Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 4. Firework Compositions and Investigation of the Sulfur/Chlorate Initiation Reaction

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ABSTRACT

Fireworks formulations were modified to produce compositions containing sulfur/chlorate mixtures, and their thermal stability and mechanical sensitiveness were studied. The results indicate that the presence of sulfur/chlorate mixtures in fireworks compositions reduces the ignition temperatures to values well below those obtained with compositions that do not contain the sulfur/chlorate mixture and generally increases the sensitiveness (this was particularly marked in iron-containing mixtures).

The sulfur/chlorate initiation reaction was examined and the mixture was shown to produce sulfur dioxide on heating. Once formed, the sulfur dioxide quickly causes potassium chlorate to decompose and pyrotechnic mixtures containing potassium chlorate to ignite.

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

Introduction

Previous papers in this series have reported thermal stability and sensitiveness studies on sulfur/chlorate mixtures and the effect of the presence of a third component in the mixtures.[1,2] Part four deals with the effect of sulfur/chlorate in a range of fireworks compositions that were modified to produce this mixture.

Several fireworks compositions were identified[3] as containing either sulfur (Table 1) or potassium chlorate (Table 2). By introducing potassium chlorate into a sulfur-containing composition or *vice versa,* it was possible to investigate the effect of the presence of sulfur/chlorate in mixtures similar to fireworks compositions. This produced a series of mixtures: based on Black Powder containing potassium nitrate and from 3 to 21% charcoal, a flash composition containing potassium perchlorate, and chlorate stars each of which had been modified to contain a sulfur/chlorate mixture.

The effect of contamination of the potassium chlorate was investigated by the inclusion of other salts whose chlorates have been identified[4–6] as being less stable than potassium chlorate.

Table 1. Fireworks Compositions that Contain Sulfur.

	Composition (% by mass)					
Component	Rocket	Gerb	Golden Streamers	Tourbillion	Flash-cracker	Pinwheel
Potassium nitrate	68	57	53	36	—	60
Potassium perchlorate	—	—	—	—	50	—
Charcoal (30–100 mesh)	21	10	3	9	—	20
Sulfur	11	10	14	9	25	10
Aluminium (200 mesh)	—	—	—	—	25	—
Meal powder	—	—	—	32	—	10
Iron filings (fine, untreated)	—	23	—	14	—	—
Dextrin	—	—	3	—	—	—
Sodium oxalate	—	—	27	—	—	—

Table 2. Fireworks Compositions That Contain Potassium Chlorate.

	Composition (% by Mass)	
Component	Red Star	Green Star
Strontium nitrate	38.7	—
Barium nitrate	—	38.7
Potassium chlorate	38.7	38.7
Charcoal	12.9	12.9
Dextrin	3.2	3.2
Shellac	6.5	6.5

Experimental

Flowers of sulfur and AnalaR potassium chlorate were used throughout this series of testing. The charcoal was provided by a UK fireworks manufacturer. The other components were purchased from chemical suppliers and were standard laboratory grade. Prior to use, individual materials were ground and sieved to produce a powder passing through a 125 μm sieve.

Loose Compositions

Loose compositions (2 g) were prepared by weighing and mixing. Thermal stability and sensitiveness testing of the compositions was carried out as previously reported.[1]

Pressed Compositions

Star compositions were additionally investigated as pressed material using a hand-operated pill press. Dry compositions were pressed into two 1 g pellets. Wet compositions had the minimum amount of water/ethanol (50:50) added to form a paste and were then pressed to form 1 g pellets. These were allowed to air dry before being tested. Two 1 g pellets with a thermocouple between them were placed into a cardboard fireworks tube and subjected to heating at 5 °C hr^{-1}.

Compositions Prepared from Co-Precipitated Potassium Chlorate

Wet compositions containing sulfur/chlorate mixtures were prepared, dried and tested to investigate the effect of contamination of potassium chlorate. Similarly, co-precipitated materials were prepared by dissolving potassium chlorate (15 g) and the salt under investigation (2–4 g) in 50 cm^3 of hot water and pouring the solution into 200 cm^3 of acetone to precipitate the salts.

Mass Spectrometer Investigation of Sulfur/Chlorate Pre-Ignition Reaction

A sulfur/chlorate mixture (2 mg, 30% S) was heated at 5 °C min^{-1} in an atmosphere of helium/argon (225 ppm Ar) to just below the ignition temperature (155 °C) determined by differ-

Table 3. Ignition Temperature (°C) of Sulfur-Containing Fireworks Compositions with Added Potassium Chlorate.

Composition	Average Ignition Temperature (°C) for % by Mass of Potassium Chlorate				
	0%	5%	10%	15%	20%
Rocket	>200	142	132	127	123
Gerb	>200	134 exo	120	118	116
Golden Streamers	>200	137 exo	123	117	116
Tourbillion	>200	147	137	133	125
Flash-cracker	>200	119 exo	120	117	115
Pinwheel	>200	157	152	144	136

Note: "exo" means a non-ignition exotherm.

ential scanning calorimetry for a similar 2 mg sample (155 °C). The evolved gases were investigated by mass spectrometry (70 eV ionisation energy) and a time profile generated for the evolved products.

Sulfur Dioxide Activated Reactions

Mixtures containing sulfur/chlorate (2 g) were heated in cardboard fireworks tubes placed in a metal block, and sulfur dioxide was passed through. Times to ignition were measured.

Results

The Thermal Stability of Sulfur-Containing Fireworks Compositions Modified To Contain Sulfur/Chlorate

Fireworks compositions listed in Table 1 were modified by replacing part of the oxidiser with potassium chlorate and were then subjected to slow heating (5 °C hr^{-1}). For most compositions, the ignition temperature was lower with increased potassium chlorate and all compositions ignited when there was 10% potassium chlorate. At 5% chlorate both non-ignition exotherms (noted as "exo" in Table 3) and ignitions were recorded. Table 3 summarises the results.

The Thermal Stability of Chlorate-Containing Fireworks Compositions Modified To Contain Sulfur/Chlorate

The compositions containing potassium chlorate listed in Table 2 were modified by the addition of sulfur and similar tests were performed. The results are reported in Table 4.

Table 4. Ignition Temperature (°C) of Potassium Chlorate-Containing Fireworks Compositions with Added Sulfur.

Composition	Processing		Ignition Temperature (°C) for Quantity of Added Sulfur	
			0%	5%
Red Star	loose	dry processed	>200	163
	pressed	dry processed	>200	152
	pressed	wet processed	>200	148
Green Star	loose	dry processed	>200	159
	pressed	dry processed	>200	152
	pressed	wet processed	>200	152

Table 5. Impact and Friction Sensitiveness of Sulfur-Containing Fireworks Compositions with Added Potassium Chlorate.

Composition	Impact Sensitiveness Limiting Impact Energy (J) for Quantity of Potassium Chlorate			Friction Sensitiveness Limiting Load (N) for Quantity of Potassium Chlorate		
	0%	10%	20%	0%	10%	20%
Rocket	20	15	15	>360	120	40
Gerb	20	>30	≤1	>360	>360	240
Golden Streamers	40	25	30	>360	>360	240
Tourbillion	25	25	2	>360	>360	160
Flash-cracker	7.5	10	25	40	60	40
Pinwheel	30	25	40	>360	>360	360

Table 6. Impact and Friction Sensitiveness of Potassium Chlorate-Containing Fireworks Compositions with Added Sulfur.

Composition	Impact Sensitiveness Limiting Impact Energy (J) for Quantity of Sulfur		Friction Sensitiveness Limiting Load (N) for Quantity of Sulfur	
	0%	5%	0%	5%
Red Star	30	40	360	60
Green Star	50	35	240	60

The Sensitiveness of Fireworks Compositions Modified To Contain Sulfur/Chlorate Compositions

The modified fireworks compositions were also subjected to mechanical sensitiveness testing and the results are reported in Tables 5 and 6. In general, the sulfur-containing fireworks composition became more sensitive (lower limiting loads) as the chlorate proportion by mass increased. Similarly, as sulfur was added (5% by mass) there was a corresponding increase in the sensitivity of the chlorate-containing compositions.

The Effects of Wet Processing of Compositions Containing Sulfur/Chlorate Mixtures

Fireworks composition may be processed in a wet state. To investigate the effect this may have on ignition temperature, a range of materials was added to a sulfur/chlorate mixture (5% sulfur) to replace part of the potassium chlorate. Table 7 lists the ignition temperatures for these mixtures after undergoing wet processing followed by air-drying.

Table 7. The Effect of Wet Mixed Additives on the Ignition Temperature of Sulfur/Chlorate Mixtures.

Additive	Average Ignition Temperature (°C) for % by Mass Additive		
	0%	20%	40%
Potassium nitrate	116	114	126
Barium nitrate	116	115	118
Calcium carbonate	115	115	115
Copper(II) chloride	115	113	114

Table 8. The Effect of Co-Precipitation of Additives with Potassium Chlorate on the Ignition Temperature of Sulfur/Chlorate Mixtures.

Precipitated Material	Average Ignition Temperature (°C) for % by Mass Sulfur	
	5% Sulfur	30% Sulfur
Potassium chlorate	114	110
Potassium chlorate/barium nitrate	99	89
Potassium chlorate/strontium nitrate	91	94
Potassium chlorate/copper(II) chloride	100	98

Thermal Stability of Sulfur/Chlorate Compositions Prepared from Co-Precipitated Potassium Chlorate

A limited number of salts were co-precipitated with potassium chlorate to give a low (but unknown) proportion of the salt in the precipitate. A similarly treated sample of potassium chlorate was also prepared and the materials were formulated into sulfur/chlorate mixtures for use in slow heating experiments. Table 8 lists the ignition temperatures of the resulting sulfur/chlorate mixtures.

Mass Spectrometry Study of the Sulfur/Chlorate Initiation Reaction

A sulfur/chlorate mixture (30:70 flowers of sulfur/AnalaR potassium chlorate), when heated to below the ignition temperature, evolved gases with mass per unit charge (m/e) ratios of 16 (O), 32 (S or O_2), 48 (SO or O_3), 64 (SO_2 or possibly S_2) and 80 (SO_3). Figure 1 illustrates the relative abundance of these ions in a typical mass spectrum from the evolved gas.

Evolution of the gas started at approximately 100 °C and reached a maximum at about 150 °C. Figure 2 illustrates the evolution of the two components of interest (m/e 64 and m/e 80) from the evolved gas (the m/e 64 trace has been scaled to fit).
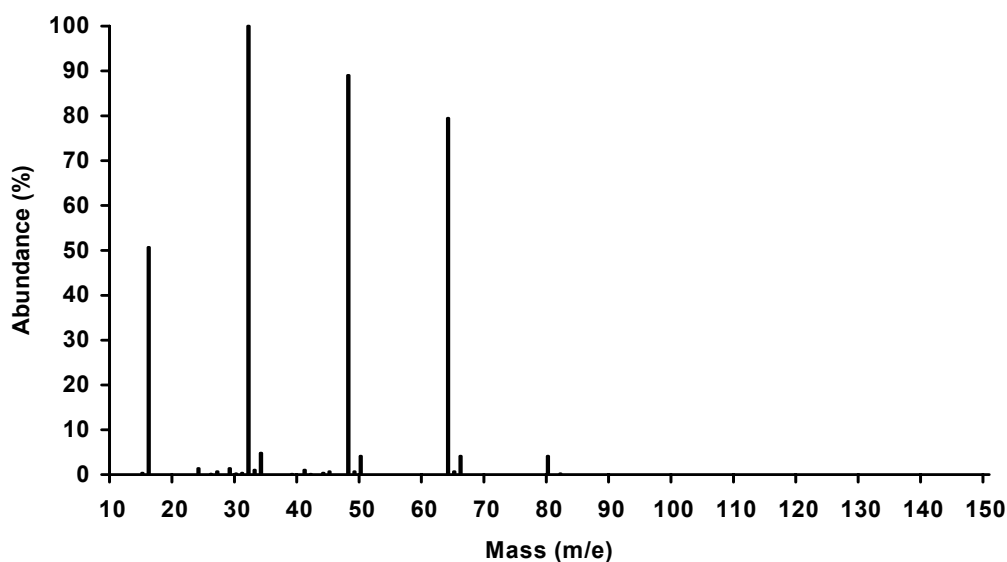

Figure 1. Mass spectrum of gas evolved during thermal reaction of sulfur with potassium chlorate at temperatures below the ignition point.
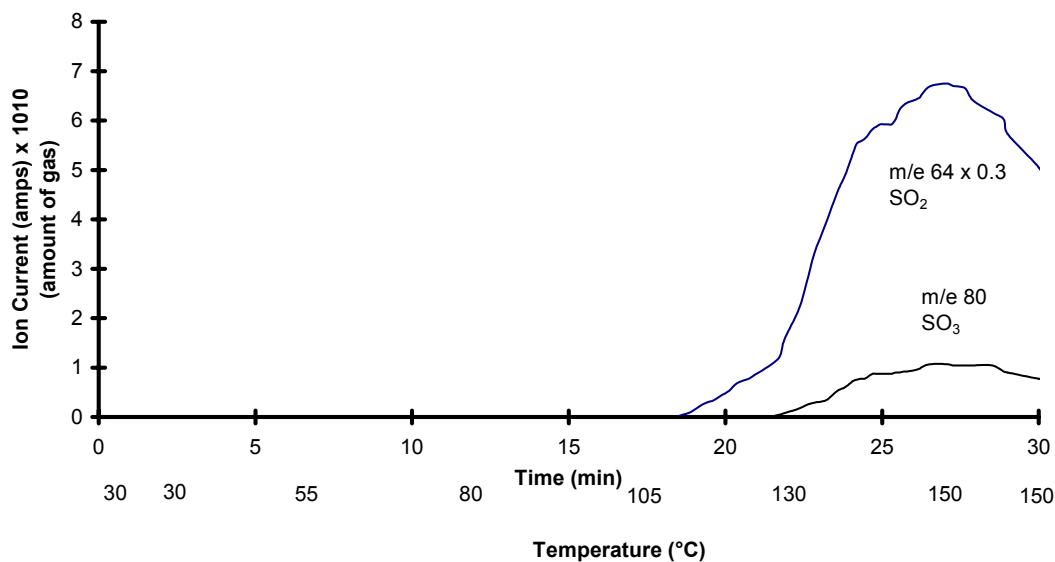
Figure 2. Evolved gas profile for primary gases from heating flowers of sulfur/AnalaR potassium chlorate. Note that the m/e 64 curve was scaled down by a factor of 30% to fit on the chart.

The Effect of Sulfur Dioxide on Sulfur/Chlorate Initiation

The effect of evolved sulfur dioxide on the reactivity of sulfur/chlorate mixtures was examined by passing sulfur dioxide through heated samples. All compositions were ignited at considerably lower temperatures than had occurred without the addition of sulfur dioxide. Table 9 summarises the effects observed.

Table 9. Effect of Passing Sulfur Dioxide through Potassium Chlorate and Mixtures Containing Sulfur/Chlorate.

Composition	Temperature (°C)	Observation
100% AnalaR KClO$_3$	80	immediate exotherm, decomposition after 290 s
	70	immediate exotherm, decomposition after 140 s
	60	immediate exotherm, no decomposition up to 900 s
30% Flowers of Sulfur 70% AnalaR KClO$_3$	80	immediate exotherm, ignition after 115 s
	70	immediate exotherm, ignition after 160 s
	60	immediate exotherm, ignition after 155 s
	50	immediate exotherm, ignition after 300 s
	40	immediate exotherm, ignition after 960 s
Rocket composition * (20% KClO$_3$)	80	immediate exotherm, ignition after 74 s
	70	immediate exotherm, ignition after 150 s
	60	immediate exotherm, ignition after 180 s
	50	immediate exotherm, ignition after 240 s
Gerb Composition* (20% KClO$_3$)	70	immediate exotherm, sample exploded violently, cardboard tube destroyed, time not recorded

* See Table 1 for basic composition.

Discussion

Thermal Stability of Fireworks Compositions Modified To Contain Sulfur/Chlorate

In recent years, a number of fireworks compositions in the UK have been found to contain sulfur/chlorate mixtures. To investigate the effect of the presence of this mixture in fireworks, a series of compositions was modified to produce the sulfur/chlorate mixture. No ignitions were observed below 200 °C in compositions that did not contain a sulfur/chlorate mixture. (This was the highest temperature attainable in the heater blocks used.) Several of the compositions were based on Black Powder, which is reported to have an ignition temperature of approximately 350 °C, while the ignition temperature of flash and star compositions may be considerably higher.[7] The addition of potassium chlorate to a sulfur-containing composition produced a significant reduction in the ignition temperature. When 20% of the normal oxidizer had been replaced by potassium chlorate, the ignition temperatures were similar to those of sulfur/chlorate mixtures alone. Those compositions with the largest amount of charcoal (rocket 21%, pinwheel 20%, and tourbillion 9% plus 32 % meal powder, Table 1) required larger amounts of potassium chlorate to achieve similar low ignition temperatures. Conversely, the flash-cracker composition, with no charcoal, was the most affected by the addition of chlorate. The added stability of charcoal-containing mixtures has been previously identified[2] and is probably due to the ability of charcoal to absorb gaseous material.

Sensitiveness of Fireworks Compositions Modified To Contain Sulfur/Chlorate

A similar trend was observed in sensitiveness testing. The addition of potassium chlorate reduced the values of the limiting impact energies and limiting loads, indicating that the materials were more sensitive. Impact energies equivalent to a mixture that is too sensitive to transport ($\leq$ 2 J)[8] were found when iron was present as a component in a composition containing sulfur/chlorate. Similar sensitisation of

fireworks compositions by hard metallic particles has been reported.[9]

Thermal Stability of Wet Processed Compositions and Compositions Prepared from Co-Precipitated Potassium Chlorate

Wet processed materials (Table 7) had similar ignition temperatures to those previously reported for dry processed samples.[2] However, when co-precipitation of potassium chlorate was carried out with salts likely to form less stable chlorates, significant lowering of the ignition temperatures was observed. Group II chlorates such as barium and strontium were cited by Amiel[4,6] as being much less stable than potassium chlorate when in the presence of sulfur (and other Group VI elements). Copper salts doped into the potassium chlorate lattice are identified by McLain[10a] as causing room temperature detonations of sulfur/chlorate mixtures.

Mass Spectrometry Study of the Sulfur/Chlorate Initiation Reaction

When small samples of sulfur/chlorate were heated in an inert atmosphere, a gas with m/e 64 was generated at temperatures above 100 °C. This corresponds to the m/e ratio for sulfur dioxide or the S_2 fragment. The main sulfur isotopes are 32 (95.0%) and 34 (4.2%) atomic mass units, and an S_2 molecule would be expected to show peaks at 64, 66 and 68 atomic mass units (M, M+2, and M+4). As there are M+2 but no M+4 peaks, the species with m/e 64 is sulfur dioxide. Additionally, at temperatures below the sulfur melting point (119 °C),[11] it is unlikely that S_2 fragments would be generated. Above the melting point there would be an increased possibility of S_2 fragments contributing to the m/e 64 signal. However, it is not until temperatures well above those investigated (ca 2200 °C)[11] that the S_2 fragment is the predominant sulfur species. Additionally, a gas with m/e ratio of 80 is generated slightly later. This corresponds to sulfur trioxide rather than to any sulfur fragment m/e ratio. Other major peaks can be attributed to breakdown products of sulfur dioxide and sulfur trioxide: m/e 48 SO, m/e 32 S, both of which show M+2 peaks, and m/e 16 O. Other species, which were con-

sidered as possibilities, [ClO$_2$ (m/e 67 and 69), Cl$_2$O (m/e 102, 104 and 106) and SOCl$_2$ (m/e 134, 136 and 138)] were not observed during the course of thermolysis.

The Effect of Sulfur Dioxide on Sulfur/Chlorate Initiation

Mechanisms for the initiation of sulfur/chlorate mixtures, as reported by Tanner,[12] suggest that it is the production of sulfur dioxide from some source that initiates the reaction:

$$SO_2 + 2\ KClO_3 + 4\ S \rightarrow$$
$$2\ SO_2 + S_2Cl_2 + K_2SO_4$$
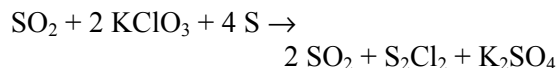
A mechanism was proposed by Rudloff[13] in which sulfur vapour reacts with potassium chlorate to generate sulfur dioxide:

$$2\ KClO_3 + S \rightarrow KClO_4 + KCl + SO_2$$

The only gaseous product of this reaction is the sulfur dioxide and therefore no chlorine-containing species would be detected in the mass spectrum as was observed in the test results. Much of the low temperature (i.e., solid state) reactivity of potassium chlorate is attributed to the low (42 °C) Tammann temperature.[14] At this temperature there is significant lattice diffusion,[10b] which would allow sulfur to migrate into the lattice and be oxidised. At low temperatures this will be a slow process and, if sufficient heat were lost, would not generate an ignition. As the temperature rises and approaches the 119 °C sulfur melting temperature, this diffusion process would accelerate and lead to an ignition. The presence of extraneous sulfur dioxide would short-circuit the initiation and produce a very low temperature, almost instantaneous, ignition. Probably the worst case would be a slow initiation with sufficient material to insulate and retain heat. This could in time lead to an ignition as the processes accelerates through self-heating.

Once sulfur dioxide has been formed, there is an exothermic reaction with potassium chlorate. Decomposition of the material was recorded at temperatures as low as 70 °C. When sulfur was also present, this was reduced to 40 °C with ignition of the mixture occurring. Similar reactions were reported for sulfur/chlorate mixtures by Storey.[15] When a rocket composition—modified to contain sulfur/chlorate—was similarly treated, a low ignition tempera-

ture was observed. However, when the composition additionally contained iron, a much more vigorous and rapid reaction resulted. We have not investigated the processes involved in causing the greater violence of the reaction but report it here as a safety warning to others who may wish to investigate these reactions further.

Conclusions

Sulfur/chlorate-containing mixtures are more likely to be initiated by accidental stimulus (friction and impact) than similar mixtures that do not contain both components. Similarly, they have considerably lower ignition temperatures than other compositions commonly found in fireworks. As such, sulfur/chlorate-containing compositions pose a greater hazard than other fireworks compositions that do not contain both components. As there are suitable compositions that do not pose these added hazards,[16] it is suggested that they are best avoided.

Acknowledgements

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