Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 3. The Effects of Stoichiometry, Particle Size and Added Materials

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ABSTRACT

The effects of stoichiometry and particle size on the thermal stability and sensitiveness of sulfur/chlorate mixtures have been investigated. Mixtures containing small particles and approximately 5% sulfur were shown to be the least thermally stable. Sulfur/chlorate mixtures containing a third component have also been investigated and compositions with up to 70% added material gave similar low ignition temperatures to mixtures of the two components. All compositions containing sulfur/chlorate were found to be friction sensitive and had limiting loads below the 80 N UN transport criterion. When iron was the third component, the compositions were also impact sensitive, with Limiting Impact Energies below the 2 J UN transport criterion.

Keywords: chlorate, sulfur, sensitiveness, thermal stability, ignition temperature

Introduction

Part 1 of this series[1] discussed the problems posed by the presence of sulfur/chlorate in fireworks compositions, and in Part 2[2] we reported initial studies on stoichiometric sulfur/chlorate mixtures (approximately 30:70 S:$KClO_3$). In this third paper we have extended the work and investigated the effect on thermal stability and sensitiveness of varying both the proportions and particle sizes of sulfur and potassium chlorate. Additionally, we have examined the effect of adding a third component to sulfur/chlorate mixtures. Both the thermal stability and sensitiveness of the resulting mixtures have been investigated.

Experimental

Mixtures were prepared from materials purchased from laboratory suppliers. The potassium chlorate was high purity (AnalaR) grade, and the other materials were standard laboratory grade. Control samples were added to each block. These were prepared from <500 µm materials and were used to monitor any changes due to extraneous effects (e.g., ambient relative humidity). Testing was carried out up to 200 °C, the maximum temperature that could be attained in the blocks. Since initial studies[2] had indicated that flowers of sulfur had similar properties to the sulfur used in Chinese production for a UK importer but was marginally more reactive, this sulfur was used in all the experiments reported in this paper. Additionally, as it was the most reactive sulfur, it was hoped that any subtle changes might be more apparent with this material.

For the majority of the testing undertaken, components were ground and sieved to obtain fractions that passed through a 0.5 mm mesh. When the effect of particle size was being investigated, potassium chlorate sieve fractions of <63, 63–125, 125–250, 250–500 μm, and a small amount of >500 μm were collected. The flowers of sulfur only yielded sufficient material for test in the <63 and 63–125 μm fractions.

Thermal stability of the sulfur/chlorate mixtures was measured in open cardboard fireworks tubes using 2 g samples, as previously reported.[2] Sensitiveness[3] measurements were made with the BAM (Bundesanstalt für Materialforschung und -prüfung) friction apparatus and Fallhammer using standard test methodologies.[4a] In our previous work we used probit[5] analysis to determine the limiting values. While this gives more information regarding the sensitiveness of the materials, a greater number of tests need to be carried out. Some compositions were found to change sensitiveness on standing (probably due to moisture uptake), and therefore the quicker standard method was adopted for the current experimental programme.

Wet Processed Materials

Some fireworks formulations are wet processed[6a] to consolidate the materials (e.g., in star production). To simulate this, compositions (2 g) were mixed dry, and then 0.5 cm^3 water was added with mixing to form a paste. Such mixtures were allowed to air-dry overnight before being cautiously crushed with the back of a non-sparking metal spatula to produce powder that was sampled for test.

Co-Precipitated Potassium Chlorate/Salt Mixtures

Samples of potassium chlorate were prepared by co-precipitation with barium nitrate, strontium nitrate or copper chloride. Potassium chlorate (15 g) was dissolved in 50 cm^3 of boiling water and 2–4 g of salt ($Ba(NO_3)_2$, $Sr(NO_3)_2$ or $CuCl_2 \cdot 2H_2O$) was added. The solution was carefully poured into 200 cm^3 of acetone to precipitate the mixed salts. The fine precipitates were filtered and air-dried prior to use.

Results

The Effect of Stoichiometry

Ignition temperatures for sulfur/chlorate mixtures containing between 1 and 70% sulfur were obtained from duplicate experiments in which 2 g samples were heated at 5 °C hr^{-1}.

Table 1. Ignition Temperatures for Sulfur/Chlorate Mixtures.

% Sulfur	Ignition Temperature (°C)	
	Sample 1	Sample 2
1	142	145
2	145	143
3	134	125
4	138	126
5	123	122
10	119	120
20	122	122
30	123	122
40	123	122
50	123	123
60	125	126
70	127	126

Effect of Particle Size

Sulfur/chlorate mixtures (30% sulfur) were prepared using the available sieve fractions of sulfur and potassium chlorate in order to investigate the effect of particle size on thermal stability, as measured by ignition temperature (Table 2).

Corresponding sensitiveness measurements were made using the available fractions to investigate the effect of particle size on friction sensitiveness (Table 3) and impact sensitiveness (Table 4). To differentiate the friction sensitivenesses, intermediate loadings were used and the "standard" BAM limiting loads are shown in parentheses.

Table 2. Effect of Particle Size on Temperature of Ignition.

Chlorate Fraction (µm)	Ignition Temperature (°C)			
	Sulfur <63 µm		Sulfur 63–125 µm	
<63	119	119	119	119
63–125	119	119	119	119
125–250	125	125	125	125
250–500	134	134	132	137
Control 1(<500)	123		124	
Control 2 (<500)	122		127	

Table 3. Friction Sensitiveness of Sieved Fractions of Sulfur/Chlorate Mixtures.

Material	Limiting Load (N) for Sulfur Fractions	
	<63 µm	63–125 µm
<63 µm chlorate	8 (10)	7 (10)
63–125 µm chlorate	5 (5)	5 (5)
125–250 µm chlorate	10 (10)	7 (10)
250–500 µm chlorate	7 (10)	14 (20)

Table 4. Impact Sensitiveness of Sieved Fractions of Sulfur/Chlorate Mixtures (63–125 µm Sulfur).

Chlorate Sieve Fraction (µm)	Limiting Impact Energy (J)
63–125	4
125–250	5
250–500	5

The Effect of Added Materials on the Thermal Stability of Sulfur/Chlorate Mixtures

Fireworks compositions generally contain a number of components. To enable a large variation in these components to be accommodated, mixtures containing 5% sulfur were selected for this part of the study.

To examine the effect of these materials on the stability of sulfur/chlorate mixtures a series of compositions containing sulfur, potassium chlorate and a third component was produced. The thermal stability of these mixtures was investigated by slow heating (5 °C hr^{-1}). Under these experimental conditions, control samples of 5% sulfur in potassium chlorate (i.e., no third component) ignited in the range 113–116 °C.

Table 5. The Effect of Oxidisers on the Ignition Temperature of Sulfur/Chlorate Mixtures (<500 μm particle size, 5% Sulfur).

Added Oxidiser	Ignition Temperature (°C) for Quantity of Oxidiser				
	10%	30%	50%	70%	90%
Potassium perchlorate	117	116	117	118	N/I
Potassium nitrate	115	117	—	117 (exo)	N/I
Barium nitrate	115	114	115	116	N/I
Strontium nitrate	115	115	116	—	N/I

N/I = no ignition

exo = non-ignition exotherm

Table 6. The Effect of Fuels on the Ignition Temperature of Sulfur/Chlorate Mixtures (<500 μm particle size, 5% Sulfur)

Added Fuel	Ignition Temperature (°C) for Quantity of Fuel				
	10%	30%	50%	70%	90%
Charcoal	120	117	128	—	—
Aluminium	115	114	115	115	N/I
Magnesium	114	114	115	116	N/I
Iron filings	114	114	113	114	118 (exo)

N/I = no ignition

exo = non-ignition exotherm

Table 7. The Effect of Other Material on the Ignition of Sulfur/Chlorate Mixtures (<500 μm particle size, 5% Sulfur).

Material	Ignition Temperature (°C) for Quantity of Material				
	10%	20%	30%	40%	50%
Potassium chloride	115	115	—	116	117
Copper chloride ($CuCl_2 \cdot 2H_2O$)	114	115	117	123	120
Barium nitrate	115	115	116	118 (exo)	124
Strontium carbonate	115	116	116	120	123
Calcium carbonate	111	113	113	113	114

exo = non-ignition exotherm

To investigate whether wet processing exerted an effect, a number of samples were prepared and their thermal stability investigated by slow heating, Table 8.

Table 8. The Effect of Wet Mixed Materials on the Ignition of Sulfur/Chlorate Mixtures (<500 µm particle size, 5% Sulfur)

Material	Ignition Temperature (°C) for Quantity of Added Material	
	20%	40%
Potassium nitrate	114	126
Barium nitrate	115	118
Calcium carbonate	115	115
Copper chloride ($CuCl_2{\cdot}2H_2O$)	113	115

To further investigate the effects of wet mixing, co-precipitated materials were prepared, and ignition temperatures of the resulting "contaminated" potassium chlorate/sulfur were measured for both 5% and stoichoimetric (30%) sulfur, Table 9.

Table 9. The Effect of Co-Precipitated Potassium Chlorate on the Ignition Temperature of Sulfur/Chlorate Mixtures (<500 µm particle size).

Material Co-Precipitated with $KClO_3$	Ignition Temperature (°C)	
	5% Sulfur	30% Sulfur
Barium nitrate	104	89
Strontium nitrate	91	94
Copper chloride ($CuCl_2{\cdot}2H_2O$)	100	98

Note: levels of co-precipitated salt are unknown.

Effect of Added Materials on Sensitiveness of Sulfur/Chlorate Mixtures

Both the friction and impact sensitivenesses of sulfur/chlorate mixtures with an added component were measured using freshly prepared materials. Additionally, some of the mixtures were also investigated either after dry storage or after conditioning at 50 °C and 70% relative humidity for 1 week.

Table 10. The Effect of Added Materials on Sulfur/Chlorate (<500 µm particle size, 30% Sulfur) Friction Sensitiveness.

Material Added to Sulfur/Chlorate Mixture	Friction sensitiveness – Limiting Load (N)		
	Freshly Prepared	Stored Dry	Temperature and Humidity Conditioned
Charcoal (30%)	40	40	20
Iron filings (30%)	20	20	40
Aluminium (30%)	20	20	40
Magnesium (30%)	40	40	40
None	10	≤ 5	≤ 5

Table 11. The Effect of Oxidisers on the Friction Sensitiveness of Freshly Prepared Sulfur/Chlorate (<500 μm particle size, 30% Sulfur).

Material Added to Sulfur/Chlorate Mixture	Friction Sensitiveness – Limiting Load for Percentage Additional Material (N)	
	20%	40%
Potassium perchlorate	40	20
Potassium nitrate	20	40
Barium nitrate	20	40
Control sample with no addition 20 N		

Table 12. The Effect of Added Materials on Impact Sensitiveness (<500 μm particle size).

Material Added to Sulfur/Chlorate Mixture	Impact Sensitiveness – Limiting Impact Energy (J)		
	Freshly Prepared	Stored Dry	Temperature and Humidity Conditioned
Charcoal (30%)	15	5	4
Iron filings (30%)	≤1	≤1	5
Aluminium (30%)	25	7.5	20
Magnesium (30%)	20	10	5
None	3	10	15

Discussion

Previous work by Conkling[7] using differential thermal analysis measurements indicated that the ignition temperatures of sulfur/chlorate mixtures were below 150 °C. Results from our early work[2] using 2 g samples of sulfur/chlorate (30:70) in fireworks tubes suggested ignition temperatures of 115–140 °C. These ignition temperatures were dependent on the sulfur used and sample history. In extending this work, other variables have now been investigated to identify their effect on both the ignition temperatures of such mixtures and their sensitiveness to mechanical stimuli.

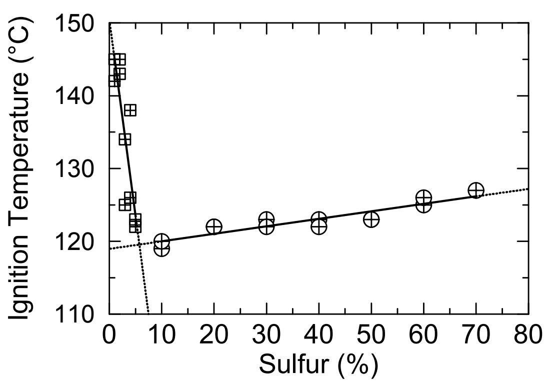

Figure 1. The effect of sulfur content on ignition temperature of sulfur/chlorate mixtures.

The Effect of Stoichiometry on the Thermal Stability of Sulfur/Chlorate Mixtures.

Sulfur/chlorate mixtures containing a low percentage (1–5%) of sulfur showed a reduction in ignition temperature with increasing sulfur content, whereas above 5% sulfur there was a gradual small increase in the ignition temperature with increasing sulfur content. Figure 1 illustrates the experimental data and indicates that the minimum ignition temperature is at approximately 5% sulfur. The majority of subsequent thermal stability testing was therefore carried out on mixtures with 5% sulfur.

The Effect of Particle Size on the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures

Similar series of experiments were carried out to ascertain the effect of the particle size of the components on the reactivity of mixtures of 30% sulfur and potassium chlorate. The sulfur fractions were limited by the small amount of material greater than 125 µm. It was possible to obtain two workable sieve fractions from sulfur and four from potassium chlorate. Table 2 shows that particle size has little effect on thermal stability when the materials are below 125 µm. When the potassium chlorate sieve fraction was larger than 125 µm there was an increase in ignition temperature, presumably due to the decreased surface area of the material reducing the reactivity. As firework compositions tend to be finely divided materials, any sulfur/chlorate mixtures present in a fireworks composition could be expected to lower the ignition temperatures of the mixtures provided that there were no specific interactions with other constituents.

All the combinations of sieve fraction that were tested for friction sensitiveness were found to be very sensitive with limiting loads below the 80 N UN transport criterion.[4a] For comparison, a typical explosive (RDX) has a limiting load of 120 N[8] and a typical primary explosive (lead azide) a limiting load of 10 N. [4b] Thus, the sulfur/chlorate mixtures in Table 3 generally have friction sensitivenesses similar to primary explosives. The impact study indicated that the materials from all the fractions tested had Limiting Impact Energies (LIE's) above the 2 J UN transport criterion.[4a] There was little variation in impact sensitiveness with particle size and no consistent trend was observed. For comparison, a typical explosive (RDX) has a LIE of 7.5 J[8] and a typical primary explosive (lead azide) has a value of 2.5 J.[4c] Hence, the sulfur/chlorate mixtures in Table 4 are less sensitive than primary explosives to impact.

The Effect of Added Materials on the Thermal Stability of Sulfur/Chlorate Mixtures

It could be anticipated that the inclusion of a third component in a sulfur/chlorate mixture would exert some effect on thermal stability and sensitiveness. There are likely to be some materials that would stabilise the mixtures, and others that would destabilise the mixtures. Also, certain materials would have no effect by interaction but would dilute the material. Bases are reported to be included in sulfur used in UK military pyrotechnics to counteract the effect of any acidity from the sulfur.[9] Conversely copper(II) salts are known[10] to destabilise potassium chlorate. Surprisingly, most tests indicated that there was little effect on ignition temperature until high percentages of a third component were added. For most compositions, the addition of up to 70% of a third added material had little effect on the ignition temperatures, which were similar to those for the basic sulfur/chlorate mixture. Beyond this level non-ignition exotherms or no reaction was observed. Charcoal showed the most marked stabilising effect, being the only fuel or oxidiser to increase ignition temperature by 10 °C at 50% addition. This may be due to the ability of charcoal to absorb materials, particularly gases. The other components found to give similar stabilising effect were the bases strontium carbonate and barium carbonate. Carbonates have been reported as stabilising sulfur/chlorate-containing compositions in military pyrotechnics.[9]

Chlorates of many metals (other than the alkali metals) mixed with sulfur are reported to be less thermally stable than potassium chlorate/sulfur mixtures.[11–13] It could be anticipated that the inclusion of barium, strontium or copper salts might lower the ignition temperature of sulfur/chlorate mixtures if there was an interaction with the salt. However, freshly prepared, dry compositions containing barium nitrate, strontium nitrate (Table 5) or copper chloride (Table 7) in sulfur/chlorate did not display reduced ignition temperatures. Copper chloride and the carbonates of both strontium and barium had a slight stabilising effect when present in high percentage in the compositions. The copper chloride presumably exerts an effect by diluting the mixture, while the carbonates may also have a chemical effect by neutralising any acidic species. Similarly, freshly prepared, wet processed materials (Table 8) did not produce compositions with lower ignition temperatures. However, when the potassium chlorate was co-precipitated with these salts, the resulting sulfur/chlorate mixtures had lower ignition temperatures (Table 10). The co-precipitated materials may equate to poor quality potassium chlorate, the inclusion of potassium chlorate having been cited as one of the main causes of many of the early fireworks accidents.[6b] In the co-precipitated materials there will be more intimate mixing of the salts and the possibility of double decomposition reactions leading to small amounts of other chlorates being formed.

The Effect of Added Materials on Sensitiveness of Sulfur/Chlorate Mixtures

Most compositions investigated had friction sensitivenesses below the UN transport criterion of 80 N and impact sensitivenesses above the 2 J criterion. However, the inclusion of iron into the composition produced material that was below both criteria. The inclusion of hard metallic components in pyrotechnic compositions has been reported to increase sensitiveness.[14] For example, when up to 25% titanium was added to Black Powder, mixtures were obtained that had enhanced mechanical sensitiveness.[15]

Conclusions

The present study has indicated that sulfur/chlorate mixtures, with up to 70% other material, are likely to ignite at temperatures below the melting temperature of sulfur (119 °C). This is low compared with normal fireworks compositions. Such mixtures are also friction sensitive, having values well below the UN transport criterion and with some compositions approaching the friction sensitiveness of primary explosives. The inclusion of hard metallic materials is likely to produce mixtures that are not only friction sensitive but also impact sensitive.

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