Harpur Hill, Buxton. SK17 9JN.
Tel: 01298 218000
Fax: 01298 218590

HEALTH & SAFETY LABORATORY

Explosive output from blackpowder/metal compositions

HSL/2005/27

Project Leader: **S. G. Myatt**
Author : **M. L. Davies**
Science Group: **Fire and Explosion**

Contents

Objective ... iv
Main Findings ... iv
Main Recommendations ... iv

1 INTRODUCTION ... 1

2 EXPERIMENTAL ... 2

2.1 Preliminary work ... 2

2.2 Tube preparation ... 2

2.3 Sample preparation ... 2

2.4 Experimental setup ... 4

3 RESULTS ... 5

4 DISCUSSION AND CONCLUSIONS ... 7

5 FURTHER WORK ... 9

EXECUTIVE SUMMARY

Objective

To determine the explosive output generated by samples of blackpowder/aluminium mixtures confined in card tubes by determining peak overpressure from noise measurements and comparing the output with a 'traditional' perchlorate/aluminium flash composition.

Main Findings

The peak overpressure generated by a sample of blackpowder is comparable to mixtures of blackpowder with various quantities of added aluminium. The pseudo-flash powders all generate a significantly smaller overpressure than the traditional perchlorate/aluminium flash powder in the mixtures investigated.

Main Recommendations

It is recommended that a literature review be completed for this subject, as the extent of the subject is much broader than the issues considered in this study.

Peak overpressure is not a sufficient quantity to fully enumerate the explosive output of an energetic material. Therefore, it is recommended that further tests be carried out to determine the explosive power index of the samples and to use this quantity to compare the test samples with the flash powder sample. The heat of explosion should also be used to more fully quantify the explosive output of pseudo-flash compositions.

It is further recommended that a systematic investigation be performed to identify the optimum quotient of blackpowder/aluminium mixtures.

An investigation of alternative manufacturing techniques should be undertaken to detemine whether a more explosive mixture can be made with these ingredients.

1 INTRODUCTION

A number of fireworks are currently being manufactured which contain mixtures of blackpowder and aluminium instead of flash powder. There is concern that the addition of aluminium to blackpowder could produce a composition with energy output approaching that of flash powders. At present, such mixtures would not be classified as UN 1.1G (as flash powder is), because the definition of flash powder for classification purposes requires an oxidiser to be available for reaction with the metal. It has been argued that the oxidiser in the blackpowder (potassium nitrate) is so intimately mixed with the other blackpowder components as a result of the corning process, that it is effectively unavailable to the aluminium powder for oxidation purposes.

HSE is concerned that mixtures of blackpowder/aluminium may pose a hazard significantly greater than blackpowder alone. They have asked that tests be performed on mixtures of blackpowder/aluminium to determine if this is the case. The tests will measure peak overpressure from samples confined in card tubes with clay plugs at one end and an igniter sealed in the other end with hot melt glue. A range of compositions with different quantities of aluminium will be compared to a ‘standard’ flash composition (perchlorate/aluminium).

2 EXPERIMENTAL

2.1 PRELIMINARY WORK

Preliminary experiments showed that graphited Henry Krank Fine (HKF) blackpowder did not mix very efficiently with the aluminium powder. The graphite coating of the polished blackpowder prevented intimate contact with the aluminium. As a result large experimental variations were observed in the results of noise experiments. An ungraphited meal powder (see section 2.2 for specification) was used as an alternative and proved to mix more satisfactorily with the aluminium.

In addition to specifying a suitable blackpowder, preliminary experiments showed that sealing a match head igniter into the tube produced more reproducible results than using a short length of fast plastic igniter cord (PIC). It was conjectured that the burning fast PIC left a hole in the glue plug thus limiting the degree of confinement. Evidence of this was given by studying the card tubes post-experiment. The tubes that had used fast cord initiators remained in one piece but the glue plug had been displaced from the end. The tubes using match head igniters burst across the diameter of the tube and both plugs remained in place.

2.2 TUBE PREPARATION

Convolute wound card tubes with the following dimensions were used:

Length: 138.7mm
Inside diameter: 10.0mm
Outside diameter: 13.7mm

Clay plugs were formed by loading each tube with 4.0g ± 0.02g of clay and compressing each load to a depth of 105.6mm using a drift and hammer. The resulting plug depth was thus:

Plug depth: 138.7-105.6 = 33.1mm

2.3 SAMPLE PREPARATION

Blackpowder

As discussed previously ungraphited meal powder was selected for its good mixing properties. The specifications for the powder are given below.

Potassium nitrate: 74.0%
Sulfur: 10.4%
Carbon: 15.6

Aluminium

Aluminium powder was obtained from The Aluminium Powder Company. The specifications are:

Purity: 99.7%
Particle size: 8 micron
Particle type: granular

Flash powder

Flash powder was obtained from a stock 3" report shell. It consists primarily of a perchlorate/aluminium mixture.

Composition preparation

Nominal mass for blackpowder/aluminium load* = 60.0g. Actual masses used are given in Table 1.

Table 1 Composition of blackpowder/aluminium mixtures

Mix	*Blackpowder*	*Aluminium*	*Total*	*Aluminium content*
1	57.60g	2.52g	60.12g	4.19%
2	56.44g	3.56g	60.00g	5.93%
3	110.42g	9.63g	120.05g	8.02%
4	45.07g	15.06g	60.13g	25.04%

Mixing procedure

Each mix was weighed into a separate plastic bottle that had been fitted with wooden baffles to aid mixing. The bottles were tumbled for 3½ hours.

Sample construction

Each tube had a match head igniter placed inside it; the head of the igniter was bent back on itself so that the head would be located inside the composition and at the same depth in all tests (Figure 1). Five tubes of each composition were prepared. Each tube had 6.00g ± 0.05g of composition added to it. A wad of tissue paper was used to cover the surface of the composition and hot melt glue was applied to seal the end of the tube.

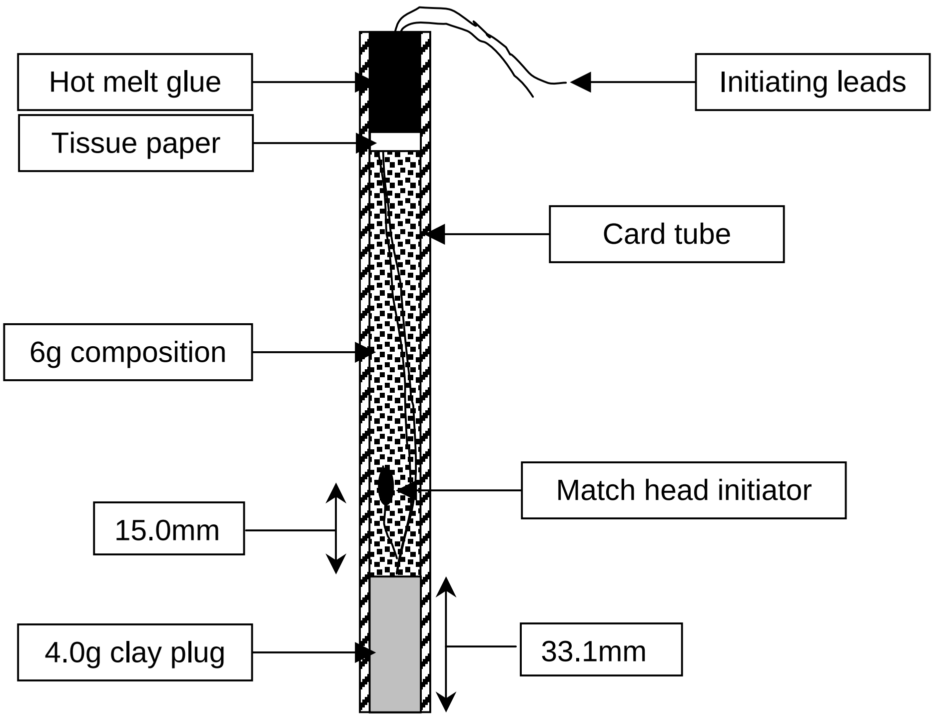

Figure 1 Diagram showing components of prepared sample

* Except mix 3 for which a double run was planned but not implemented.

2.4 EXPERIMENTAL SETUP

All tests were carried out in the same day over a two-hour period. The wind speed was negligible and the ambient air temperature was 8°C. The test set up is shown in Figure 2.

Two sound meters were positioned at a distance of 15m from the sample, at 90 degrees to each other. The sample was suspended in the air by fixing the initiating leads to a suitable support. Noise levels were recorded from both sound meters after each article had been ignited.

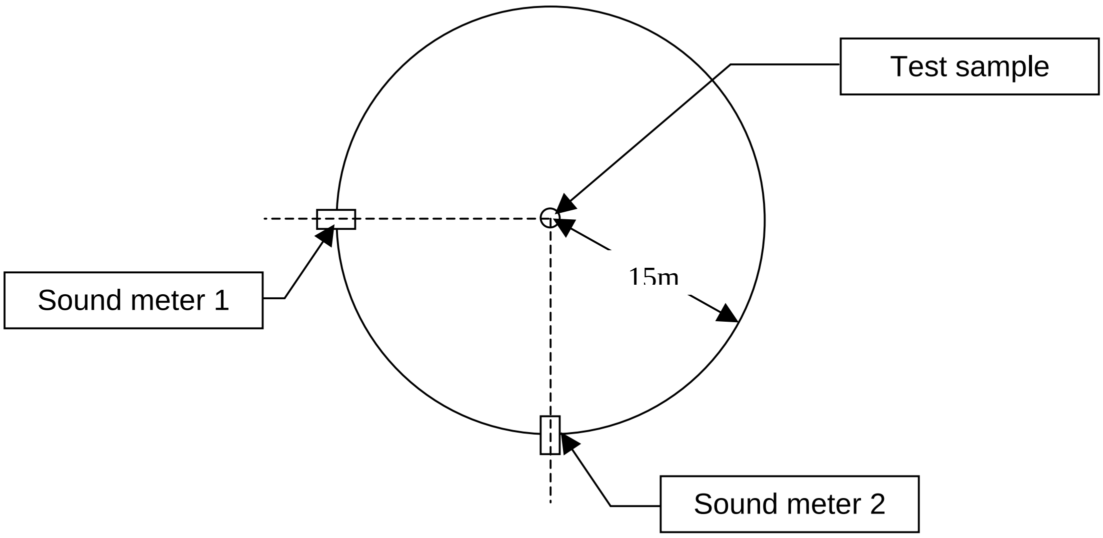

Figure 2 Experimental set up showing relative positions of the sample and the sound meters

The sound meters employed are Brüel and Kjær 2238 Mediator integrating sound level meters with basic SLM software. This meter complies with the coming IEC 1672 Class 1 standard that will supersede the IEC 651 and IEC 804 type 1 standards. This implies that the Mediator complies with current international and national standards. The mediator is a self-contained battery-operated instrument that requires no external connections to other apparatus to measure sound levels i.e. it is a Group X sound level meter according to IEC 1672. The Mediator also comprises of a microphone preamplifier and a pre-polarised free-field ¼" condenser microphone.

One of the main features of the Mediator is that it contains two detectors with independent frequency weighting functions. One is an RMS detector dB(A) and the other a peak detector dB(C).

3 RESULTS

Each test was repeated five times and the dB(C) reading was used to calculate the peak overpressure according to the following equation:

$$p_{calc} = p_o 10^{dB(C)/20}$$

where $p_o = 2 \times 10^{-8}$ kPa; the mean of the overpressure was calculated. Table 2 and Figures 3 and 4 summarise the test results.

Table 2 Mean overpressure obtained from blackpowder metal compositions confined in card tubes

	Soundmeter 1		***Soundmeter 2***		***Average***
Sample	***dB(C)***	***Pressure/Pa***	***dB(C)***	***Pressure/Pa***	***Pressure/Pa***
Bp only	137.1	143.9	134.9	111.4	127.7
Bp/4%Al	136.3	130.0	135.5	119.1	124.6
Bp/6%Al	137.4	148.3	136.7	137.1	142.7
Bp/8%Al	136.8	138.0	137.2	145.6	141.8
Bp/25%Al	140.7	215.8	140.4	209.9	212.8
$KClO_4$/Al	152.6	855.1	151.9	783.5	819.3

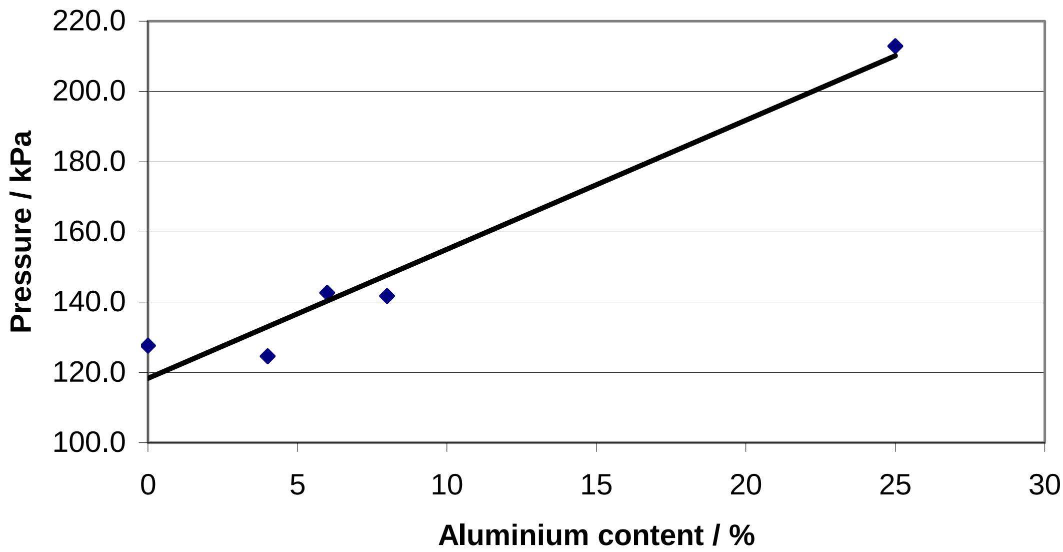

Figure 3 Variation in peak overpressure with proportion of aluminium in the composition

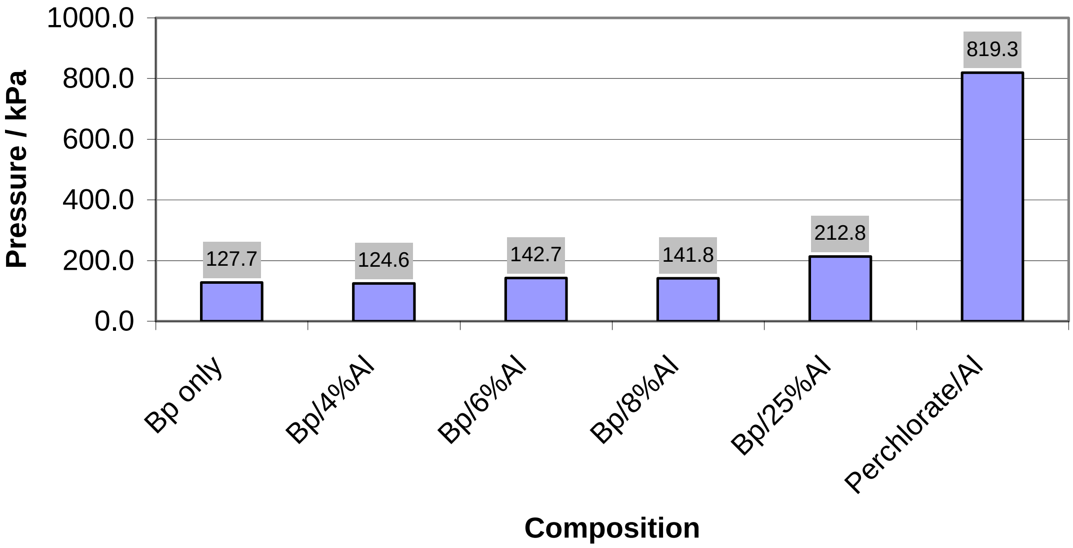

Figure 4 Variation in peak overpressure with composition contd.

Figure 3 shows the dependence of the peak overpressure on the aluminium content of a pseudo flash composition. There is an upward trend, and this follows the following relationship:

$$\textbf{Pressure / kPa = 3.7 x Aluminium content / \% + 118.3} \qquad \textit{Equation 1}$$

However, without a statistical analysis of the data it is not possible to fully determine the validity of this relationship and in the absence of further data, it is not possible to speculate whether the relationship holds over a wider range of parameter values. Therefore it should be used with caution. It is presented to demonstrate the apparent general trend.

From Figure 4, it is clear that the pseudo-flash powders all generate a significantly smaller overpressure than the traditional perchlorate/aluminium flash powder in the mixtures investigated. According to Equation 1 (assuming it is valid over the entire range), for a blackpowder/aluminium mixture to generate the same noise output as the flash powder, a metal content of 190% is required! This is clearly not feasible. Indeed, the maximum possible pressure according to the relationship is for the 100% aluminium case, which generates a peak overpressure of 488kPa. However, without the presence of an oxidiser, this would be unlikely to generate such a pressure. It is highly likely that the relationship is not valid over the full range but it is also possible that a blackpowder/aluminium mixture cannot generate an overpressure comparable to flash powder. Further investigations are required to develop the relationship over a wider parameter range and to verify if it is indeed the case that a pseudo-flash composition cannot be as energetic as a flash composition.

4 DISCUSSION AND CONCLUSIONS

Two of the possible explanations for the observations made in this investigation are outlined below; following this will be a proposal for further work. It is important to determine the mechanism by which the addition of aluminium increases acoustic output so that improved manufacturing techniques can be identified and the optimum explosive output determined.

In traditional flash compositions, the aluminium acts as a fuel and reacts with the perchlorate oxidiser. It is possible that this is the case when aluminium is added to blackpowder. In this case, aluminium and carbon will compete for the potassium nitrate and this will result in an oxygen deficiency. Oxygen would be drawn from the surrounding atmosphere and the reaction rate will be slower. This would explain why the process is less efficient than perchlorate/aluminium mixtures.

However, although the above arguments are valid for many explosives, the fuel and oxidiser in blackpowder are so thoroughly mixed as a result of the corning process, and are probably present in quantities close to stoichiometry that the favoured reaction pathway is probably the reaction between potassium nitrate and carbon. In this case, it could be argued that the increase in acoustic output with increasing metal content with the blackpowder/aluminium mixtures is due to a two stage process involving the reaction of blackpowder followed by dispersion in air and rapid oxidation of aluminium powder by atmospheric oxygen. This would also explain why the process is less efficient than perchlorate/aluminium mixtures.

It follows that if the aluminium can be mixed more intimately with the blackpowder ingredients, such that the selection of a reaction pathway is not so clear, it could be possible to significantly increase the acoustic output of the blackpowder/aluminium mixtures studied thus far. The preferred reaction pathway will be determined by the enthalpy change that is required to initiate the reaction.

A second explanation is that the addition of aluminium to blackpowder creates an energised explosive. Adding to the explosive composition another fuel that has a high heat of combustion can increase the heat of explosion. Such fuels can be found in the lighter elements of the periodic table. Aluminium is a relatively cheap and useful element and can be used to increase performance of other explosives such as ammonium nitrate and TNT.

The oxidation of aluminium is highly exothermic producing –1590 kJ/mol of heat[1]:

$$2Al(s) + 1\tfrac{1}{2}\, O_{2(g)} \rightarrow Al_2O_{3(s)} \qquad \Delta H_c = -1590 \text{ kJ/mol}$$

In an explosive composition, such as blackpowder, the aluminium reacts with the gaseous products particularly in oxygen-deficient compositions where no free oxygen exists[2]:

$$3CO_{2(g)} + 2Al_{(g)} \rightarrow 3CO_{(g)} + Al_2O_{3(s)} \qquad \Delta H_c = -741 \text{ kJ/mol}$$
$$3H_2O_{(g)} + 2Al_{(g)} \rightarrow 3H_{2(g)} + Al_2O_{3(s)} \qquad \Delta H_c = -866 \text{ kJ/mol}$$
$$3CO_{(g)} + 2Al_{(s)} \rightarrow 3C_{(s)} + Al_2O_{3(s)} \qquad \Delta H_c = -1251 \text{ kJ/mol}$$

The volume of gas does not change in the first two reactions; consequently the increase in the output of heat from the oxidation of aluminium prolongs the presence of high pressures.

[1] Chetah, ASTM computer program for chemical thermodynamic and energy release evaluation, ver. 7.3
[2] Knock, C., Lecture Notes "Explosives Ordnance and Engineering Thermodynamics", Department of Environmental and Ordnance Systems, RMCS, Cranfield University, 2004.

The energy of the explosion, being proportional to the area under the pressure time curve, is thus also increased (Figure 5).

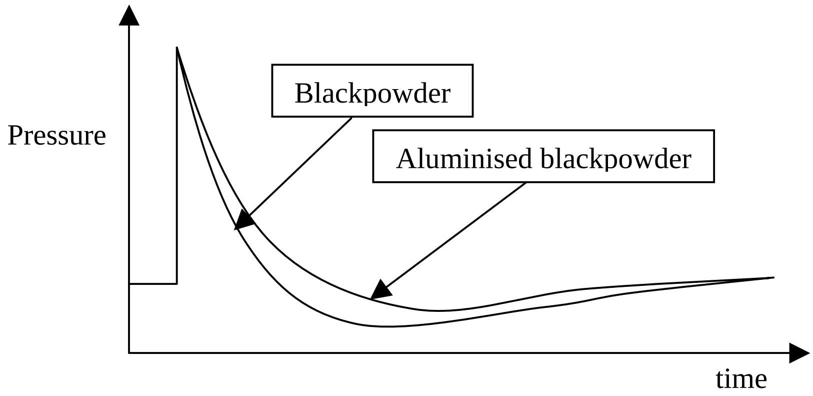

Figure 5 Representation of the effect on the pressure time curve of energising blackpowder with aluminium

There is a limit to the amount of aluminium that can be added to an explosive composition. The heat of explosion (Q) increases with an increase in the quantity of aluminium but the gas volume (V) decreases. This results in the power (Q x V) reaching a maximum at some critical value.

5 FURTHER WORK

Peak overpressure is not a sufficient quantity to fully enumerate the explosive output of an energetic material. Therefore, it is recommended that further tests be carried out to determine the explosive power index of the samples and to use this quantity to compare the test samples with the flash powder sample. The heat of explosion should also be used to more fully quantify the explosive output of pseudo-flash compositions. It is further recommended that a systematic investigation be performed to locate the optimum quotient of blackpowder/aluminium mixtures.

A more detailed study would investigate the processes involved in the combustion of blackpowder/aluminium mixtures. It was suggested in Section 4 that combustion may proceed by a two stage process. Experiments could be designed and performed to see if this is the case. A positive result (confirming a two-stage process) could confirm the hypothesis that the components of the blackpowder are so intimately mixed that the oxidiser is unavailable to react with the aluminium. This would lead to the conclusion that manufacturers are unlikely to be able to produce blackpowder/aluminium mixtures that are more hazardous than flash powder.