

Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures

Part 1. Introduction

D. Chapman*, R. K. Wharton* and G. E. Williamson**

* Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom

** HM Explosives Inspectorate, Health and Safety Executive, Magdalen House, Trinity Road, Bootle, Merseyside, L20 3QZ, United Kingdom

ABSTRACT

The presence of sulfur/chlorate mixtures in fireworks compositions has been proposed as the cause of numerous accidents in production and storage. A series of accidents after the introduction of the 1875 Explosives Act led to additional legislation to prohibit such mixtures in the UK. In this paper, as part of an ongoing programme to quantify the hazards associated with the presence of the mixture in fireworks compositions, we have reviewed previously published work and give an outline of the approach we will take in our current research.

Keywords: sulfur, chlorate, pyrotechnics, fireworks, reactivity, accidents, safety

Introduction

Sulfur/chlorate mixtures have, for many years, been known as potential causes of the accidental initiation of pyrotechnics. In the period 1875 to 1894 there are numerous incidents recorded in the United Kingdom (UK) HM Inspectors of Explosives reports that are attributed to the presence of sulfur/chlorate mixtures. The majority of these incidents, which resulted in 11 deaths along with many injuries, were believed to be caused by the spontaneous ignition of the mixture while the remainder were thought to be due to the sensitiveness^[1] of the mixtures.

An accident^[2] in 1887 was attributed to a green star composition where both barium and potassium chlorates were present with sulfur (KClO_3 47%, $\text{Ba}(\text{ClO}_3)_2$ 9%, $\text{Ba}(\text{NO}_3)_2$ 24%,

S 14%, shellac 4%, charcoal 2%), whereas an accident^[3] in 1890 was attributed to a green lance manufactured using two compositions. These comprised a green fire which contained both potassium and barium chlorates and a white fire containing sulfur. It was believed that filling was not carried out carefully and that the two compositions were able to mix and form a sulfur/chlorate mixture. Similar ignitions were reported^[4] involving a green fire composition containing 62% barium chlorate with 8% sulfur.

The acidic nature of the materials used at that time was proposed as a possible cause of the accidents.^[5] The occurrence of such events led to an Order in Council in 1894 prohibiting the manufacture, import, keeping, conveyance or sale of fireworks containing mixtures of sulfur with any chlorate except with the consent of a Government Inspector. Such restrictions on fireworks have been and continue to be in place for fireworks manufactured in or imported into the UK.

In a more recent review of accidents, in this case to minors from chemical experimentation in the 1950s, Burns^[6] reported that 36% of the incidents were attributed to handling sulfur/chlorate mixtures in conjunction with carbon.

In recent years a number of fireworks have been examined by the Health and Safety Laboratory for the presence of sulfur/chlorate mixtures, both qualitatively^[7] and quantitatively.^[8] A proportion of the fireworks tested was found to contain sulfur/chlorate mixtures to different extents within a component composition, and in many cases this necessitated both removal of

the item from sale and destruction of the fireworks. While there have been no recent reported manufacturing or storage incidents in the UK, there are reports of accidents with pyrotechnic materials in many countries (e.g., Peru,^[9] China^[10,11] and India^[12] that could be attributable to the presence of sulfur/chlorate mixtures.)

Role of Sulfur and Chlorate in Fireworks

Sulfur is one of the commonly used fuels in fireworks manufacture and is said to act as a “tinder”, and its low temperature exothermic reactions with a variety of oxidisers are used to initiate other higher temperature reactions.^[13]

Chlorates are present in compositions to either:

- a) act as an oxidiser and/or
- b) act as a chlorine source.

The presence of chlorate is said to generate compositions with relatively low ignition temperatures, in the region of 200 °C for many compositions.^[14] Conkling reports a strong exotherm for sulfur/potassium chlorate mixtures corresponding to ignition at temperatures well below 200 °C.^[15] It is further suggested by Conkling that the low Tammann temperature (defined as 0.5 T where T is the melting temperature in Kelvin) of 42 °C, the exothermic decomposition of potassium chlorate, and the melting temperature of sulfur of 119 °C are responsible for the low ignition temperature. At the Tammann temperature, a solid has 70% of the vibrational freedom present at the melting temperature and considerable diffusion into the lattice is likely. Similar ignitions have been observed with thiourea/potassium chlorate mixtures in processing^[16] where reactivity was attributed to migration of loosely bound sulfur from thiourea into the potassium chlorate lattice producing a material that was both highly sensitive to mechanical stimulus and had temperatures of ignition of about 150 °C.

Previous Work

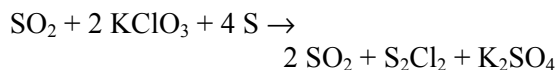
Several previous studies have investigated the reaction of sulfur and metallic chlorates. All workers have found the mixtures to be readily ignited at low temperature or with low mechanical stimulus. As early as 1881, acidity of the sulfur was cited by Dupré^[17] as a major contributing factor in the auto-ignition of sulfur/chlorate mixtures. Additionally, where barium salts were present under moist conditions with potassium chlorate, a double decomposition reaction could occur to produce barium chlorate. Barium chlorate was also shown to be more susceptible to auto-ignition than the potassium salt when mixed with sulfur. Later work by Dupré^[18] concluded that under conditions of heat retention it was a matter of when not if mixtures containing sulfur and chlorate would spontaneously ignite.

Amiel^[19] attributed the spontaneous ignition of chlorates and sulfur to the production of chlorine dioxide (ClO₂). Chlorates, other than alkali-metal chlorates, were shown to produce ClO₂ at temperatures around 60 °C in the presence of water. Additionally, the chlorates of magnesium, nickel, cobalt, cadmium and zinc were reported to react very suddenly.

Taradoire^[20] focused his studies on potassium, barium and lead chlorates. Under wet conditions the production of sulfuric acid followed by the formation of chloric acid (HClO₃) was proposed as the cause of spontaneous ignition of mixtures. The mixtures formed by sulfur with the chlorates of barium and lead were said to ignite at “ordinary” temperatures.

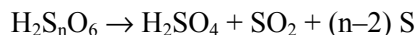
In a further paper, Amiel^[21] reported the effect of sample size, indicating that for large (unspecified) quantities, self-reaction was immediate rather than taking minutes or hours as for smaller (unspecified) quantities.

Tanner^[22] has demonstrated that sulfur dioxide can initiate sulfur/chlorate mixtures. He proposed that the exothermic reaction:



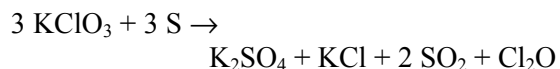
was responsible for the ignition of the material. This chain reaction would be capable of self sustaining once the initial sulfur dioxide had

been generated from polythionic acids ($H_2S_nO_4$) by the equation:



Polythionic acids form on the surface of sulfur crystals, particularly at elevated temperatures due to surface oxidation. Decomposition of polythionic acids occurs when evaporation of surface moisture or a temperature rise make the acid unstable.

An alternative mechanism was proposed by Rudloff^[23] from thermal analysis work carried out on the reaction of sulfur vapour and potassium chlorate. The overall reaction for the complex mechanism was reported as:



Storey^[24] reported friction sensitiveness of sulfur/chlorate mixtures and the results of a number of thermal techniques that were used to assess the likelihood of the ignition of sulfur/chlorate mixtures. Stoichiometric mixtures of sulfur and potassium chlorate were shown to have a Figure of Friction 0.12, compared to 0.84 for lead azide. Since low Figure of Friction values indicate a more sensitive composition, this illustrates that under certain circumstances sulfur/chlorate mixtures can be more sensitive to friction than primary explosives commonly used as initiator compositions. Mixtures containing less than 2.5% sulfur with potassium chlorate were shown to be insensitive to friction.

Hot stage microscopy of mixtures containing 1–5% sulfur with potassium chlorate indicated that they started to decompose at temperatures in the range 165–178 °C, dependent on sample size and percentage of sulfur. Differential thermal analysis on 20 mg samples reduced the initiation temperature to the range 130–155 °C for similar mixtures, again depending on the percentage of sulfur and, in this case, the source of the sulfur. Times to autoignition for stoichiometric mixtures were also considered. Sulfur/potassium chlorate mixtures (1 g samples) were sealed in glass test tubes and the time to ignition was recorded. Sulfur from two sources produced similar results taking 2.5–3 hours for ignition at 90 °C, while the sulfur from a third source ignited in 13.5 minutes at the same temperature. The sulfur samples were

from three different UK manufacturers and were representative of the materials used in fireworks manufacture. Unfortunately no measurement of acidity was reported.

Calorimetry (Seteram C80) on 0.5 g samples of stoichiometric sulfur/potassium chlorate mixtures indicated that exothermic reactions were initiated within a few hours at temperatures below 60 °C under isothermal conditions. Using a heating rate of 0.1 °C min⁻¹, exotherms were observed for similar mixtures at temperatures as low as 62 °C. Mixtures with low sulfur percentage showed higher onset temperatures, but generally these were below the sulfur melting temperature. The addition of sulfur dioxide to a mixture was shown to initiate the reaction almost instantaneously.

Research Plan

Thermal Studies

The early papers by Amiel and Tara-doire^[19,20,21] do not report the sizes of the samples taken, the ratio of sulfur to chlorate in the experiments, nor the conditions under which the experiments were carried out. However, they do indicate an early appreciation of the thermal instability of this mixture. Tanner's work^[22] utilised an almost stoichiometric mixture (33:67) and the acidity of the sulfur was measured.

A previous study,^[24] which defines the conditions employed for the experimental work, used samples contained in glass or metal containers, many of which were sealed systems. The use of a sealed system will prevent the dispersion of any sulfur dioxide produced which could in turn accelerate the autocatalytic reaction yielding unrealistically low reaction temperatures or times to ignition. Tanner's work,^[22] on the other hand, utilised cardboard tubes made from match books after the striker composition had been torn off. This provided an open containment system and the samples tested would therefore not suffer from any effects of confinement. However, his use of a heat lamp and thermocouple positioned in the centre of the sample may have led to unrepresentatively low measured temperatures of ignition since the reaction surface of the material would have

been at a significantly higher temperature than that indicated by the thermocouple. Additionally, it may be possible that some phosphorus contamination remained from the matches.

Our studies will investigate the initiation of sulfur/chlorate mixtures in containers that are similar to those used in the fireworks industry (i.e., cardboard tubes sealed with a clay plug at the bottom and either open at the top or sealed with a further clay or cardboard disk.) Temperature measurement of the samples will be made using a thermocouple inserted into the composition. The cardboard tubes will be heated in a metal block to achieve uniform temperature throughout the sample. To fully understand the reactivity of sulfur/chlorate mixtures in fireworks a number of variables will be systematically examined. These include:

1. the acidity of the sulfur,
2. the stoichiometry of the mixture,
3. the size of sample,
4. the degree of sample compaction,
5. the moisture content of the mixture,
6. the particle size of the components of the mixture, and
7. the inclusion of other fireworks materials such as barium or strontium salts and metal particles.

Sensitiveness Studies

While the majority of accidental ignitions of compositions containing sulfur/chlorate mixtures have been attributed to thermal instability, Dupré^[2] reported that he could initiate a sulfur/chlorate containing "green Roman" composition by friction using the wooden plunger used in filling, particularly when the material had been heated. He concluded that the composition "possesses a degree of sensitiveness which renders it in the highest degree a hazardous composition to deal with especially in hot weather". Therefore, in parallel with our proposed thermal studies, the sensitiveness of different sulfur/chlorate mixtures to mechanical stimuli will also be quantified using the same matrix of variables identified for the thermal stability work.

Friction has previously been shown to be a major cause of accidental ignitions for explo-

sives in general^[25] and pyrotechnics^[26] in particular. However, for completeness both friction and impact sensitiveness will be examined. This will be carried out using the BAM friction and BAM Fallhammer apparatus to gain data using the UN recommended test methods^[27] for friction and impact, respectively.

Future Work

This paper has outlined the problems associated with the presence of sulfur/chlorate mixtures in fireworks and forms the introduction to a series of papers where we intend to report the findings of our research programme. Part 2^[28] will deal with the early work carried out on dry stoichiometric mixtures. Future papers will cover other variables considered in the study.

References

- 1) R. K. Wharton and D. Chapman, "Use of the Term Sensitiveness to Describe the Response of Pyrotechnic Compositions to Accidental Stimuli", *Journal of Pyrotechnics*, in press.
- 2) Special Report of HM Explosives Inspectors LXXX, 1887.
- 3) Special Report of HM Explosives Inspectors XCIV, 1890.
- 4) Special Report of HM Explosives Inspectors CII, 1892.
- 5) R. Lancaster, "Chlorate: Can We Really Exist without It?", *Proceedings of the 3rd International Symposium on Fireworks*, Walt Disney World® Resort, Lake Buena Vista, Florida, September 16–20, 1996, p 272.
- 6) C. Burns, "Chemical Accidents Involving Minors", *Journal of Chemical Education*, Vol. 33, 1956, p 508.
- 7) BS7114: Part 3: Appendix C, 1988, p 23. (ISBN 0 580 17028 4)
- 8) D. Chapman, "Techniques for the Quantitative Analysis of Sulfur and Chlorate in Fireworks Compositions", *Journal of Pyrotechnics*, No. 5, 1997, p 25.

- 9) Reuter Economic News, "Two Dead, 17 Hurt in Peru Fireworks Factory Blast", November 8, 1995.
- 10) Lloyds List, Lloyds Information Casualty Report, "China: Fires and Explosion; Firework Factory, Linquan, China", October 31, 1996.
- 11) Reuter-News-Services-Far-East Report "Explosion in Store for Materials Used in Fireworks", Xichong, China, February 4, 1997.
- 12) Lloyds List, Lloyds Information Casualty Report, "Fires and Explosion; Fireworks Factory, Southern India", May 6, 1997.
- 13) J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, New York, 1985, p 70.
- 14) K. L. Kosanke, B. J. Kosanke, C. Jennings-White and W. D. Smith, *Lecture Notes for the Chemistry of Pyrotechnics, Pyrotechnic Reference Series No. 2*, Journal of Pyrotechnics, 1996, p II-22.
- 15) Ref. 13, p 102.
- 16) R. K. Wharton and A. J. Barratt, "Observations on the Reactivity of Pyrotechnic Compositions containing Potassium Chlorate and Thiourea", *Propellants, Explosives and Pyrotechnics*, Vol. 18, 1993, p 77.
- 17) Annual Report of HM Explosives Inspectors, 1881.
- 18) Annual Report of HM Explosives Inspectors, 1892.
- 19) J. Amiel, "Action of Chlorates on Sulfur, Selenium and Tellurium", *Comptes Rendus de l'Académie des Sciences*, Vol. 198, 1934, p 1033.
- 20) F. Taradoire, "Action of Sulfur on Chlorates" *Comptes Rendus de l'Académie des Sciences* Vol. 199, 1934, p 603.
- 21) J. Amiel, "Damp Mixtures of Chlorates and Sulfur and Some Other Reactions of Damp Chlorates", *Comptes Rendus de l'Académie des Sciences* Vol. 199, 1934, p 787.
- 22) H. G. Tanner, "Instability of Sulfur-Potassium Chlorate Mixture", *Journal of Chemical Education*, Vol. 36, 1959, p 58.
- 23) W. K. Rudloff, "Thermal Analysis of the Reaction between Sulfur Vapor and Chlorates", *Proceedings of the 4th International Conference of Thermal Analysis*, Budapest, 1974, p 555.
- 24) P. D. Storey, "Identification and Assessment of Hazardous Mixtures in Pyrotechnics", *Proceedings of the 13th International Pyrotechnics Seminar*, Grand Junction, Colorado, USA, July 1988, p 765.
- 25) A. Bailey, D. Chapman, M.R. Williams and R. Wharton, "Handling and Processing of Explosives", *Proceedings of the 18th International Pyrotechnics Seminar*, Breckenridge, Colorado, USA, 13-17 July 1992, p 33.
- 26) F.L. McIntyre, "Incident/Accident Survey of Pyrotechnic Compositions", *Proceedings of the 6th International Pyrotechnics Seminar*, Denver, Colorado, USA, 1978, p 392.
- 27) "Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria", ST/SG/AC.10/11/Rev 2, 2nd revised ed., United Nations, New York and Geneva, 1995, p 105-6.
- 28) D. Chapman, R. K. Wharton, J. E. Fletcher and G. E. Williamson, "Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures. Part 2. Dry Stoichiometric Mixtures", *Journal of Pyrotechnics*, in press.