and-down method and the results were analyzed. The increment of force in the experiment is 0.1 log unit. The 50% ignition mass (M_{50}) and the standard deviation of log M were calculated.

2.2.6 Electric Spark Sensitivity Test

The electric spark sensitivity test is a method for determining the ignition sensitivity of energetic materials to an electric spark. The tester used was developed by Dr. Mizushima for low- and medium-sensitive energetic materials.[10] Sample parts of the tester are shown in Figure 6. The structure of the electrode in the tester is a fixed pipette plate electrode according to Dahn et al.[11] This tester can give the sample from 10^{-1} to 80 J in capacitor energy depending upon the selection of capacitance and voltage. Experiments were carried out twenty times using the Bruceton up-and-down method with 0.1 log unit intervals of capacitor energy. Values of the 50% ignition energy (E_{50})

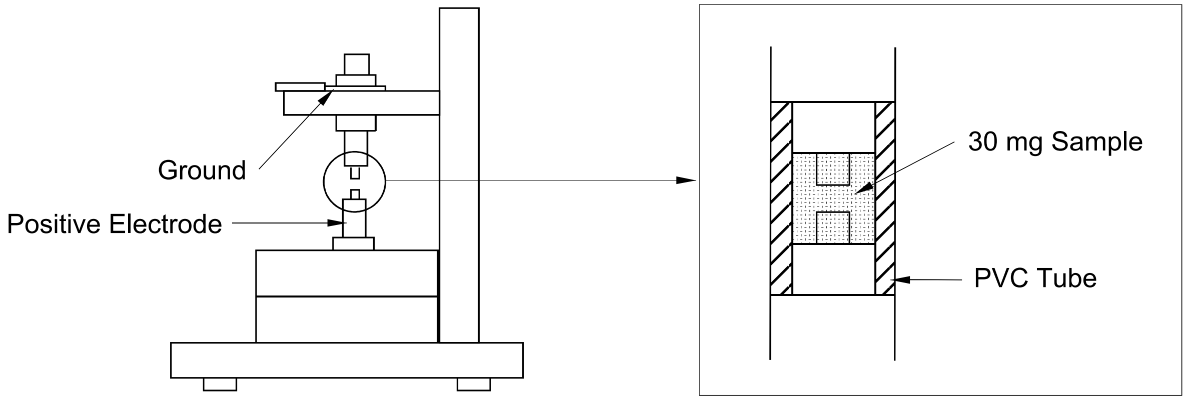

Figure 6. Electrodes of the electric spark sensitivity tester.

and standard deviation of log E were calculated.

2.2.7 VP 30 PVC Tube Burning Test

The VP 30 PVC tube burning test evaluates both the ability of energetic materials and pyrotechnic compositions to propagate combustion as well as the violence of that combustion. The sample is placed in the 0.1 m long VP 30 PVC tube and ignited by a 0.6 mm diameter Ni–Cr wire heated with an electric current of 10 A. Whether it is ignited or not is noted and, if ignition is observed, the burning time is measured. The sample assembly for the test is shown in Figure 7. When no ignition is noted, a 5 g mixture of 37:63 ratio of urazole and $KClO_4$ is used as an ignitor.

2.2.8 Conical Pile Burning Test

The conical pile burning test is a method for examining the effect of sample size on the violence of the combustion of pyrotechnic compositions. There is a suggestion that the combustion of pyrotechnic compositions becomes more violent as the mass of the composition is increased.[12] The test method is similar to that for oxidizing solids according to the Japanese Fire Services Law.[13] A sample of 25, 50, 100 or 200 g is piled conical on a heat resistant plate, a 0.6 mm diameter Ni–Cr wire is touched to the base of the cone and the sample is ignited. The duration of the combustion is observed. The setup of the experiment is shown in Figure 8. If the sample is not ignited by the Ni–Cr wire, the experiment is repeated using a 5 g mixture of ADCA–$KClO_4$–CuO as the ignitor.

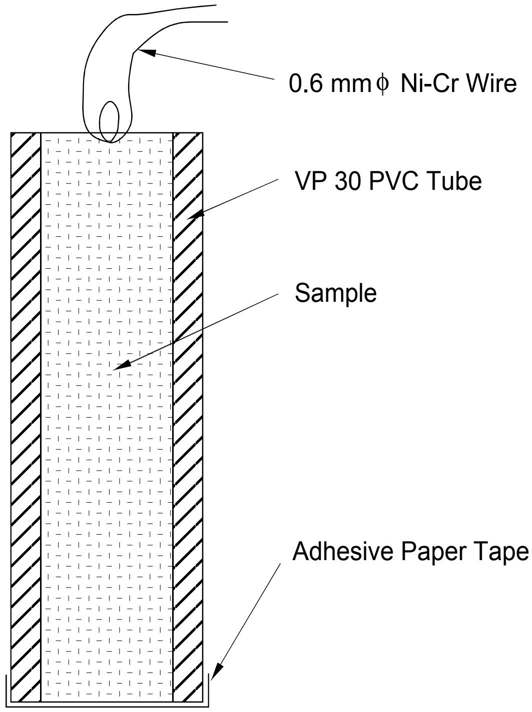

Figure 7. VP30 PVC tube burning test.

2.2.9 SC–DSC Test

The sealed cell-differential scanning calorimetry (SC–DSC) test is a screening method for examining the thermal stability of self-reactive materials including energetic materials. If a relationship between the SC–DSC data and the data from any practical test method is known, the practical test data can be estimated from the SC–DSC data.[14]

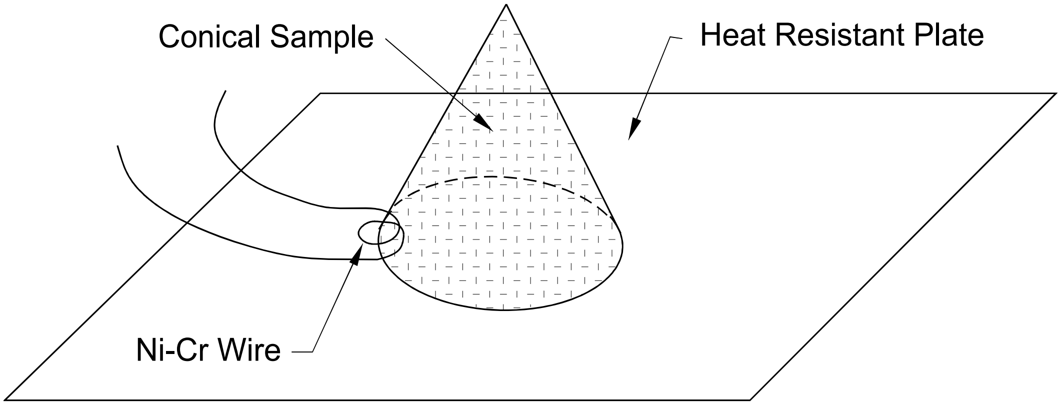

Figure 8. Conical pile burning test.

A sample of about 1 mg is weighed accurately in the sealed cell. The sealed cell containing the sample is placed in the DSC (Seiko Denshi) and heated at a rate of 10 ºC/min. The DSC extrapolated decomposition temperature (T_{DSC}) and DSC decomposition heat (Q_{DSC}) are recorded. Additional information is also obtained from the appearance of the DSC curve.

2.2.10 Pressure Vessel Test

The pressure vessel test evaluates the violence of the reaction of a self-reactive material when it is subjected to heating in an essentially closed container with a single small orifice of defined size. A pressure vessel in accordance with the Japanese Fire Service Law was used in this study.[15] A 5 g sample is placed in the pressure vessel which is equipped with either a 1.0 mm or 9 mm diameter orifice and is heated at a rate of 40 ºC/min. Less than ten trials are carried out for each size orifice. The bursting times of the rupture disk are noted as being either smaller or larger than five.

3. Results

3.1 Drop Hammer Test

Results of the JIS drop hammer test are listed in Table 3. Urazole reacted with the tin foil by the impact of the 5 kg drop hammer, and the apparent impact sensitivities of materials containing urazole were higher with the tin foil than without it.

Table 3. Results of the JIS Drop Hammer Test.

Material	With tin foil		Without tin foil	
	E_{50} (J)	$\sigma_{\log}E_{50}$	E_{50}	$\sigma_{\log}E_{50}$
Urazole	8.5	0.30	21.4	0.30
UNSSi	7.4	0.08	11.8	0.13
UKS	14.8	0.16	20.0	0.04

3.2 Shock Ignitability Test

Powdered UKS exploded in the shock ignitability test with a No. 0 detonator inserted and with the top covered. The bottom cover separated, but the explosion did not fragment the steel tube. This indicates that the explosion was not a detonation but a deflagration. The sample did not explode in the test with a No. 0 detonator in contact with the surface of the sample but without the cover. Powdered urazole, UNSSi and the 50:50 mixture of UKS/UNSSi did not explode in the test with a No. 6 detonator inserted in the top cover. Granules of UKS and UNSSi did not explode in the test.

3.3 VP 30 PVC Initiation Test

The VP 30 PVC initiation test with a No. 6 detonator inserted results in no propagation of explosion and unreacted material remaining in the tester for urazole, UKS, UNSSi and the mixture of both materials.

3.4 United Nations Gap Test

Powdered UKS propagated detonation in the United Nations gap test, whereas powders of UNSSi and urazole propagated neither detonation nor deflagration, and unreacted material remained in the tester.

3.5 Friction Sensitivity Test

Urazole and UNSSi reacted once in ten trials in the BAM friction tester under a load of 36 kgf (360 N). UKS reacted once under the a load of 32.4 kgf (324 N).

3.6 Electric Spark Sensitivity Test

Fifty percent ignition energy (E_{50}) of urazole, UNSSi and UKS by the tester for medium-sensitivity are listed in Table 4.

Table 4. Results of the Electric Spark Test.

Material	E_{50} (J)	$\sigma_{\log}E_{50}$
Urazole	51 (3/10) *	—
UNSSi	38.1	0.04
UKS	25.2	0.20

* Urazole reacted three times in ten trials with 51 J capacitor energy.

3.7 VP 30 PVC Burning Test

In this test, urazole did not ignite, but the 100 mm strands of UNSSi and UKS burned for 198 s and 139 s, at the burning rates of 0.50 mm/s and 0.72 mm/s, respectively.

3.8 Conical Pile Burning

The conical pile burning test on 25 g each of powders and granules of urazole, UKS and UNSSi did not show sustained burning with either the hot Ni–Cr wire or the 5 g ignitor.

3.9 SC–DSC

The SC–DSC curves of urazole, UNSSi and UKS are shown in Figures 9 (a), (b), and (c), respectively. Each material showed an endothermic peak before the first exothermic peak which is assigned to the decomposition of urazole. For UNSSi and UKS, other exothermic peaks follow the decomposition peak of urazole.

The DSC onset temperature T_{DSC} of urazole, UNSSi and UKS were 284, 225 and 241 ºC, respectively.

3.10 Pressure Vessel Test

The pressure vessel test for urazole was carried out seven times, and the rupture disk burst five times. However, when the rupture disk burst, it was noted that the orifice had been plugged with sublimed material. When the disk did not burst, the orifice was open and smoke came out through the hole. When a 9 mm diameter orifice was used, it was not plugged with sublimed materials, and the decomposition products came out slowly through the orifice.

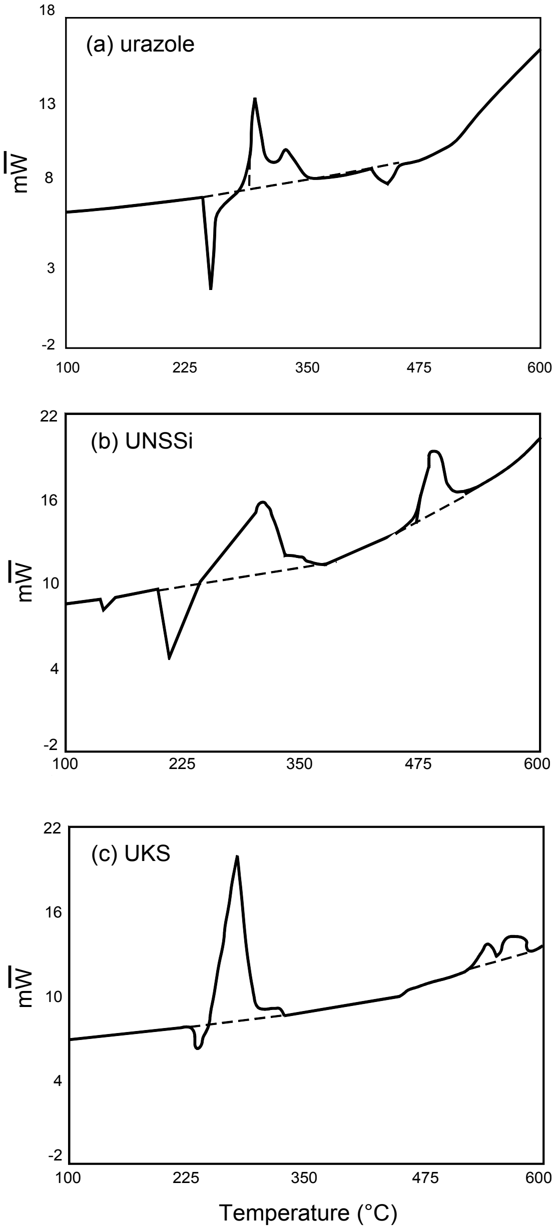

Figure 9. SC–DSC Curves of urazole (a), UNSSi (b) and UKS (c).

4. Discussion

4.1 Impact and Shock Sensitivity and Explosion Propagation by Urazole, UNSSi and UKS

All three samples were low-sensitive to the JIS drop hammer impact test. Only UKS among these three materials exploded in the shock ignitability test with the top cover in place and with a No. 0 detonator inserted. This explosion was classified as deflagration, not detonation, because the steel tube was not fragmented. Only the bottom cover separated.

Powders of all three materials were not initiated by the VP 30 PVC initiation test with a No. 6 detonator inserted, and unreacted sample remained in the tester. Only UKS powder propagated detonation in the United Nations gap test. In conclusion, UKS can propagate detonation under the severe conditions in the United Nations gap test, and urazole and UNSSi propagate neither detonation nor deflagration even under these severe conditions.

The impact and shock sensitivity of urazole and UNSSi are classified as negligible (D level). Urazole and UNSSi are also classified as combustible materials. The impact and shock sensitivity of UKS is low (C level), and UKS is classified as a deflagrating material.[2]

4.2 Friction Sensitivity of Urazole, UNSSi and UKS

Urazole, UNSSi and UKS reacted in the BAM friction tester. However, urazole did not propagate combustion by the burning test. Therefore, the reaction by the friction test will be not propagative and is not hazardous. In the burning tests urazole is classified as not hazardous. The friction sensitivity of urazole is negligible (D level), and the friction sensitivity of UNSSi and UKS are low (C level).

4.3 Electric Spark Sensitivity

All three samples are low-sensitive in the electric spark tester for low- and medium-sensitivity materials. The sensitivities of urazole, UKS and UNSSi are low (C level).

4.4 Ignitability, Propagation of Combustion and Violence of Combustion

Urazole is not ignitable by small heat sources. This material is only ignitable by an external fire and therefore is poorly combustible. The ignitability of urazole is negligible (D level), UNSSi and UKS can be ignited by a hot wire or ignitors in a tube but not in bulk. Self-reactive materials such as UNSSi and UKS were shown to burn more easily in a tube than in bulk. Ignitability depends on the ignition source. The 5 g ignitors were stronger ignition sources than the Ni–Cr wire.

The ignitability of UNSSi and UKS is low (C level). UNSSi is classified as a combustible material, but UKS as a deflagrating material, because it can be detonated by a strong initiator if in a closed container.

Granules of UKS burn more easily and more quickly than the corresponding powders.[12] All forms of UKS burn more quickly at high pressure than at atmospheric pressure. The powders, granules and pellets should not be handled in a tightly sealed vessel, because when ignited, the speed of combustion increases remarkably under those conditions.

4.5 Thermal Stability and Violence of Decomposition

The 107 ºC–400 hr test is used for evaluating the thermal stability of a gas generant for automotive airbag inflators. In this test, an inflator containing the gas generant is kept at 107 ºC for 400 hr. The 60 L tank test is applied to the inflators before and after heating. The test criterion is that no significant difference between the 60 L tank test results before and after the heating be observed. The 107 ºC heat and mass reduction test simulates the 107 ºC–400 hr test. A composition having a DSC onset thermal decomposition temperature (T_{DSC}) greater than 200 ºC is known to pass the 107 ºC heat and mass reduction test based on experience with the ADCA gas generant compositions.[16] The T_{DSC} of UNSSi and UKS are 225 and 241 ºC, respectively. These values are significantly higher than those for the ADCA gas generant compositions. The heat sensitivities of UNSSi and UKS are low (C level).

In the pressure vessel test for urazole, the rupture disk burst at an orifice size of 1 mm. In this case, however, the orifice was plugged with sublimed material. When the orifice was not blocked, the rupture disk did not burst and the decomposition gases did not blow out violently. Therefore, the thermal decomposition of urazole is not considered violent as long as sublimed material does not block the orifice, thereby sealing the container.

References

1) K. Hara, T. Misawa, T. Maekawa, S. Iyoshi, T. Yokoyama, M. Hayashi, T. Yoshida, "Concept and Performance of a Non-Azide Propellant for Automotive Airbag Inflators", *Proceedings of the 19th International Pyrotechnics Seminar*, Christchurch, New Zealand, 21–25 Feb. 1994.
2) K. Hara, Y. Shimizu, Y. Higashi, T. Nojima, T. Hasegawa, T. Yoshida, "Hazard Analysis of Manufacture of Non-Azide Propellant for Automotive Airbag Inflators", *Proceedings of the 20th International Pyrotechnics Seminar*, Colorado Springs, USA, 25–29 July 1994, p 381.
3) W.J. Dixon, F.J. Masseg, *Introduction to Statistical Analysis*, McGraw–Hill, 2nd ed., 1957, p 318.
4) K. Aoki, K. Hara, J. Peng, T. Yoshida, H. Hatano, F. Hosoya, "Shock Ignitability Test for Medium-Sensitive Pyrotechnic Compositions", *Proc. 18th International Pyrotechnics Seminar*, 13–17 July 1992, Breckenridge, USA, p 1.
5) Y. Wada, H. Yabashi, M. Tamura, T. Yoshida, T. Matsuzawa, F. Hosoya, "Shock Sensitivity Test of Blasting Explosive Cartridges", *Journal of Energetic Materials*, Vol. 9, 1991, p 105.
6) T. Okitsu, J. Suzuki, K. Aoki, K. Hara, T. Yoshida, "Shock Sensitivity Tests for Commercial Explosives and Low-Sensitive Explosive Materials", *Proc. 9th Symposium on Chemical Problems Connected with the Stability of Explosives, Margretetorp, Sweden*, Aug. 23–27, 1992, p 107.
7) United Nations, *Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria*, 2nd Rev. ed., 1995.
8) A. Bailey, D. Chapman, M. R. Williams, R. Wharton, "The Handling and Processing of Explosives", *Proc. 18th International Pyrotechnics Seminar*, Breckenridge, Colorado, USA, 13–17 July, 1992, p 33.
9) H. Koenen, K. I. Ide, K. H. Swart, "Sicherheitsteche Kenndaten Explosionstahlgen Stoffe", *Explosivestoffe*, Vol. 9, 4, 1961.
10) S. Amari, K. Sato, T. Yoshida, Y. Mizushima. F. Hosoya, "Electric Spark Sensitivity of Reductive Element–Oxidizer Mixtures", *Journal of Pyrotechnics*, No.3, 1996, p 1
11) C. J. Dahn, A. Kashani, M. Nguyen, "New Concepts in Studying Electrostatic Discharge Hazards of Propellants, Pyrotechnics and Explosives", *Proc. 17th International Pyrotechnics Seminar* Connected with the 2nd International Symposium on Pyrotechnics and Explosives, Beijing, China, 28–31, Oct. 1991, p 941.
12) T. Kazumi, K. Hara, Y. Yu, Y. Yamato, T. Takashi, Y. Shimizu, T. Yoshida, "Safety Aspect of a Non-Azide Propellant for Automotive Airbag Inflators", *Energetic Materials*, Vol. 14(2), 1996, p 81.
13) T. Yoshida, N. Foster, Y. Wada, *Safety of Reactive Chemicals and Pyrotechnics*, Elsevier, Amsterdam, 1995, p 75.
14) T. Yoshida, *Safety of Reactive Chemicals*, Elsevier, Amsterdam, 1987, p 237.
15) T. Yoshida, N. Foster, Y. Wada, *Safety of Reactive Chemicals and Pyrotechnics*, Elsevier, Amsterdam, 1995, p 269.
16) Y. Ohtsuka, E. Kawashima, Y. Yu, K. Hasegawa, K. Hara, Y. Shimizu, T. Yoshida, "Evaluation of Thermal Stability of Energetic Materials", *The 10th Symposium on Chemical Problems Connected with the Stability of Explosives*, Margretetorp, Sweden, 29 May–2 June, 1995.

Progress in Developing a Fuel-Air Salute

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ABSTRACT

In a fuel-air salute a fine metallic fuel is first dispersed into the surrounding air, then ignited. Such a salute is much safer than a conventional salute as the salute fuel must be mixed with air to obtain the oxygen needed to function. It can not explode violently in bulk or in a mortar tube because the salute contains only fuel. Even if fired while lying on the ground, its explosive power is reduced. This preliminary paper summarizes progress achieved to date in fuel-air salute construction and suggests areas for future study.

Keywords: fireworks, salutes, fuel-air, safety, dust explosions

Introduction

Fuel-air explosives have been used by the military for over 30 years. In a fuel-air explosive the air surrounding the explosive is used to supply the oxygen for the reaction. The fuel (such as ethylene oxide, C_2H_4O, with a wide explosion concentration range) is first dispersed by a small explosive charge. When the fuel has expanded to the desired volume, a second charge is fired to initiate the explosion of the fuel-air mixture. Due to the large size of these devices, the delay between the dispersing charge and the initiating charge can be on the order of two seconds. For a given mass of explosive, the absence of oxidizer allows greater explosive efficiency. A second advantage is that the large volume of the resulting explosion can lead to the efficient production of a powerful shock wave that can extend over a great distance, creating overpressure damage.

A fuel-air salute for pyrotechnics would offer unique advantages. The primary advantage would be in the greatly increased safety in storage, transportation, and in the use of the salutes. With conventional salutes, bulk storage of salutes can result in mass detonation should one device function. This may have contributed to the ruling in the United States that bulk salutes must be treated as Explosives 1.1, even though a single salute may be classified as Explosives 1.3. A properly designed container of bulk fuel-air salutes could not mass detonate. In fact it may be possible to package the dispersing and delay charge separate from the fuel, and then ship the fuel component as a flammable solid and the dispersing charge as Explosives 1.4. They would then be combined at the point of use.

The premature explosion of salutes within mortars have caused many serious accidents. The absence of adequate air within the mortar tube would prevent the fuel-air mixing required for explosion in the barrel. Also, the dispersing charge can probably be designed so that no damage to the mortar would occur. Salutes have also been known to return to the ground before exploding, sometimes in the midst of a crowd. The expected reduction in strength of a fuel-air salute ignited while lying on the ground should reduce the danger of injury to spectators.

Fuel-air explosions have been reported by others in the general field of pyrotechnics. A fuel-air blast of magnesium powder from a concussion mortar has been reported[1]. This work is the first, however, that I am aware of in which the subject of investigation is an aerial salute, where the fuel is dispersed in three dimensions making the dust concentration drop very fast with distance. This paper is a progress report on the present status of that work. The device is not yet perfected, and it must be developed further before it will become a commercially viable replacement for the conventional salute. The author hopes that this preliminary paper will stimulate interest in others to help achieve this goal.

Theory

Dust Explosions of Fine Metallic Fuels

A cubic meter of air at STP (Standard Temperature and Pressure) contains approximately 299 g of oxygen. This is the same amount of oxygen contained in 648 g of potassium perchlorate, the most commonly used oxidizer in aerial salutes. For metallic fuels, Table 1 lists the amount of fuel that can be oxidized by the oxygen in one cubic meter of air.

Table 1. Oxidation of Metal Fuels by Air.

Fuel	Grams Oxidized by 299 g Oxygen (1 m^3)*
Aluminum	336
Titanium	449
Magnesium	445
Zirconium	852

* Reactions with nitrogen will be ignored.

From the numbers in Table 1 it is apparent that the required diameter of the fuel-air mixture prior to ignition is small. This presents a complication. The required delay between the dispersing charge and the initiating charge must then also be very small, probably on the order of a millisecond. Conventional fuses are much too slow, thus some other technology must be employed. While electrical timing and firing can be used to achieve such short delays, the cost constraints on the fireworks industry require that a non-electric delay be employed.

Parameters of interest in designing a fuel-air salute are the minimum explosive concentration (MEC), the maximum explosive concentration, the peak pressure produced, the rate of pressure rise, and their variation with fuel type and particle size. The minimum explosive concentration for fuels of interest in this study are listed in Table 2.

Table 2. MEC of Selected Fuels in Air.

Fuel	MEC (Wt. %)	
Magnesium	4*	2.7**
Aluminum	6*	3.0**
Mg/Al	—	1.3**

* from reference 2.

** from reference 3.

Quite surprising is the fact that aluminum and magnesium dusts have a minimum explosive concentration comparable to ethylene oxide vapor, which is reported[4] to be 3%. The disagreement in minimum explosive concentration for aluminum and magnesium between references 2 and 3 is probably due to differences in test initiation and particle morphology (shape) and size. The report[3] of a lower minimum explosive concentration for magnalium than either magnesium or aluminum is not unexpected as alloys between 35 and 67.7 weight percent magnesium have a much lower melting temperature than either magnesium or aluminum as shown in Figure 1. In this system the auto ignition temperature in air closely follows the melting temperature.[3]

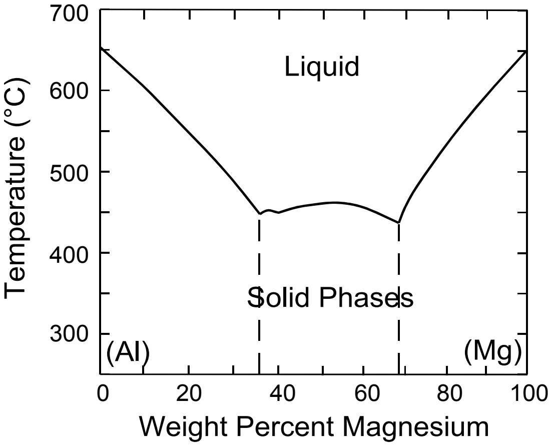

Figure 1. Simplified phase diagram of the Mg-Al system. Compositions of interest lie between the eutectics at 35 and 67.7 weight percent magnesium. See reference 5 for a more complete diagram.

Many studies on metallic dust explosions have been performed at the US Bureau of Mines Pittsburgh Research Center. Their interest in studying dust explosions is understandable in view of the many coal dust explosions that have occurred in coal mines. The following discussion is based primarily on the research of K. Cashdollar[2] and other Bureau of Mines publications.[3,6] Figures 2 and 3 show the explosion properties of various aluminum dusts in air. Similar results should occur for both magnesium and magnalium compounds.

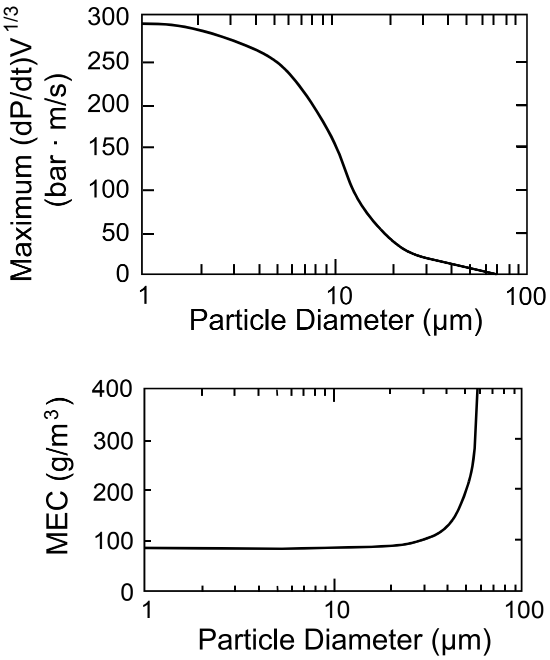

Figure 2. Explosibility data for aluminum dust as function of median particle diameter.[2]

Figure 2 shows the variation of minimum explosive concentration and the pressure rise rate of various aluminum dusts as functions of particle diameter. While the minimum explosive concentration decreases with particle size down to about 30 microns, it is relatively independent of particle size below 30 microns. The maximum rate of change of pressure with time increases strongly as the particle size decreases. The best results occur with the smallest particles. The apparent saturation near 1 micron may be due to the increased fractional concentration of aluminum oxide on the smallest particles. Dayu[7] reports similar results. Therefore, potentially the loudest sound will be produced by a fuel-air salute (FAS) with the smallest particle size, as long as the particle size is not so small that prior oxidation greatly reduces the percentage of fuel available or inhibits the reaction rate.

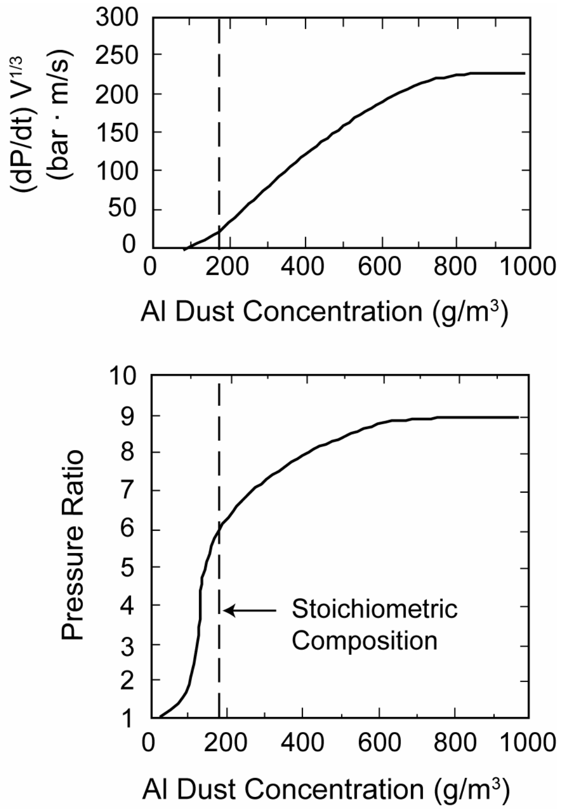

Figure 3. Explosibility data for Alcoa 1401 Aluminum.[2]

Figure 3 shows the variation of pressure rise rate and test chamber peak pressure as functions of aluminum dust concentration. The data was obtained using Alcoa 1401 atomized aluminum, with a mass weighted median particle size around 12 microns.[8] For these particles both the peak pressure and pressure rise rate with concentration reach their highest values at concentrations far over the stoichiometric aluminum/air concentration. Therefore, for aluminum, the best salute results should be obtained using fuel-rich mixtures. No data was reported for finer grades of aluminum, but one would expect that the greater surface to mass ratios of smaller particles would produce maximum explosion effects at lower concentrations. The aluminum producing the highest pressure rise, reported in reference 2, was obtained with an ultra-fine flake aluminum with a median thickness of 1 micron and flake widths ranging from 3 to 30 microns as measured with a scanning electron microscope.[8] This US Bronze/US Aluminum 807 aluminum is coated with about 3 percent stearic acid. The effect of this coating on the experimental results has not been determined.

As might be expected, very fine flake aluminums perform better than atomized aluminums, due to their larger surface areas. Figure 4 shows the results[3] for flake and atomized aluminum. The data presented on these curves was normalized to compare more directly with the later work of Cashdollar.[2] (The explosion chamber used in reference 3 was of different geometry than that in the later work in reference 2, so that absolute comparisons with the two works are not possible.) The data plotted were for the average results obtained for 15 of the finest atomized and flake aluminum samples reported in this reference. The flake aluminums clearly outperform the atomized samples, both in peak pressures and pressure rise rates.

An index of explosivity (I_{ex}) of dust clouds has been defined:[3]

$$I_{ex} = \frac{P_m \left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_m}{T_i \bullet E_i \bullet MEC}$$

where:

P_m is the maximum chamber explosion pressure,
$\left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_m$ is the maximum $\mathrm{d}P/\mathrm{d}t$,
T_i is the minimum ignition temperature,
E_i is the minimum ignition energy, and
MEC is the minimum explosive concentration.

While this is a useful parameter for relatively large dust particle sizes (200 mesh) it becomes less useful for ultrafine powders, because the denominator goes to zero as particles approach the point of being pyrophoric. Calculated explosivity index numbers for a few selected metal dusts are listed in Table 3. Reference 3 did not include values for ultrafine flake aluminums, which may out perform the atomized sample.

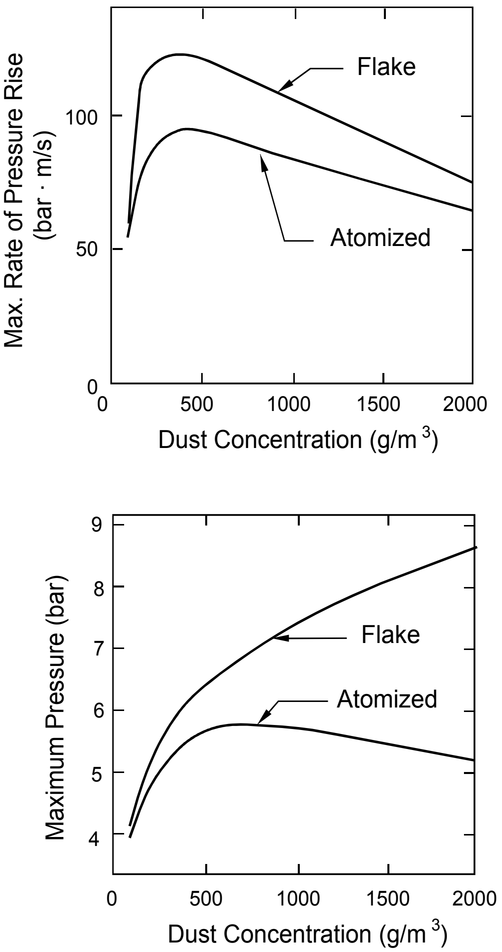

Figure 4. Explosion data comparing finest atomized aluminum with finest flake aluminum[3].

Table 3 . A Few Selected Explosivity Index Numbers Calculated from Data Provided in Reference 3.

Sample	Explosivity Index
Al (atomized, 6 µ diameter)	998
50:50 Mg/Al (milled powder, <44 µ)	1250
Mg (milled powder, <74 µ)	817
Ti (10 µ diameter)	1037

The most likely candidates for use in a fuel-air system are :

- Ultrafine magnalium
- Ultrafine flake aluminum
- Ultrafine atomized aluminum
- Ultrafine titanium

Ultrafine magnesium is not included in this list because of potential long term stability problems. Also the high cost of titanium may remove it from this list. To become commercially successful material costs are very important.

Dust Explosions in an Expanding Cloud

A fuel-air system can be constructed by surrounding an energetic dispersing charge with fuel. Following ignition of the dispersing charge the fuel expands outward. Initially the dust concentration is too great for ignition or for rapid combustion to take place. As the cloud expands to a certain point, the mixture becomes explosive. When the fuel cloud over expands, the concentration drops below the minimum explosive concentration and it will no longer burn. Thus, after explosion of the dispersing charge, there is an optimum delay before igniting the cloud to achieve the maximum pressure rise with time and hence sound. Complicating this picture is the fact that the dust particles are rapidly being slowed by the air. The rate at which they slow will vary with the morphology and size of the particles. Small particles will slow quicker than large particles, and flakes will slow quicker than atomized particles .

The optimum delay before ignition will depend on many parameters: the strength of the dispersing charge, the amount of the fuel surrounding the charge, the morphology and size of the fuel particles, and the type of fuel. If the dispersing charge also initiates combustion of the fuel, the entire scenario changes. While this complex problem could, in principle, be solved analytically to optimize the performance of the fuel-air system, it would require a considerable effort. I have therefore attempted optimization of the fuel-air system by empirical means.

Experimental Results

All test results reported here were obtained using the fuel-air system configuration shown in Figure 5. The exact container dimensions were varied for some tests to accommodate greater or lesser fuel and/or burst charge amounts. The fuel is contained in the outermost compartment, varying in weight depending on the density of the fuel used. Inside the fuel compartment is the dispersing charge. The charge was a fuel rich flash mixture containing 7 parts by weight 20 micron potassium perchlorate, 4 parts of 12 micron atomized aluminum (Alcoa 1401), and 1 part sulfur. For Tests 1 through 13 the charge was held constant at 24 g. This may not be the optimum dispersing charge; however, because of the many parameters in the fuel-air system, some parameters had

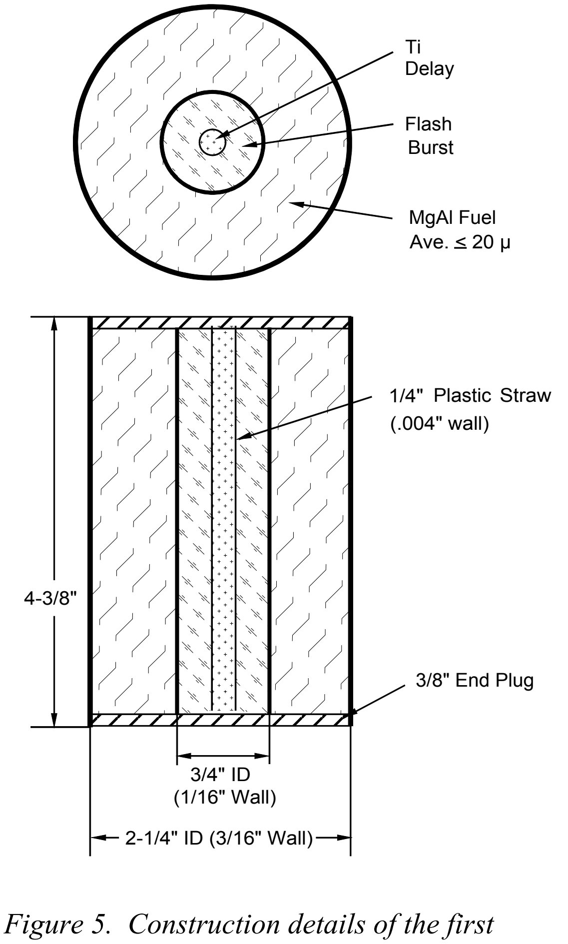

Figure 5. Construction details of the first generation fuel-air salute.

to be fixed in the first iteration. Tests 14 through 16 used reduced burst weights

At the center of the dispersing charge is a plastic tube containing titanium, used as the ignition element. The amount of titanium depends on the compaction of the grade used. Typically 4 to 5 grams of granular titanium were used, or about 8 grams, if spherical titanium. In all cases the three compartments were completely filled. The delay ignition of the titanium is due to the fact that since it is located at the center of the dispersing charge, it will first be compressed, ignited, then follow the outward moving fuel cloud at a later time. A greater delay time would be expected for large titanium particles than for small particles. This was one of the parameters varied in the tests, and it had a significant effect on the strength of the fuel-air system salutes in the tests.

To date only 16 tests have been performed. The first two preliminary tests were July 4, 1996. Although they showed that the fuel-air system could be made to function in principle, no instrumentation was available to yield quantitative results. The next seven tests were done at the Pyrotechnics Guild International (PGI) Convention at Muskegon MI in August 1996. By that time I had obtained 4 Anderson Blasgages to yield a rough quantitative measurement of overpressure. These gauges are described in the appendix. Since there were only four gauges and seven tests, the last three tests were not monitored. The seven tests after the PGI convention were monitored using blast gauges. All salutes were suspended 3 feet above the ground, except Test 2, which was fired while the salute was lying on the ground to test the effect that lack of air would have on the blast. (In all honesty, the fuse burned through the supporting string by accident, but the results were interesting!). The tests results are summarized in Table 4 (on next page).

Discussion of Test Results

Test 1 was the first successful test of the fuel-air system principle. The analysis of the titanium used in the delay, designated as "40 mesh", is shown in Table 5.

Table 5. Size Distribution of the "40 Mesh" Granular Titanium.

Mesh Size	Wt. %
10 to 20	3.4
20 to 40	7.7
40 to 60	11.3
pass 60	77.6

As tests at Muskegon would show, the "40 mesh" material was a poor choice for delay titanium for magnalium. However, since it did allow the fuel-air system to function, it was used in several of the following tests as I was afraid to vary a parameter that functioned.

Test 2 was identical to Test 1 except that the fuel-air system was lying on the ground when it exploded. Very little fuel-air boost occurred, showing that unless the fuel-air system is mixed with air it is ineffective. A large amount of unburned magnalium was found on the ground following the test.

Test 3 established a baseline for the overpressure produced by just the 24 g of burst charge. The distance of 3 feet to the gauges used at Muskegon turned out to be too close, 5 or 6 feet would have been better. The overpressure at 3 feet for the burst charge alone was between 2.4 and 4.1 psi.

Test 4 recorded an increased overpressure of 3.3 to 5.6 psi. The front of the blast gauge was covered with heavy burns, indicating that the fireball extended beyond 3 feet.

Test 5 used spherical titanium of 20 to 40 mesh, and the overpressure was greater than 6.5 psi.

Test 6 used spherical titanium of 40 to 60 mesh. The overpressure was so high at 3 feet that not only were all of the measurement holes completely sheared, but shear also occurred in even the small (.281") holes used for mounting the gauge. By extrapolation of the Anderson calibration data to a hole of this size, I estimate the pressure to be greater than 10 psi. This extrapolation is discussed in the Appendix.

Tests 7, 8, and 9 used the lesser performing "40 mesh" granular titanium delay with larger quantities of fuel. They exhibited very bright

Table 4. Results of the Fuel-Air System Tests.

Test	Fuel – Particle Size and Type	Ti Delay Size	Over-pressure (psi)	Dist. (ft)	Burst Charge (g)	Visual Observation
1	200 g Mg/Al	"40 mesh"	—	—	24	Very strong flash and blast
2	200 g Mg/Al	"40 mesh"	—	—	24	Weak explosion, ineffective*
3	Burst charge only	none	2.4 – 4.1	3	24	Baseline blast, not bright
4	200 g Mg/Al	"40 mesh"	3.2 – 5.6	3	24	Very bright flash
5	200 g Mg/Al	20 – 40 sph.	>6.5	3	24	Very bright flash
6	200 g Mg/Al	40 – 60 sph.	>10	3	24	Most impressive at PGI
7	330 g Mg/Al[a]	"40 mesh"	—	—	24	Bright but 6 better noise
8	285 g Mg/Al[a]	"40 mesh"	—	—	24	Similar to 7
9	360 g Mg/Al[a]	"40 mesh"	—	—	24	Similar to 7
10	180 g Mg/Al	40 – 60 sph.	1.3 – 2.4	5	24	Burns on gauge at 5 ft
11	180 g Al 635	40 – 60 sph.	<1.3	5	24	No evidence of ignition
12	80 g Al 807	40 – 60 sph.	3.7 – 6.5	3	24	Bright flash, unburned aluminum deposits on front of gauge
13	80 g Al 807	60 – 100 sph.	2 –3.7	3	16	All aluminum consumed.
14	180 g Al 105	60 – 100 sph.	2.7 – 4.9	3	16	Subjectively, blast sounded like a good quality 3" salute.
15	180 g Al 105	60 – 100 sph.	2.4 – 4.1	3	7	Produced non-uniform dispersion pattern.
16	135 g Al 807[a]	60 – 100 sph.	3.2 – 5.6	3	14	Flash impressive in bright sunshine. Good report.

* This salute was on the ground.

Al 635 = US Aluminum/US Bronze 635 (Ampal) atomized aluminum with average particle size of 8 µ.

Al 807 = US Aluminum/US Bronze 807, a flake aluminum, average thickness 1 µ, diameter 3 – 30 µ.

Al 105 = Alcan/Toyo 105 atomized aluminum, average particle size is 5 µ.

[a] A larger fuel compartment was used with 3" inside diameter and 1/8" wall.

flashes but were not noticeably louder than Test 6. No gauges were available for these tests.

Photo 1 shows the perforations obtained with the Anderson Blasgages for the burst charge only, Test 3. Photo 2 shows the perforations for the fuel-air system from Test 6. Richard Berris who attended the demonstration at Muskegon took video pictures of the blasts. He supplied me with frame photos of several tests. Photo 3 shows the explosion of Test 3, the burst charge alone. Photo 4 shows one frame of the explosion of Test 5. The titanium delay particles can be clearly seen emerging from the explosion at the top of this frame. Many of the frame photos were overexposed from the intense light emission of the explosions.

Test 10, after the convention, was a repeat of Test 6 (at slightly reduced fuel weight) with the blast gauge located 5 feet from the explosion to obtain a reading that could be more accurately related to future tests. At a distance of 5 feet the gauge showed smoke deposits indicating that the fireball was at least 10 feet in diameter.

Test 11 was the first test using aluminum as the fuel. The aluminum was Ampal 635 (a US Aluminum/US Bronze product). Its mass weighted median particle size is 8 microns (atomized). The burst charge and delay titanium were those found to work well for magnalium. No evidence of fuel-air boost or even ignition of the aluminum was observed.

In Test 12, a sample of US Aluminum/US Bronze 807 flake aluminum was used as a fuel. This material was reported[2] to have a thickness of one micron and a flake width varying from 3 to 30 microns. Due to the low density of these

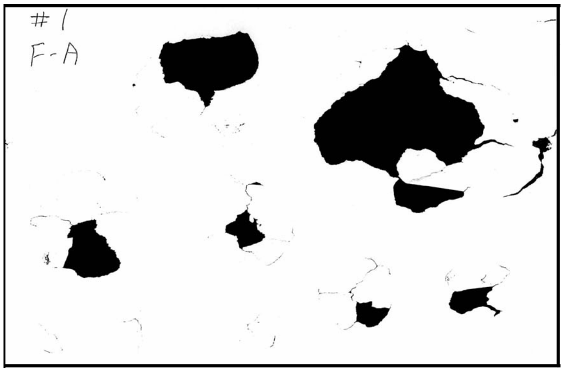

Photo 1. Perforations obtained with the Anderson Blasgage located 3 feet from only 24 g of Burst charge, Test 3.

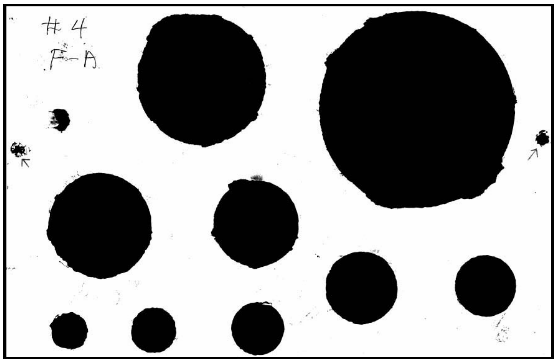

Photo 2. Perforations obtained with the Anderson Blasgage located 3 feet from 24 g of Burst and the Fuel-Air Burst of Test 6.

flakes only 80 grams of charge would fit into the standard container. The burst and titanium ignition charge were the same as for the preceding test. In this case there was obvious ignition of some of the aluminum. A bright flash was observed and the blast gauge showed an increase in the overpressure. The force of the dispersing charge and/or the igniter charge was certainly not optimum as unburned deposits of aluminum covered the front of the blast gauge. This test showed that magnalium is not the only fuel that can be utilized. The lack of complete burning of the aluminum indicated the burst and/or delay elements should be varied for flake aluminum compared to magnalium.

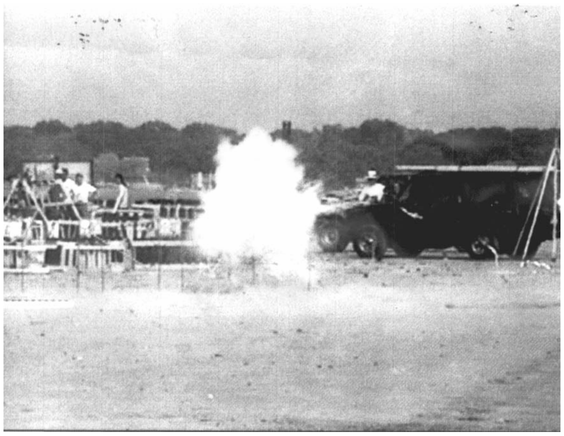

Photo 3. Explosion from Test 3, the burst charge only [from R. Berris].

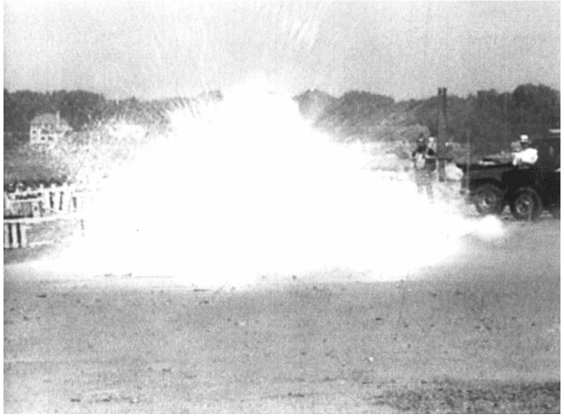

Photo 4. Explosion from Test 5. Titanium delay particles can be seen exiting the explosion. The apparent close proximity of spectators is an optical illusion [from R. Berris].

Test 13 was similar to Test 12 except that the burst charge was reduced from 24 to 16 g, and the spherical titanium delay size was 60 to 100 mesh. The smaller size was used to attempt to achieve more complete combustion with the US Aluminum 807 flake aluminum. In this test all of the aluminum was consumed with no unburned deposits visible on the blast gauge. Shear on the gauge, however, indicated an overpressure of 2 to 3.7 psi, lower than Test 12. The reliability of the Anderson Blasgage for making such comparative measurements on the fuel-air salute is discussed in the appendix.

Test 14 was similar to Test 11 except that Alcan/Toyo 105 atomized aluminum was used as the fuel. This aluminum has a mass-weighted median particle size of 5 microns, finer than the aluminum used in Test 11. The burst charge was reduced to 16 g and 60 to 100 mesh spheri-

Photo 5. Electron microscope picture of milled Mg/Al alloy used in this study.

cal titanium delay was used. Gauge shear indicated an overpressure of between 2.7 and 4.9 psi at 3 feet. Subjectively, the blast sounded to be the equal of a good quality three-inch standard salute.

Test 15 was similar to Test 14 except that the burst charge was further reduced to 7 g. The titanium delay was about 8 g of 60 to 100 mesh spherical material. This produced a very non-uniform dispersion pattern as the small separation between the inside diameter of the burst tube (1/2 inch) and the outside diameter of the delay tube (1/4 inch) made symmetry in the dispersion pattern impossible to achieve. A smaller delay tube and less titanium delay would have been preferable. Additionally, the thick wall of the outer fuel container was not well and uniformly ruptured by this reduced burst charge, disturbing the symmetry of the dispersion pattern. A thinner outer wall should be used as the burst charge is made weaker. Even with the non-uniform dispersion pattern as visually observed from the blast pattern, ignition occurred and an overpressure of 2.4 to 4.1 psi occurred at 3 feet.

In Test 16 a larger fuel compartment was used with three-inch inside diameter and a wall thickness of 1/8 inch. This allowed the amount of US Aluminum 807 flake aluminum to be increased to 135 g, which can be compared more directly with the 180 g of Alcan/Toyo 105 atomized aluminum used in Test 14. The burst charge was 14 g and the delay was 8 g of 60 to 100 mesh spherical titanium. Overpressure from 3.2 to 5.6 psi was recorded at 3 feet. The flash was impressive in bright sunlight and the report was subjectively felt to be at least as loud as a good three-inch conventional salute.

WARNING: Do not attempt to mill magnalium to obtain ultrafine particles. The magnalium fuel used in these tests was produced by reducing 50:50 Mg/Al, 200 mesh material in a ceramic mill. Since I was trying to produce a new effect I chose to use the most reactive material (magnalium) in a very small particle size. This turned out to be a very dangerous operation as some particles of 1 micron or even finer are invariably produced during the milling operation. Magnalium becomes pyrophoric as the particle size drops below 1 micron and the mill will either explode or catch fire. Most of the material produced had a mass weighted median particle size of 20 microns. An electron microscope picture of this material is shown in Photo 5. EDAX (electron excited X-ray fluorescence) measurements on individual particles showed that even particles 10 microns in diameter were 10% oxidized after milling and removal to air. The size distribution of an even finer sample is shown in Figure 6, which had a mass weighted median particle diameter of less than 6 microns. Material of this type is very pyrophoric. It is far too dangerous an operation to be performed by anyone except for commercial producers experienced in handling such hazardous material. It is possible that a successful fuel-air system can be constructed with larger magnalium particles. For example, 50:50 Mg/Al, –325 mesh size (all less than 44 µ) is commercially available from Mapcoa Inc. in Cleveland, Ohio. I have also been informed that in about six months Hart Metals intends to start production of atomized magnalium for a newly emerging commercial need. At that time 10 or 20 micron material should be available, and it would be expected that it will be non-pyrophoric. The commercial availability of satisfactory aluminum powders and flakes, negates the need for attempting any dangerous milling of magnalium.

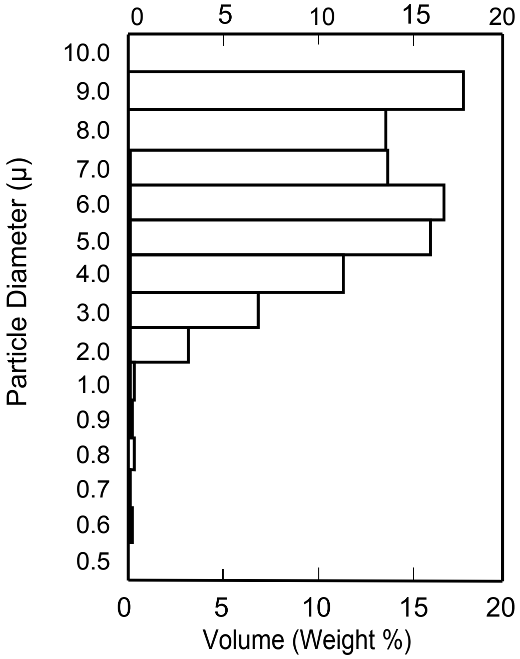

Figure 6. Milled sample of Mg/Al, Horba CAPA–700 Particle Analyzer. Median volume weighted particle diameter = 5.71 µ, std. dev. = 2.03 µ.

Discussion

For the fuel-air system to become a reality, commercial factors as well as theoretical factors must be dealt with. Fireworks is a microscopic business in comparison to other commercial interests. It must rely on using products that are available at a reasonable cost due to their use in other markets. Although the possible savings in liability costs of a safer aerial salute could permit somewhat higher material and manufacturing costs than a conventional salute, they are still important considerations. Areas of concern are the use of ultrafine magnalium which is not yet commercially available, and the additional complexity of a centrally located delay ignition source. Therefore, I see the future development of the fuel-air system as proceeding in the following directions :

1. Eliminate the need for the central delay element. Perhaps the dispersing charge could be located at the center, with the delay element located inside the fuel, possibly consisting of relatively large particles of Black Powder. It might also consist of relatively large particles of Mg/Al. With the lower ignition temperature of magnalium compared to aluminum, see Figure 1, it could also serve to promote the ignition of Aluminum. If the delay composition was so located, one of the manufactured components could be eliminated. If the delay element was Black Powder, the fuel compartment could probably still be classified as Explosives 1.4.
2. Reduce the strength of the dispersing charge to Explosives 1.4. Test results indicate that the 24 g of burst charge used in these tests was excessive. Future tests will be performed with Black Powder burst with the goal of achieving Explosives 1.4 status.
3. Study the effects on performance of the fuel-air salute in extreme conditions of temperature, humidity, and reduced air density at high altitudes. Most of the tests to date were performed at an elevation of 1300 feet above sea level, at temperatures ranging from 50 to 85 ºF, and at relative humidities ranging from 40 to 90 percent.

Values far outside of these ranges may require modification to the fuel-air salute.

4. Have a dialogue with the fine metal suppliers to inform them of our interests. This has already started. If a market analysis justifies it, they will be willing to produce new materials for this purpose. However, cost might be a problem.
5. Use a spherical (ball) shell as the container for the fuel-air system instead of a cylindrical container. With the dispersing charge located in the center of the sphere, a more uniform fuel-air mixing should be obtainable.

Acknowledgments

The author would like to extend thanks to the members of the Western Pennsylvania Skylighters for their assistance in this project, to W. Blair for performing a literature search, to R. Berris for supplying test photos from Muskegon, to R.C. Miller for the calculation in the Appendix, to R. Watson and K. Cashdollar of the US Bureau of Mines Pittsburgh Research Center for technical discussions, to Bonnie Kosanke for transforming my sketches into legible figures, and to K. Kosanke for loaning me the blast gauges and for sharing my enthusiasm for new pyrotechnic effects.

References

1) K. L. & B. J. Kosanke and T. DeWille, “Concussion Mortar Internal Pressure, Recoil, and Overpressure as Functions of Powder Mass”, *Journal of Pyrotechnics*, No. 1, 1995, p 26.

2) K. L. Cashdollar, “Flammability of Metals and Other Elemental Dust Clouds”, *Process Safety Progress,* Vol. 13, No. 3, 1994, p 139.

3) M. Jacobson, A. R. Cooper, and J. Nagy, “Explosibility of Metal Powders”, US Bureau of Mines Report No. 6516 [TN23.07 - 6516 622.06173], 1964.

4) *Handbook of Chemistry and Physics*, Chemical Rubber Company, 51st ed., 1970, p D–82.

5) Max Hansen, *Constitution of Binary Alloys*, McGraw Hill, 2nd ed., 1958, p 106.

6) M. Hertzberg, I. A. Zlochower, and K. Cashdollar, “Metal Dust Combustion: Explosion Limits, Pressures, and Temperatures”, *24th Symposium (Int.) on Combustion*, The Combustion Institute, 1992, p 1827.

7) D Dayu, W. Boliang, T. Mingjuin, and P. Viking,“Influence of Particle Size on Explosion Characteristics of Aluminum Dust Clouds”, *Proceedings of the 17th International Pyrotechnics Seminar*, Beijing, China, 1991, p 577.

8) K. Cashdollar, Personal Conversation.

9) R. C. Miller, Personal Communication.

Appendix

The Anderson Blasgage was originally developed by Paul W. Cooper of Sandia National Laboratories. It consists of two aluminum plates sandwiching a single sheet of standard copier paper. Holes of various diameters are machined into the two plates. A rough measure of overpressure can be determined if the paper exhibits shear at the circumference of a given hole size. Lower pressures cause shear only at the larger holes. Higher overpressures cause shear to occur at smaller holes. This gauge is no longer produced by the Anderson Effects Company but is now produced by the Defense Technology Corporation of Casper Wyoming.

The extrapolation of the Blast Gauge calibration to a smaller hole as used in Test 6 follows the calculation of R.C. Miller.[9] Consider a hole in the plate of diameter *d*, the force on the paper within the hole is the differential pressure (*p*) multiplied by the area of the hole and when the paper yields, the opposing force is the perimeter of the hole multiplied by the shear strength (*s*) per unit length of the paper, thus

$$\frac{\pi d^2}{4} \bullet p = \pi d \bullet s$$

or simply,

$$p = \frac{4s}{d}$$

If the maximum and minimum pressures of a given hole are plotted as functions of the reciprocal of the hole diameter in inches, a linear relationship is obtained which fits the minimum strength values for a shear strength value of the paper of 0.8125 pounds/inch. The minimum strength values can thereby be extrapolated to smaller holes with some confidence, although shadowing by the hole of the paper and accuracy of fit between the two plates will limit this extrapolation at some size (one would expect the extrapolation to yield conservative values for the minimum strength). The maximum values for a given hole size do not follow such a simple relationship and are probably the highest observed values in a series of tests.

During the latest tests it became apparent that the Anderson Blasgage is not a reliable indicator of performance of the fuel-air salute. To obtain shear on the gauge, it must be located within the burning explosion zone of the fuel-air salute, which can exceed ten feet in diameter. It is therefore in the “near field” region of the explosion and inhomogenieties in the shape of the explosion will produce variations in readings. It is desirable to use a pressure gauge in the “far field” region, where these effects are averaged out. Hopefully such gauges can be used in further experiments.

Pyrotechnic Whistles

NOTE: This article originally appeared in
Fourth Symposium (International) on Combustion, 1952.

W. R. Maxwell

Introduction

The fact that certain pyrotechnic compositions when pressed into a tube and ignited burn with a loud whistling noise has been known and used by firework manufacturers for many years. The two compositions most widely employed appear to be (a) a mixture of dry powdered potassium picrate and potassium nitrate in the proportions of about 60/40 and (b) a mixture of powdered gallic acid and potassium chlorate in the proportions 25/75. Whistling compositions have occasionally been used for military purposes. Thus in World War II the Germans had a whistling cartridge (pfeif-patrone) for signaling and the Canadians used a whistling thunderflash for training purposes. In October, 1943, the author was instructed to investigate in collaboration with the Admiralty the use of pyrotechnic whistles burning under water as a possible counter measure to the acoustic homing torpedo then being used by the Germans. As little was known about the factors influencing the intensity and frequency of the sound made by pyrotechnic whistles or their mode of action an investigation into this subject was made and is described in the present paper. A number of measurements were also made on pyrotechnic whistles burning under water, but as they are mainly of acoustical interest only, they will be dealt with very briefly.

Measurement of Frequency

The measurement of the main component of the frequency was accomplished by means of a Rothermel BR 2S crystal microphone connected through an amplifier detector and driver amplifier to the Y-plates of a cathode ray tube. The X-plates of the tube were connected to an amplified time base. This time base was usually set to traverse the tube in about one five hundredth of a second by connecting the input from a thousand cycle tuning fork oscillator to the Y-plates and adjusting so as to get the required number of waves on the screen. The time base could be locked to the incoming signal from the microphone so that the nearest whole number of waves appeared on the screen. These waves could be counted and the fundamental frequency of the whistle determined. To determine the frequency more exactly or to examine the wave-form for the presence of harmonics the time base was not used but the wave-form was obtained by photographing the movement of the oscillograph spot on a rotating drum camera. To get a record of the wave-form for an appreciable length of time the shift knob on the oscillograph was turned so as to move the spot across the screen while taking the record so that a spiral trace was obtained. Immediately before or immediately after taking a record a time base was put on near one edge of the paper by means of the fork oscillator.

Measurement of Intensity

The amplifier detector unit to which the crystal microphone was connected contained a rectification stage which could be switched into the circuit when it was desired to measure the intensity. The output in millivolts was then proportional to the root mean square pressure in the sound wave and the intensity was proportional to the square of this value. The instrument was fitted with a sensitivity switch so as to cover different ranges of intensity, the output was fed into an oscillograph unit and the motion of the spot photographed on a drum camera. A record from a time marker giving ten marks per second was obtained at the same time. The amplifier detector was fitted with a calibrating switch which enabled a known voltage to be applied to the oscillograph where the deflection of the spot was recorded by the drum camera. Since the sensitivity of the microphone and the characteristics of the instrument were known, the value of the calibrating pulse in terms of RMS (root mean square) dynes/cm^2 could be calculated. The output from whistles of the coachman's lamp type (see below) was usually fairly constant, and the mean intensity could then be taken as proportional to the mean value of the root mean square pressure which was obtained by integrating the record with a planimeter.

It was found that, to obtain consistent results, measurements designed to investigate any particular effect had to be carried out on the same day under the same conditions; also if the effect of some physical factor such as tube diameter was being investigated for a particular composition then the composition used had to be all from the same batch and preferably consolidated at the same time. Similarly the ingredients of compositions containing varying proportions had to come from the same batch. Unless all these precautions were taken, inconsistencies which might amount to several hundred per cent were likely to be experienced. All measurements described in this paper were made over grassland with the micro-phone and whistle at a height of about 5 ft above the ground.

Variation of Frequency with Tube Length

When a tube filled with a whistling composition is burned in air it is obvious to the ear that the frequency of the main component of the sound falls continuously as the length of the tube above it increases. To study this effect quantitatively it is necessary, or at any rate very convenient, to use whistles in which the length of the tube above the burning composition remains constant. This is most easily achieved by using a principle similar to that employed in the old-fashioned coachman's lamp and can be most readily understood by reference to Figure 1. It was necessary to coat the pellets of whistling composition very carefully in order to prevent ignition down the sides and consequent explosion. The method which was extensively used for this purpose consisted of coating the cylindrical surface of the pellets with three coats of enamel paint followed by two layers of insulating tape and then a layer of lassolastic tape to give a smooth finish. In addition, a layer of clay was usually pressed at the bottom of the pellet to prevent ignition at the base end. The three knife edges against which the pellet pressed were necessary to cut through the charred remains of the coating materials.

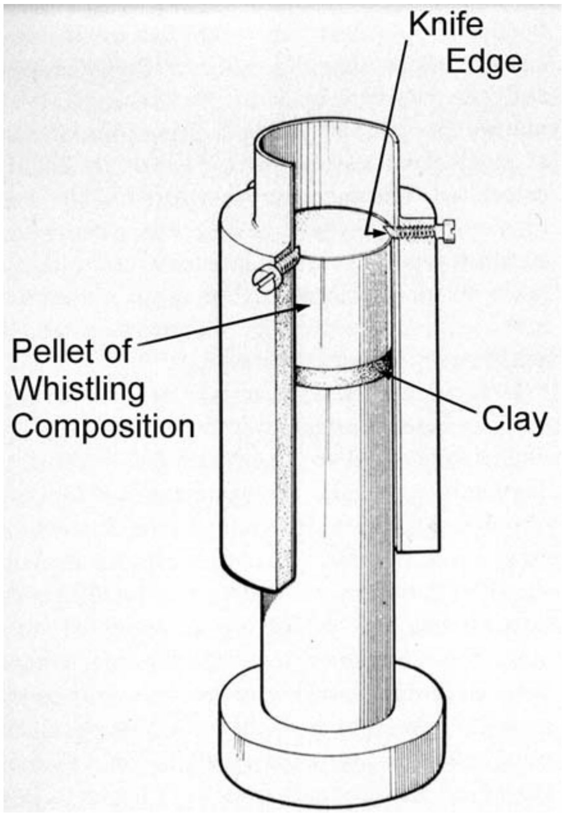

Figure. 1. Constant frequency whistle using principle of coachman's lamp.

The determination of the frequencies produced by different tube lengths were carried out with the following composition (120 BS means that the powdered material had all passed through a 120 BS sieve).

Potassium benzoate, 120 BS	30 parts
Potassium perchlorate, 120 BS	70 parts

Two diameters of steel tubing were used and the result are shown in Figure 2. It will be seen that except for short lengths the frequency is approximately inversely proportional to the length of tube above the composition. The acoustic system is thus similar to that in an open organ pipe. It is a coupled system in which the frequency is controlled mainly by the length of the resonance tube above the burning composition. The frequency is not exactly inversely proportional to the length of tube, but there is an end correction as with an organ pipe. This end effect becomes of major importance for short lengths of tube. For an organ pipe the correction for a tube of radius R is 0.786R (Helmholtz) or 0.824R (Rayleigh), the tube being assumed to have an infinite flange. For pyrotechnic whistles the correction is more complicated, but it is greater, the greater the diameter of the tube. When the length of the tube falls below a certain value, the composition ceases to whistle. The critical whistling frequency varies somewhat with the composition. For the composition containing 30 parts of potassium benzoate and 70 parts of potassium perchlorate this frequency is about 5000 cycles/sec and for most other compositions is below this value. No composition which will whistle at an appreciably higher frequency than this is known to the author.

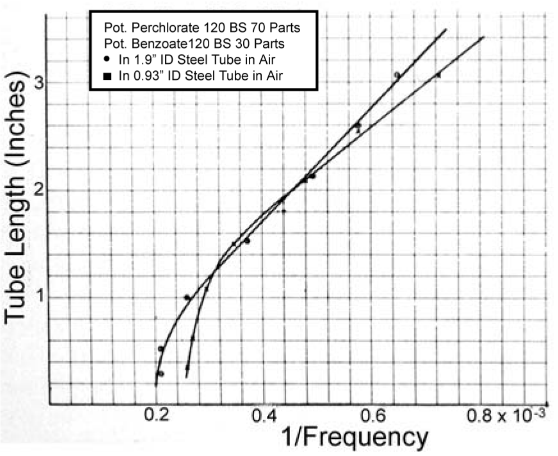

Figure. 2. Effect of tube length on frequency.

Variation of Frequency with Composition

Since the resonating frequency of a tube is dependent on the velocity of sound in the gas in the tube it is to be expected that any change in the ingredients or in the proportion of the ingredients of a whistling composition will lead to a change in the frequency given by a definite tube length, because the composition of the products of combustion and probably the temperature will be different. This variation has been experimentally verified. For example a composition consisting of 70 parts of potassium 2:4 dinitrophenate and 30 parts of potassium nitrate gave a frequency of 2380 cycles/sec when burned in a coachman's lamp type tube, 0.93 inches in diameter and with 1.52 inches of tube above the burning surface. Whilst a composition consisting of 70 parts of potassium perchlorate and 30 parts of potassium benzoate when burned under the same conditions gave a frequency of 2700 cycles/sec.

Effect of Frequency on Rate of Burning

If a composition is ignited in a tube which is too short for it to whistle in, it burns at a rate appreciably greater than it would do if it whistled. This effect can be simply demonstrated by pressing 4 g of 70/30 potassium perchlorate/ potassium benzoate composition already referred to into each of two half-inch diameter tubes three inches long under a dead load of two tons, so that the composition is 0.10 inch down the tube at the one end (Figure 3). If the two tubes are lit from different ends, it will be found that the tube which whistles (i.e., the one in which the composition was ignited at the end furthest in the tube) takes about 1.4 times as long to burn as the one which does not whistle. Some such effect as this might be expected since, as will be shown later, the whistling composition in all probability stops and starts burning alternately so that it is burning for only a part of the time. The difference between the two rates is not nearly so great when the whistle is burning at high frequency. The marked difference between the whistling and non whistling flames is apparent from the photograph shown in Figure 4.

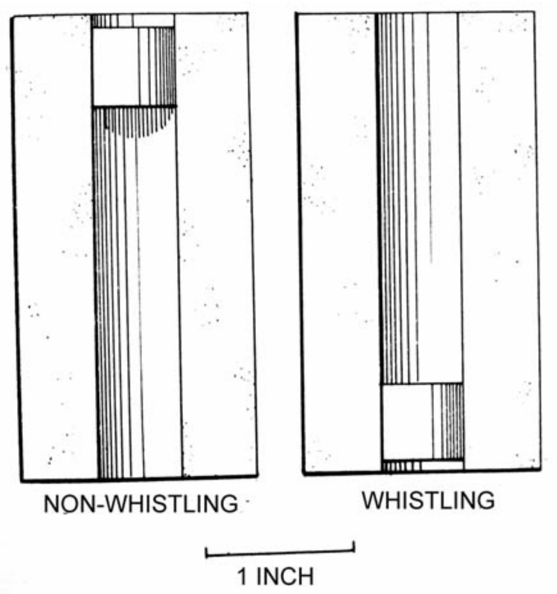

Figure 3. Experiment to show that a whistling composition burns faster under conditions when it cannot whistle.

The effect of the frequency of the whistle on the rate of burning of the composition was investigated by burning short lengths at various depths in a 0.93 inch diameter steel tube. The frequency corresponding to any particular depth was taken as the mean between the values corresponding to the top and bottom of the composition determined from the curve in Figure 2. The results are plotted in Figure 5. It will be seen that the composition burns fastest at high frequencies and that the rate of burning changes much more slowly with frequency at low frequencies.

Acoustic Output of Pyrotechnic Whistles

If the RMS pressure is measured at a considerable distance from the source, the energy flow per unit of surface can be regarded as being the same as for a plane wave, i.e. = $\frac{1}{2}(\delta p \max)^2/\rho c$, where δp max is the maximum variation in pressure in the wave, ρ is the density of the air and c the velocity of sound in air.

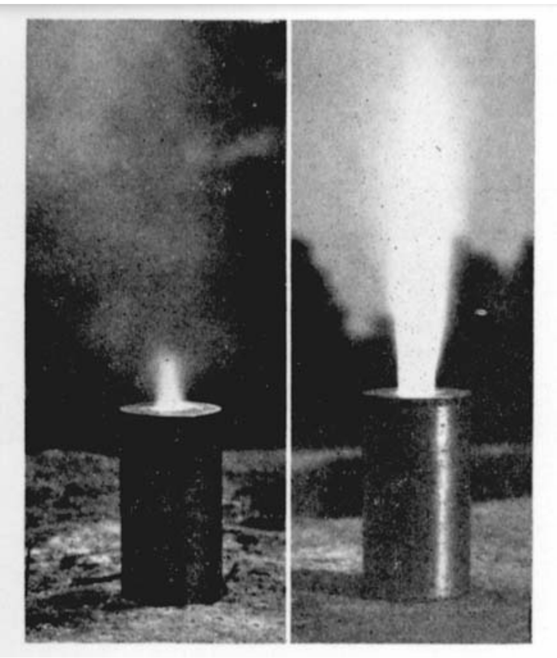

Figure 4. Photographs of whistling and non-whistling flames (Exposure time ca 1/50 sec). Left: Whistling. Right: Non-whistling.

The total energy output of the whistle, if it is assumed that all the sound which strikes the ground is absorbed (which is not true, but the error introduced should be fairly constant)

$$= \frac{4\pi r^2 (\delta p \max)^2}{2\rho c}$$

It is the RMS pressure δp RMS which is actually measured, and since

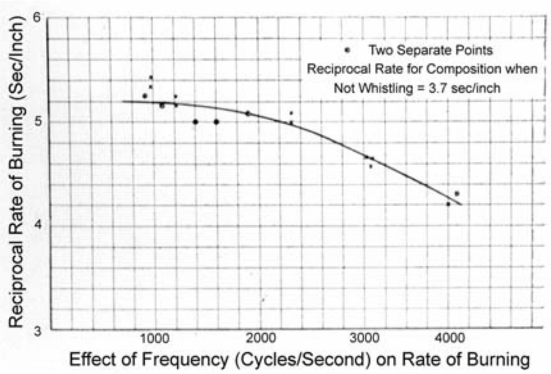

Figure 5. Effect of frequency (cycles/second) on rate of burning.

$$(\delta p\ \mathrm{RMS})^2 = 1/2(\delta p\ \max)^2$$

then

$$\text{Output} \quad = \frac{4\pi r^2 (\delta p \mathrm{RMS})^2}{\rho c}$$

If the above terms are expressed in CGS units, the output is obtained in ergs/sec. This gives an inconveniently large number, and it is usual to convert it to watts by dividing by 10^7. Most of the intensity measurements were made at a distance of 20 ft from the whistle.

Variation of Output with Diameter of Tube

The output of a number of whistles made by pressing the same composition into a series of steel tubes of different diameters was measured. The tubes were all four inches long and the composition was pressed to within 1.5 inches of the open end of the tube. The results are given in Table 1 and plotted in Figure 6. The composition used consisted of 30 parts of potassium benzoate and 70 parts of potassium perchlorate. From elementary reasoning it might be considered that the output would be proportional to the square of the diameter of the tube (i.e., the surface area of the burning composition) or, what is the same thing, the amount of composition consumed per second. In actual fact it will be seen that over the range of tube diameters investigated it varies approximately as the cube of the diameter.

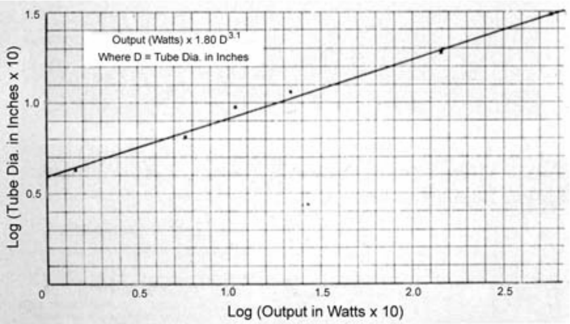

Figure 6. Effect of tube diameter on acoustic output.

Table 1.

Tube Diameter *in.*	Wall Thickness *in.*	RMS Pressure at 20 ft *dynes/sq cm*	Output *watts*
3.01	0.08 – 0.09	72.0	57.6
1.9	0.048	36.3	14.6
1.16	0.048	14.0	2.18
0.94	0.03	10.0	1.11
0.64	0.03	7.3	0.592
0.34	0.03	3.59	0.143

The composition used in the above experiments was found to whistle in steel tubes of as low a diameter as 0.2 inches.

Quality of the Sound from Tubes of Different Diameter

The notes obtained from whistles of diameter not greatly exceeding one inch were in general very pure and the wave-forms obtained from the oscillograph record or direct observation on a cathode ray tube with synchronised time base were sinusoidal. An exception was furnished by a composition containing 70 parts of potassium 2:4 dinitrophenate and 30 parts of potassium nitrate which in a "coachman's lamp" type of tube 0.93 inch in diameter gave a peculiar wave-form with alternate high and low peaks (frequency 2380). The notes obtained from larger whistles of diameter approximately three inches were very raucous and the wave-form was no longer purely sinusoidal but very irregular in shape.

Effect of Material of Tube on Output

Several different materials including aluminum and bakelised paper were used for the tubes, but they made little difference to the output.

Variation of Output with Proportion of Ingredients

A series of compositions containing different proportions of potassium benzoate and potassium perchlorate were burned in a coachman's lamp type of whistle with a constant length of resonating tube and the output measured. The results are plotted in Figure 7 together with a rate of burning curve. It will be seen that the proportions of ingredients for the maximum output are quite critical. The maximum output does not correspond to the maximum rate of burning, but the proportions of the ingredients are quite close to those required for complete combustion.

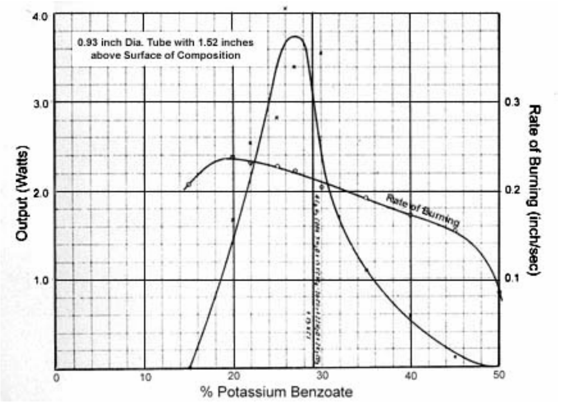

Figure 7. Effect of proportion of ingredients of acoustic output. [Ed. Note: The text on the line at about 29% Potassium Benzoate is $4\ C_6H_5COOK{\cdot}3H_2O + 15\ KClO_4 \rightarrow 26\ CO_2 + 22\ H_2O + 2\ K_2CO_3 + 15\ KCl$.]

Photography of Flames of Pyrotechnic Whistles

A photograph of a pyrotechnic whistle taken in a rotating mirror of the Wheatstone type is shown in Figure 8. The intermittent nature of the flame is clearly visible. A sequence of direct photographs of a pyrotechnic whistle taken on a special form of high speed camera is shown in Figure 9. In order to increase the light output from the flame so that a good image could be obtained with very short exposure time, the potassium benzoate/potassium perchlorate mixture was modified slightly by the inclusion of 5 percent of fine magnesium powder. The composition was pressed to a depth of two inches in a steel tube about 1 inch in diameter and 8 inches long. The whistling frequency was about 1000 cycles/sec and the photographs were taken at about 1500 frames a second with an exposure time of approximately 1/25000 sec. In order to try to get some information on the movement of the flame inside the tube, a narrow longitudinal slot 0.03 inch wide was cut in the wall of a whistle of the above type from the top of the tube almost to the surface of the composition and the burning whistle photographed on a drum camera. A portion of the record is shown in Figure 10. It is clear from this that the intermittent flame starts at or very near to the surface of the composition.

Figure 8. Photograph of pyrotechnic whistle in rotating mirror.

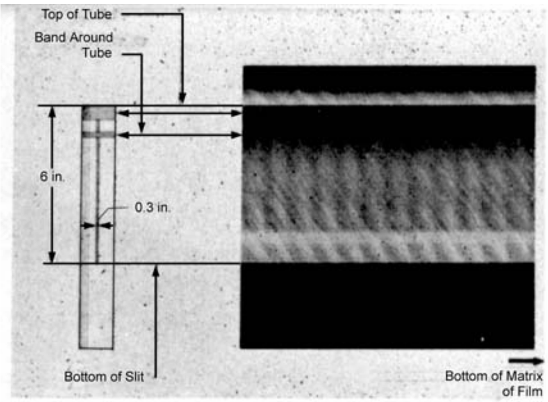

Figure 10. Drum camera photograph of a whistle with a slit in tube.

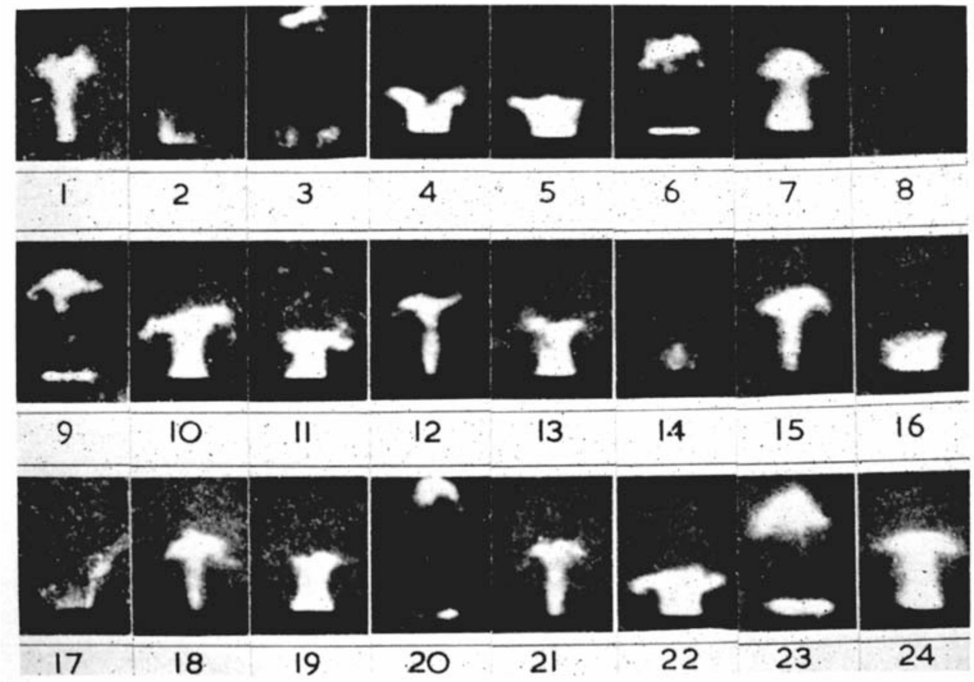

Figure 9. High speed photographs of flame of pyrotechnic whistle.

Effect of Crystal Size of Ingredients

The general effect of crystal size was not investigated. The compositions consisting of potassium perchlorate 70 parts / potassium benzoate 30 parts and also potassium dinitrophenate 70 parts / potassium nitrate 30 parts were found to whistle either much more faintly or not at all if either of the ingredients were only coarsely ground. One series of experiments with the latter composition gave the following results [See Table 2]. The batches of composition were pressed in half-inch diameter steel tubes under a dead load of two tons. The length of the column of composition was about 1.5 inches and the initial depth of the burning surface from the top of the tube about 1.25 inches.

Table 2. Effect of Crystal Size.

	Potassium Dinitrophenate Particle Size	Potassium Nitrate Particle Size	Reciprocal Rate of Burning	Whistling Properties
A	Passing a No. 120 BS sieve	Passing a No. 120 BS sieve	3.0 sec/in	Composition whistled strongly
B	Passing a No. 25 BS, retained on a No. 40 BS sieve	Passing a no. 120 BS sieve	3.0 sec/in	Composition whistled somewhat less intensely than A
C	Passing a No. 120 BS sieve	Passing a No. 25 BS, retained on a No. 40 BS sieve	3.5 sec/in	Low intensity whistle
D	Passing a No. 25 BS, retained on a No. 40 BS sieve	Passing a No. 25 BS, retained on a No. 40 BS sieve	4.3 sec/in	Very low intensity whistle, just faintly audible

The Effect of Lowering the Pressure on the Rate of Burning of Pyrotechnic Whistles

The effect of reducing the atmospheric pressure on the burning of pyrotechnic whistles filled potassium perchlorate 70 parts, potassium benzoate 30 parts, was examined down to a pressure of 10 inches of mercury. The compositions continued to whistle down to this pressure and the rate of burning decreased as shown in Figure 11 where the reciprocal of the rate of burning is plotted against the pressure.

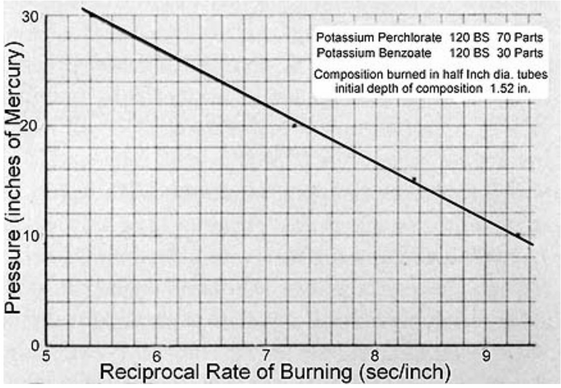

Figure 11. Effect of pressure on the rate of burning of a whistling composition.

Effect of Spin on Whistling Compositions

It is a well known fact that many pyrotechnic compositions when spun about on axis perpendicular to the plane of the burning surface, burn considerably more rapidly. The effect can be explained as due to an increase in burning area resulting from the action of centrifugal force on molten reactants in the burning surface. Compositions which burn with a solid surface do not show the effect. A number of shell tracer bodies consisting essentially of a thick walled tube of 0.375 inch internal diameter were filled with the potassium perchlorate / potassium benzoate composition and spun about their longitudinal axis in an electric spinning machine at speeds up to 30,000 rpm. The spin had no appreciable effect on the rate of burning and the composition whistled normally at all speeds of rotation. It can therefore, be concluded that the burning surface is solid.

The Mechanism of Burning of Pyrotechnic Whistles

It can be inferred and it has been proved above that a whistling composition burns intermittently. Every time the surface is ignited a wave of condensation passes down the tube and is reflected as a wave of rarefaction from the open end. This wave of rarefaction strikes the surface of the composition where it is reflected without change of phase back to the mouth of the tube. At the mouth of the tube it is reflected with change of phase, i.e., as a wave of condensation and travels down to the surface of the composition. It is evident that it is these waves of condensation and rarefaction which cause the composition to burn intermittently, but the exact mechanism is not clear. The variation in pressure which they produced on the surface of the composition are quite small (usually a few ounces per square inch and at the most one or two pounds per square inch) and cannot account for the violent fluctuations in the rate of burning by the simple effect of pressure on rate of burning which is normally observed with propellants and other compositions, since the rate of burning of whistling compositions is not abnormally sensitive to pressure. Now, as already mentioned, the fact that spin has no significant effect on the rate of burning of whistling compositions suggests that they burn with a solid surface. This is confirmed by the almost complete lack of solid residue in the tube of a burnt out whistle. Further, whistling compositions are porous since they consist of consolidated crystals. There would thus appear to be some connections between whistling power and the presence of a solid porous[1] burning surface com-

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[1] Wax would be expected to destroy the porosity of the surface and thus reduce the power to whistle. A small proportion of wax in the composition does in fact have the effect of reducing the power to whistle — the greater the proportion of wax the lower the frequency at which whistling commences. Unfortunately wax also has the normal effect of reducing the rate of burning, and slow burning compositions only whistle at low frequencies. It is difficult to separate the two effects.

posed of fine crystals. (It will be recalled that compositions containing only coarse crystals do not whistle satisfactorily.) All whistling compositions known to the author contain a chlorate, a perchlorate or the salt of an organic acid, and small crystals of one or other of the ingredients will be found to decrepitate in a flame. On the basis of these facts it is suggested that the mechanism of combustion of pyrotechnic whistles is roughly as follows. The combustion of a whistling composition whether in a tube or in the form of a pellet involves the explosion of crystals as an essential part of the process. If the composition is not contained in a suitable tube, these crystals will explode in a random fashion and the products of combustion will flow from the surface at a uniform rate and no definite note or indeed any sound of appreciable intensity will result. If, however, the composition is contained in a suitable resonating tube, the flame will be forced in and out of the surface by alternate waves of compression and rarefaction and every time it is forced into the surface a fresh mass of crystals will explode.

Reaction of Pyrotechnic Whistles

It had been observed in the course of the work described in the present paper that pyrotechnic whistles pressed in light tubes tended to wander about if knocked over on their side and to possess a reaction greater than would be obtained from an ordinary pyrotechnic composition burning at a comparable speed. Accordingly some measurements were made on the reaction of such whistles. The apparatus employed consisted of a small condenser gauge dynamometer used in conjunction with a cathode ray oscillograph and a drum camera. The whistles were fired vertically and since the reaction must alternate between positive and negative and the instrument could not record the negative reaction, it was necessary to weight the whistle so that the total downward force was always positive. As would be expected the mean resultant reaction is positive and can be measured by putting a suitable low pass filter into the electrical recording circuit. It was found that this resultant reaction first increased directly with the length of the resonating tube, or inversely with the frequency, and then became steady. The potassium perchlorate / potassium benzoate mixture pressed in a steel tube, 1.9 inches in diameter gave a resultant reaction of about 6.4 oz for a tube length of 1.5 inches and 20.2 oz for a tube length of approximately 3.5 inches. There appeared to be no significant increase in thrust with a tube length of 5.5 inches. A similar tube filled with gun powder meal gave an almost steady reaction of 4.0 oz. The reaction for the gunpowder calculated from the momentum of the products, which can be deduced approximately from chemical and thermal data, was 3.6 oz so that agreement between theory and practice is quite good. The corresponding reaction for the potassium chlorate/potassium benzoate composition burning smoothly (i.e., without whistling) at the same rate as when whistling was calculated to be 3.8 oz which is considerably less than that observed. The detailed explanation of the reaction is not simple. It is known that a resonator exposed to a source of sound gives a resultant thrust but this explanation is inadequate in the present case.[1]

Most of the thrust probably arises from a somewhat similar mechanism to that in the impulse jet motor as fitted, for example, to the German VI, except that combustion is independent of a supply of atmospheric air. The rapidity with which the composition burns at each impulse causes the pressure inside the tube to build up above atmospheric, owing to the inertia of the gases above the composition; the subsequent expansion of the combustion products results in their having a greater momentum than in smooth combustion. After each impulse the pressure inside the tube will fall below atmospheric and result in a negative reaction. The theory of reaction due to a pulsating gas stream is of interest in a negative reaction. The theory of reaction due to a pulsating gas stream is of interest in connection with the back pressure in the exhaust pipes of internal combustion engines and has been investigated to some extent from this point of view.[2]

The Burning of Pyrotechnic Whistles under Water

This aspect of the work on pyrotechnic whistles will only be mentioned briefly. It was soon established that several pyrotechnic compositions when pressed in open tubes of the same type as those used in experiments in air, would burn under water. When a whistle burns under water, it can be distinctly heard above the surface, although the intensity is greatly reduced: (a) The low transmission coefficient between gas and water; (b) The low transmission coefficient between water and air. The sound is also changed in quality for it is intermittent and very much like the chirping of a canary. The most probable explanation of this is that before the tube of the whistle can behave as an open ended pipe, there must be a certain volume of gas surrounding the open end. But the gaseous products of combustion escape in a series of bubbles so that the end conditions vary continuously and are frequently not satisfactory for resonance. The problems of getting the best end conditions formed part of the wider problem of getting the maximum amount of sound energy with the correct frequency distribution into the water, but this will not be dealt with here.

References

1) J.W.S. Rayleigh, *Theory of Sound*, Vol. 2, Dover, 1945, p 42.

2) H. Martin, *Auto-Technische Zeit*, Vol. 10, 1935, p 243.

Events Calendar

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23rd Annual Conference on Explosives and Blasting Technique

February 2 – 5 1997, Las Vegas, NV, USA

Contact: Int'l Soc. Explosives Engineers
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