Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 2. Stoichiometric Mixtures

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ABSTRACT

The sensitiveness and thermal stability of stoichiometric sulfur/chlorate mixtures (approximately 30:70) have been investigated. The mixtures were found to be very sensitive to friction, with BAM limiting loads below 40 N. Some ignitions occurring at the lowest measurable level of 5 N result in limiting loads of ≤ 5 N. When the mixtures were heated slowly in cardboard fireworks tubes, they gave ignition temperatures in the region of 115–160 °C depending on the source and treatment of the sulfur.

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

Introduction

Part 1 of this series[1] discussed the problems posed by the presence of sulfur/chlorate mixtures in fireworks compositions. In this second paper we report initial studies on stoichiometric sulfur/chlorate mixtures (approximately 30:70 S:$KClO_3$). The work has involved measurement of the acidity of the sulfur samples used to formulate the mixtures and determination of both the sensitiveness and thermal stability of the resulting mixes.

Experimental

Sulfur/chlorate mixtures were prepared from samples of potassium chlorate and sulfur purchased from laboratory suppliers or supplied by a United Kingdom (UK) manufacturer and importer of fireworks. The two potassium chlorate samples used were a high purity (AnalaR) laboratory material and a sample typical of that used by a Far Eastern manufacturer. Sulfur samples were standard laboratory grade (flowers of sulfur), and two samples representative of the materials used by a UK and a Far Eastern manufacturer. Additionally, samples of the oxidisers—potassium nitrate and potassium perchlorate—were included in the study for comparison.

Components were ground and sieved to obtain fractions for test that passed through a 0.5 mm mesh. Testing was performed on the sieved materials without further treatment and on samples dried at 100–105 °C, which were then stored in a desiccator. A series of mixtures was prepared from the oxidiser and sulfur samples. The components were weighed and then added to sample bottles where mixing took place, remotely, using a tilting roller mixer.

The mixtures produced were then subjected to thermal or sensitiveness testing.

Table 1. pH Measurement of Sulfur Samples.

Sulfur	Treatment	pH
Flowers	none	6.15–6.31
Flowers	dried 100 °C 2 hrs	5.76–6.05
Flowers	overnight heating at 105 °C	3.91–3.99
Far Eastern manufacturer's	none	5.92–6.36
Far Eastern manufacturer's	dried 100 °C 2 hrs	5.91–6.11
UK Manufacturer's	none	7.97
UK Manufacturer's	dried 100 °C 2 hrs	7.29–7.75

Acidity Measurement

Acidity of the sulfur samples was estimated from pH measurements. A portion of the sulfur, 5.0 g, was placed in a conical flask containing 250 cm^3 distilled water with 1 drop of surfactant added. The mixture was placed in an ultrasonic bath and agitated for 30 minutes, then removed and allowed to cool to room temperature before measuring pH. Measurements were made using a combined electrode which had been calibrated at pHs of 4.01 and 7.01.

Thermal Stability

Cardboard fireworks tubes (70 mm × 10 mm id and 2 mm wall thickness) were prepared with a pressed clay plug (approximately 10 mm) at one end. To measure temperature of ignition, duplicate sets of 2 g samples of the sulfur/chlorate mixtures were placed in cardboard tubes, thermocouples (type T) inserted into the samples and tissue paper plugs loosely inserted into the top. The filled tubes were placed into heated aluminium blocks set to give a temperature rise of 5 ℃ hr^{-1}. A similar thermocouple was placed in the metal block to monitor the block temperature. Temperatures were calculated to ±0.5 °C using a PICO TC-08 combination thermocouple amplifier and analogue-to-digital converter with electronic cold junction. Block temperature was calibrated against a platinum resistance thermometer, which in turn was calibrated and traceable to national standards. The digital data were collected every 10 s using the provided software.[2] Ignition of the sample was recognised by a sharp increase in the recorded temperature compared with that of the block.

Sensitiveness Measurement

The friction and impact sensitivenesses[3] of sulfur/chlorate mixtures, in powdered form, were measured using standard BAM (Bundesanstalt für Material-forschung und -prüfung) apparatus and sample sizes.[4] The criteria for positive events were a visible flash or audible crack for both impact and friction. In no case was there any difficulty in ascertaining a positive result. In the investigation of friction sensitiveness, a number of test samples did not initiate on the forward run but did so on the return; these were considered as giving a positive result. The method utilised to analyse the data was the conventional limiting energy or limiting load, either measured directly or via probit[5][a] studies which involved determining the probability of reaction at a minimum of three points. These data points were usually evaluated from 16 events.

Results

Acidity Measurements

The acidities of the sulfur samples ranged from 3.91 for a sample that had been heated at 105 °C for a prolonged period to 7.97 for the UK manufacturer's sulfur in its "as received" state. Table 1 lists the measured pH for the samples.

Table 2. Ignition Temperatures (°C) for 30:70 Sulfur/Chlorate Mixtures Prepared from "As Received" Materials.

Material	Flowers of sulfur		Far Eastern manufacturer's sulfur		UK manufacturer's sulfur	
Potassium chlorate AnalaR	115.0	115.5	115.5	115.5	158.5	155.5
Potassium chlorate Far Eastern	116.5	115.5	115.5	115.5	152.5	155.5

Table 3. Ignition Temperatures (°C) for 30:70 Sulfur/Chlorate Mixtures Prepared from Dried Materials.

Material	Flowers of sulfur		Far Eastern manufacturer's sulfur		UK manufacturer's sulfur	
Potassium chlorate AnalaR	119.0	119.0	118.5	117.5	159.5	147.5
Potassium chlorate Far Eastern	117.0	118.5	115.0	114.5	149.0	149.5

Table 4. Friction Sensitiveness (Limiting Load, N) for 30:70 Sulfur/Chlorate Mixtures Prepared from "As Received" Materials.

	Type of sulfur		
Oxidiser	Flowers	Far Eastern manufacturer's	UK manufacturer's
Potassium chlorate AnalaR*	10	10	≤5
Potassium chlorate Far Eastern	10	10	≤5
Potassium perchlorate SLR*	60	—	—
Potassium perchlorate Far Eastern	60	—	—
Potassium Nitrate SLR	360	—	—

* AnalaR = analytical reagent.
SLR = specified laboratory reagent for general laboratory applications.

Thermal Stability

Ignition temperatures of slowly heated (5 °C hr^{-1}) sulfur/chlorate mixtures prepared from as received materials without drying are listed in Table 2.

Similar experiments were performed with sulfur and other oxidisers, however the heater system used could only achieve 180 °C, and this was insufficient to ignite these mixtures. Tests were also carried out after drying the materials at 100–105 °C. The ignition temperatures are listed in Table 3.

Sensitiveness Measurements

Friction sensitiveness of 30:70 mixtures of sulfur with the oxidisers was measured for the materials "as received", the only treatment being sieving through a 0.5 mm sieve. The results are presented in Table 4.

Table 5. Impact Sensitiveness (Limiting Impact Energy, J) for Sulfur/Chlorate Mixtures Prepared from "As Received" Materials.

Oxidiser	Type of sulfur		
	Flowers	Far Eastern manufacturer's	UK manufacturer's
Potassium chlorate AnalaR	15	15	15
Potassium chlorate Far Eastern	20	25	20
Potassium perchlorate SLR	20	—	—
Potassium perchlorate Far Eastern	30	—	—
Potassium nitrate SLR	40	—	—

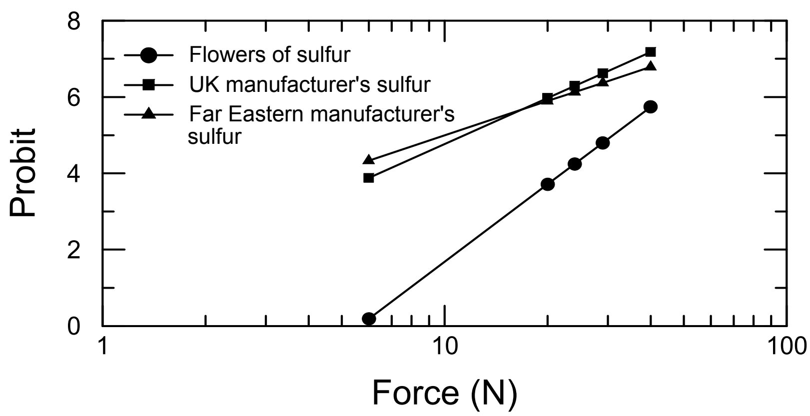

Figure 1. Typical probit plots for friction sensitiveness (mixtures made up from AnalaR potassium chlorate and the indicated sulfur).

Similarly, Limiting Impact Energies were measured and are reported in Table 5.

Dried samples were prepared and their sensitiveness determined by probit analysis. Typical probit lines generated from friction testing are shown in Figure 1.

The probit lines were used to calculate the limiting load applied in the BAM Friction test[4] which corresponds to a 0.17 probability. Table 6 reports the results.

Table 6. Calculated BAM Friction Sensitiveness for 30:70 Sulfur/Chlorate Mixtures Prepared from Dried Materials.

Materials used in formulating mixture		Calculated Limiting Load (N)
Sulfur	Chlorate	
Flowers	AnalaR	40
UK	AnalaR	10
Far Eastern	AnalaR	10
Flowers	Far Eastern	10
UK	Far Eastern	20
Far Eastern	Far Eastern	10

Similarly, the probit lines generated from impact data were used to calculate the limiting impact energies from the BAM Fallhammer test, Table 7.

Table 7. Calculated BAM Impact Sensitiveness for 30:70 Sulfur/Chlorate Mixtures Prepared from Dried Materials.

Materials used in formulating mixture		Calculated limiting impact energy (J)
Sulfur	Chlorate	
Flowers	AnalaR	5
UK	AnalaR	15
Far Eastern	AnalaR	15
Flowers	Far Eastern	10
UK	Far Eastern	20
Far Eastern	Far Eastern	20

Discussion

Tanner[6] has cited the acidity of sulfur in the form of polythionic acids as one cause of the instability of sulfur/chlorate mixtures. He has suggested the reaction

$$SO_2 + 2\,KClO_3 \rightarrow 2\,ClO_2 + K_2SO_4$$

to be the initiation step for a chain reaction leading to ignition. The release of sulfur dioxide from the polythionic acids by the action of heat or friction was proposed as the "trigger" for the reaction. Storey[7] has shown that sulfur and potassium chlorate held at 80 °C spontaneously ignite when sulfur dioxide is blown into the mixture. Additionally, Weingart[8] has reported that the thermal stability of sulfur/chlorate mixtures is increased by the addition of base. The samples of sulfur used in our study had pH values between 3.91 and 7.97. With this large range in acidity it was anticipated that there would be an effect on both thermal stability and sensitiveness of mixtures formed with potassium chlorate.

Ignition temperatures for the sulfur/chlorate mixtures indicate a difference between the UK manufacturer's sulfur and the other samples for both "as received" and dried materials. The alkaline pH measured from extracting the UK manufacturer's sulfur with water suggests that this type of sulfur may contain a small amount of base, possibly intended as an anticaking agent. The addition of base to sulfur is reported as being required in UK military pyrotechnics to stabilise sulfur/chlorate mixtures.[9] Interestingly, heat treatment when drying the sulfur reduces the ignition temperature of sulfur/chlorate mixtures produced from the UK manufacturer's sulfur while for the other sulfur samples the ignition temperature increases with heat treatment. With the acidic samples it would appear that the acidity as measured by pH is not the critical factor. As the sulfur is heated, acidity in the form of sulfuric acid is increased but the weaker, less stable polythionic acids will be decomposed in the heat treatment, removing or reducing the sulfur dioxide-producing material from the reaction until oxidation of the sulfur produces sufficient sulfur dioxide for the reaction to be triggered.

It may be possible that two ignition mechanisms could operate. The sulfur samples which were acidic formed sulfur/chlorate mixtures, which ignited at or below the melting temperature of 119 °C for orthorhombic sulfur, S_α.[10] On the other hand, the sulfur which was found to be slightly alkaline formed sulfur/chlorate mixtures which had higher ignition temperatures (approaching 160 °C). At lower temperatures the action of sulfur dioxide on chlorate has been suggested as the trigger mechanism.[6] An alternative mechanism at temperatures above 140 °C has been proposed by McLain:[11] this involves S_8 molecules breaking into smaller units which can penetrate the potassium chlorate lattice. The temperature at which this occurs is well above the Tammann temperature[12] for potassium chlorate, and there will be significant diffusion of the sulfur fuel into the oxidiser lattice. Ignition should occur at, or before, 159.1 °C, which is the reported temperature for maximum rate of formation of S_3 fragments.[11] This suggests that in our experiments the UK manufacturer's sulfur is reacting by fragmenting its S_8 rings and suppressing any reactions due to sulfur dioxide. Conversely, the other sulfur samples are likely to be reacting via the formation of sulfur dioxide, initially from polythionic acids. If the polythionic acids have been decomposed prior to mixing then the reaction requires sulfur dioxide to be generated by oxidation.

The standard procedures for measuring impact and friction sensitiveness calculate the stimulus required for a single probability of initiation. For the BAM methods this is a limiting value corresponding to a level of approximately 0.17 (or less) probability of initiation. In the corresponding UK methods, 0.50 probability of initiation is found by a "Bruceton Staircase" method.[13] Typically, 15–25 samples would be used for the BAM method and 50 samples for a "Bruceton Staircase" method. In this study we investigated the whole response curve by probit[5] transformation and "standard" BAM methodology.

Storey[7] has reported a Figure of Friction of 0.12 for an unspecified sulfur/chlorate mixture tested using the Rotary Friction apparatus.[14] An approximate BAM limiting load of 6.6 N can be calculated from this value using the relationship for explosives reported by Wharton and Chapman.[15] This limiting load falls within the range measured for the "as received" materials, which were below 10 N (Table 4). Acidity in the form of the sulfur pH does not seem to have a major influence on the sensitiveness of the materials. All samples had BAM limiting loads below 40 N which would correspond to a Figure of Friction of less than 1. Materials having Figures of Friction less than 3 are regarded as being "very sensitive" in the UK.[16] Similarly, the mixtures were below the UN criterion of 80 N for transport in the form tested. Heat treated sulfur samples, which had more acidic pH, appear to be marginally less sensitive to friction. This is probably due to polythionic acid levels being reduced by heating. Further work will be carried out to investigate this.

Impact sensitiveness results for the 30:70 sulfur/chlorate mixtures were all above the 2 J threshold in the UN scheme, indicating that the main mechanical hazard posed by the mixtures is the response to friction stimuli.

Conclusions

Initial work with stoichiometric mixtures (30:70) of sulfur and potassium chlorate indicate that the material can be extremely friction sensitive depending on the source of the sulfur and its treatment. Sulfur/chlorate mixtures in cardboard fireworks tubes have been shown to ignite at temperatures below the sulfur melting temperature when subjected to slow heating. Added materials, of the type likely to be found in fireworks compositions, could affect the reactivity of sulfur/chlorate mixtures and this will form the basis for our next paper.

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Notes

[a] Probit analysis is a statistical treatment used for quantal or all-or-nothing response systems and is particularly useful in extrapolating data to very low or very high probability where an S-shaped response curve is generated. For example, it has been used in studying biological systems to find the mortality rate from insecticide at different concentrations (see reference 5). The insects are either killed or survive. In our case the test sample initiates or does not.

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