# Communications

Brief technical articles, comments on prior articles and book reviews

## Particle Size Effect in Pyrotechnic Compositions Containing Potassium Chlorate

M. Fathollahi, S. G. Hosseini, S. M. Pour-mortazavi, and F. Farahani

Material and Chemical Engineering Excellency Ctr., Malek Ashtar University of Technology, PO Box 16765-3454, Tehran, Iran

**ABSTRACT**

*In this research, the effect of potassium chlorate particle size on the heat of reaction and the ignition temperature was studied. Potassium chlorate of known particle size was prepared by crystallizing saturated solutions of potassium chlorate at various cooling rates and then isolating crystals of the desired particle size by sieving. The heat of reaction was measured using a bomb calorimeter. The ignition temperature was determined by thermal analysis.*

*The results indicate the heat of reaction increases non-linearly as the particle size decreases. The maximum change, however, was only about 4%.*

*The experimental results indicate that 100 to 250 microns is the best range of particle sizes for potassium chlorate intended for use in pyrotechnic compositions for vaporizing organic materials.*

**Keywords:** potassium chlorate, particle size, heat of reaction, ignition temperature

### Introduction

The particle size effect is universal and affects all reactive systems: fuels, oxidizers, propellants, pyrotechnics, and explosives. The reactive systems can be powders, slurries, or solid or liquid dispersions in a gas. In the case of liquids, the droplet size must be taken into consideration. For solids, whether the particles are nearly spherical or jagged, the particle size is very important. From a more fundamental point of view, it is the surface area, expressed as surface-to-mass ratio, that must be considered.[1] In this paper, it is assumed that reference to particle size refers to the diameter of a hypothetical spherical particle.

Most effort has been expended in the investigation of particle size effects with regard to liquid fuels, monopropellants and explosives. At first glance, the results of these investigations[1] do not seem to be consistent. On the one hand, it is well known[2] that atomization of a fuel greatly aids in decreasing its auto ignition delay. On the other hand, it has also been shown[3,4] that each fuel, under otherwise identical conditions, has an optimum particle size that results in minimum ignition delay; whereas larger particles evidently are not heated sufficiently fast. Another investigation has demonstrated that the auto ignition temperature for a particle increases with decreasing particle size.[5]

These effects, however, are not actually inconsistent but are the result of various physical and chemical processes that occur concomitantly and, in many instances, competitively. This is particularly true where an endothermic phase change absorbs some of the exothermic combustion energy.[6]

Heat of reaction is an important parameter of pyrotechnic compositions, being one of the factors that controls the maximum temperature attained during combustion. This is especially important for pyrotechnic compositions that are used to vaporize organic material, such as a smoke dye. The organic material decomposes at relatively low temperatures; the combustion temperature must therefore be high enough to vaporize the material, but low enough to ensure that the material is not destroyed.

In this paper, we will present the effect of potassium chlorate particle size on heat evolved and ignition temperature of a mixture containing potassium chlorate and lactose.

## Experiments

### Apparatus

#### *Bomb Calorimeter*

An IKA adiabatic/quasi-adiabatic calorimeter system C 4000 thermometer was used in the determinations of heat of reaction. This calorimeter has the advantage that it contains a sensitive control and an integrated heating and cooling system. It consists of a stainless steel bomb, an inner chromium-plated copper calorimeter, an outer water jacket and an adiabatic jacket, a measuring sensor in the calorimeter water, and controls for making adjustments. It was calibrated in the normal way using standard thermochemical benzoic acid pellets, ignited with platinum wire and cotton under 30 atmospheres of oxygen.

#### *DTA/TG Apparatus*

A Stanton Model TR-01 thermobalance, with a sensitivity of 0.1 mg, with a Stanton 780 differential thermal analysis (DTA) attachment, was used for the ignition temperature study.

### Materials

The potassium chlorate was laboratory reagent grade material from Merck Chemical Ltd.

The lactose used as fuel was laboratory reagent grade material from Merck Chemical Ltd. (sieved to pass a 72 BS sieve).

### Procedure

#### *Preparation of Potassium Chlorate Particle Size*

The various particle sizes of potassium chlorate were prepared by recrystallizing saturated solutions of potassium chlorate at several thermal programs of cooling. They were separated into nine fractions (average particle size of 25, 50, 75, 90, 130, 160, 200, 290, and 350 microns) by means of a sieving machine. Particle sizes were checked with a Topocon Electron Microscope model SR-50.

#### *Preparation of Samples*

Pyrotechnic mixtures of 73.1% potassium chlorate and 26.9% lactose were prepared by carefully sieving small quantities of the components through a slightly coarser sieve (i.e., with larger holes) than the particle size of the potassium chlorate being used in that sample.

#### *Calorimetry of Samples*

Each sample was weighed into a steel tube [1.5 × 5.8 in. (38 × 147 mm), closed at one end] and consolidated using a ram under hand pressure. The sample was ignited by electrically heating a coil of nichrome wire buried in the composition at the open end of the tube and burned with a self-sustaining reaction similar to that which normally takes place in a pyrotechnic generator. For a composition that was difficult to ignite, a layer (1g) of igniter composition of known exothermicity was used. The experiments were carried out in air.

#### *Determination of Ignition Temperature*

DTA/TG thermograms were used to obtain the ignition temperature for samples (all 9 mixtures) of pure potassium chlorate and lactose.[7]

## Discussion and Conclusions

### Heat of Reaction

Figure 1 shows that a decrease in the particle size results in an increase in the heat of reaction. The total reaction between potassium chlorate and lactose is as follows:

$$8\ KClO_3 + C_{12}H_{22}O_{11}\cdot H_2O \rightarrow 8\ KCl + 12\ CO_2 + 12\ H_2O \qquad \Delta H = -4515\ J/g$$

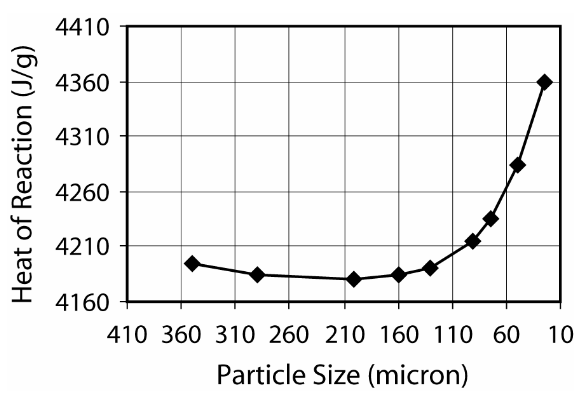


*Figure 1. Change in heat evolved relative to particle size. (Note that the range of change is approximately 1%.)*

The type of reactants and their percentages are the same for all samples; therefore, the propagation reaction and its products are the same for all determinations. The division of crystals into smaller pieces does not contribute significantly to bond breaking or loosening of the crystal structure, as measured by the exposure of relatively larger numbers of atoms at the particle surfaces. It is easy to show by calculation that the increase in the ratio of surface atoms to the total number of atoms is negligible compared to the increase in the heat of reaction.[7]

The lattice looseness, which results from defects in the crystal lattice, is the principle factor in the pyrochemical reactions.[8] The preparation of potassium chlorate of known particle size from chemicals by the method used in this work is likely to cause the formation of crystals with imperfect structures including dislocations, cracks, and other discontinuities, particularly for the smaller crystals. With smaller crystals, the lattice defects increase and those lattice defects operate as reactive sites. They increase the heat of reaction by reducing the energy required to break up the crystal lattice. This is consistent with the heat of reaction being somewhat greater with the smallest particle sizes than with the largest ones.[8]

### Ignition Temperature

Figure 2 shows that a decrease in particle size, results in a lower ignition temperature. The smaller the particle size is, the lower the ignition temperature.

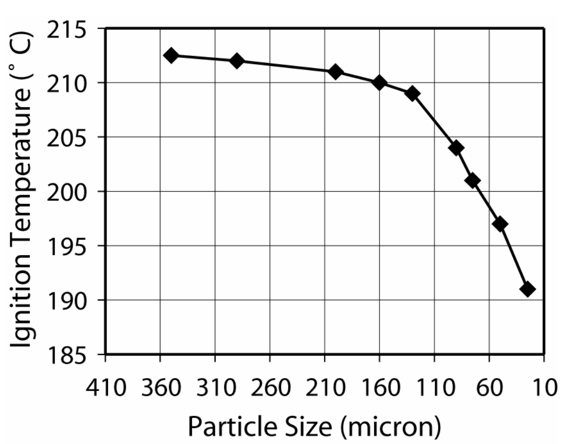


*Figure 2 Change of ignition temperature relative to particle size.*

The formation of localized regions of high temperature ('hotspots') is known to be an important step in the ignition of energetic materials. When the particles in a pyrotechnic mixture are small and jagged, lesser amounts of thermal energy (or other type energy, such as frictional or impact energy) are needed to produce hotspots. This is because energy is localized at the stress points. Dislocations, cracks, and other discontinuities in the crystal structure of the particles provide sites favorable to the formation of hotspots. These sites may come about from structural dislocations that run between grain boundaries or other discontinuities. These form as the growing crystal acquires more molecules that do not fit properly in to the normal pattern. The faults do not heal with continued overgrowth.[9]

Some crystal faults may be due to the inclusion of impurities. Impurities that occupy sites for which they are too large or too small, compared to the normal occupants, may generate defects that propagate through the crystal like a run in a nylon stocking. Cracks and dislocations in the crystal structure contribute to the chemical reactivity of solids. At crystal decomposition temperature, material is lost first at edges or corners.[10]

In the preparation of potassium chlorate particles of different sizes by recrystallization at various temperatures, it is likely that conditions used to obtain smaller particle sizes caused the crystals to be formed with imperfect structures including: dislocations, cracks, and other discontinuities. As crystals become smaller, these imperfections increased. Therefore, the reactivity increased and ignition temperature decreased with decreasing particle size.

Based on the curves in Figures 1 and 2, 100 to 250 microns appears to be the best potassium chlorate particle size range for this pyrotechnic application.

## References

1) Allen J. Tulis, "The Particle Size Factor in Explosives and Pyrotechnics", *Proc. 10th Symp. Explos. Pyrotech.*, 1979, Paper No. 39, 9 pp.

2) B. P. Mullins, "Studies of Spontaneous Ignition of Fuels Injected into Hot Air Streams", *Fuel*, Vol. 32 (1953) pp 211–252, 327–379.

3) H. L. Wood and D. A. Charvonia, "The Ignition of Fuel Droplets Descending Through an Oxidizing Atmosphere", *Jet Propulsion* (1954) pp 162–165.

4) J. A. Browing, T. L. Tyler, W. G. Krall, "Effect of Particle Size on Combustion of Uniform Suspensions", *Ind. and Eng. Chem*., Vol. 49, No. 1 (1967) pp 142–147.

5) S. R. Mott, R. L. Peskin, and D. G. Levine, "Effect of Fuel Molecular Weight of Particle Ignition", *Combustion and Flame*, Vol. 16 (1971) pp 17–27.

6) L. V. de Yong and G. Wilson, *Comparison of Several Techniques for Measuring the Particle Size of Powder Used in Pyrotechnics*, RAAF General Ammunition Dept., Kingswood, NSW 2750 Australia, 1986.

7) F.S. Scans, "Thermal Analysis of Pyrotechnic Compositions Containing Potassium Chlorate and Lactose", *Combustion and Flame*, Vol. 23 (1974) pp 363–371.

8) D. M. Griffiths and J. A. Oliver, "The Reaction of Potassium Chlorate with Lactose: Analysis of Combustion Gases", *Combustion and Flame*, Vol. 24 (1975) pp 21–25**.**

9) J. H. McLain, *Pyrotechnics from the Viewpoint of Solid State Chemistry*, The Franklin Institute Press, 1980, pp 26–37.

10) J. Akhavan, *The Chemistry of Explosives*, The Royal Society of Chemistry, 1998.