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Water induced thermal decomposition of pyrotechnic mixtures – Thermo kinetics and explosion pathway

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ABSTRACT

Pyrotechnic mixtures are susceptible to explosive decompositions. The aim of this paper is to generate thermal decomposition data for flowerpot tip, which is a mixture used in the tip of flowerpot fireworks for easy ignition. Several accidents were reported by using this mixture. The mixture is prepared by mixing barium nitrate, potassium nitrate, aluminum (666) and dextrin in a slurry manner with water. In the manufacturing process 40% water wt/wt is added to the mixture. The thermal characteristics of pure sample and water added sample were studied. Differential Scanning Calorimeter is used for screening tests and Accelerating Rate Calorimeter is used for detailed studies in adiabatic and isothermal mode. The self heat rate data obtained showed onset temperature for pure sample at 170.62 °C and the sample with water showed a much earlier onset at 95.71 °C in adiabatic mode. Also it gets decomposes even at 40 °C and starts exothermic characteristics with a substantial rise in system pressure of 32 bar in isothermal mode. The heats of exothermic decomposition and Arrhenius kinetics were computed.

1. Introduction

Fireworks industry is one of the most vulnerable industry in which frequent accidents are known to occur. Accidents during processing, storage and transportation have been reported (Clive and Ken, 1995; Krone & Treumann, 1990, Sivapirakasam, Surianarayanan, Venkataratnam, & Nagaraj, 2003). This is because fireworks mixtures are energetic compounds susceptible to explosive degradation on ignition, impact and friction. These mixtures decompose at low temperatures and the decomposition mechanism is yet to be explored. Inadequate knowledge on exothermic hazards and reactive nature of these chemicals is yet another reason for explosive incidents, causing casualties and material loss. Fireworks Industries in India can be categorized as small scale and unorganized with almost no opportunity for sophistication due to a number of limitations such as sensitive nature of the chemicals to any mechanization of the process, which prohibit modernization of the shop floor, lack of awareness, adequate infrastructure, and research and development for improving safety. Raw materials are often stored and handled by workforce with no formal education. This leads to lots of difficulties in imparting training and maintain a sustainable system for housekeeping. Thermal sensitivities of fireworks composition and its vulnerability to cause explosive accidents have not been fully understood.

Nevertheless, the sensitivity of a mixture to explosion cannot be theoretically predicted as it depends on the reactive nature of the mixture components and the conditions employed during its preparation and handling (Fathollahi, Pourmortazavi, & Hosseine, 2004; Hidetsugu & Miyako, 1998). Though material safety data sheets of pure materials are available, no such data are available for mixtures. Moreover the mixture composition varies from company to company for the same type of fireworks. Due to non-availability of standard manufacturing equipment, tools, manufacturing procedures, and inadequate understanding of the thermo chemistry of fireworks and their explosive nature, accidents continue to occur (Sivapirakasam, Surianarayanan, & Chandrasekran, 2010; Sridhar, Surianarayanan, Sivapirakasam, & Mandal, 2012).

Generally the composition of fireworks is a mixture of oxidizer, fuel, igniter, binder, and color enhancing chemicals. These mixtures have high sensitivity to temperature, impact, friction and electrostatic stimuli (Chapman, Wharton, & Fletcher, 1998). A thorough knowledge of thermal stability, auto ignition temperature, impact

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sensitivity, frictional sensitivity and electrostatic sensitivity of these materials is imperative to assess the hazard potential (Herder, Weterings, & de Klerk, 2003; Sivapirakasam, Surianarayanan, Venkataratnam, & Nagaraj, 2005).

Chemical reactions of fireworks produce large amounts of heat when confined to a closed system and result in thermal explosion. Although there are numerous thermal measurement techniques to characterize the hazardous nature of pyrotechnic mixtures, Accelerating Rate Calorimetry (ARC) is at present the only adiabatic and versatile Calorimetry that produces reliable data. As the ARC measurements are conducted adiabatically (Hou, Duh, Lee, & Shu, 2009; Roy et al., 2010; Sivapirakasam et al., 2010; Sridhar et al., 2012) the result can be effectively correlated with the behavior of energetic materials handled in bulk. The information obtained from ARC experiments includes the onset temperature, self-heat rates, and pressure for an exothermic reaction.

The previous studied on the reactivity hazards of fireworks are briefly discussed below. Ottaway (1986) reported that the Accelerating Rate Calorimeter (ARC) could be used to study fireworks compositions to determine the storage and transportations parameters. Laye and Charsley (1987) gave an extensive review of the widely studied fireworks compositions. The review also stated that thermal analysis, in conjunction with analytical techniques like Fourier Transform Infrared analyzer (FTIR), X-Ray Diffraction meter, could be used to study the reaction mechanism. Many accidents in fireworks are due to unintentional ignition during careless handling and storage. The energy required to induce a sustained exothermic reaction is commonly referred to as the Activation energy. Hence, Kosanke and Kosanke (1997) motivated the researchers to determine the activation energy of fireworks compositions to establish the hazardous nature. A hazard assessment provides important information for determining safe conditions for the manufacture, storage and transportation of firework. Sensitivity to thermal stimuli is an important aspect of an overall hazard assessment.

Lightfoot, Fruchard, Turcotte, and Kwok (2001) described a number of laboratory techniques to determine thermal properties of fireworks and other energetic materials. These included Differential Scanning Calorimeter (DSC), Accelerating Rate Calorimeter (ARC), Thermogravimetry (TG) and simultaneous TG/DTA. He suggested that no technique was without limitation, and a combination of techniques, providing complementary information was often the best approach. For example, DSC would provide enthalpy change for an exothermic decomposition, allowing an assessment to be made based on heat that could be generated by a runaway reaction. Although, DSC could measure onset temperature, ARC along with would provide a much better estimate of the temperature at which thermal runaway took place. Through pressure measurement, ARC could also be used to estimate the volume of gaseous products generated and the rate at which pressure was built up. Surianarayanan, Vijayaraghavan, Swaminathan, and Rao (2001) proposed work on "Micro Calorimetry and its role in thermal hazard quantification" which clearly explained the different thermal techniques for thermal hazard analysis using DSC and ARC. Smitha, Surianarayanan, Seshadri, Lakshman, and Mandal (2012), Sridhar et al., 2012, Vijayaraghavan, Surianarayanan, Armel, MacFarlane, and Sridhar (2009), used ARC for evaluating thermal hazards of high energy materials. Recently researchers have studied the thermal stability and kinetics of fireworks mixtures using Differential Scanning Calorimeter (DSC) (Sivapirakasam et al., 2010; Sridhar et al., 2012). While DSC data can be used for screening purposes, they are not as good for determining safe operating temperatures. It is because under non adiabatic conditions small quantities of samples (2–5 mg) used in the DSC experiments result in poor reproducibility. Thus the literature review suggests that there are no studies on the thermal hazards of flowerpot tip composition.

In this study, thermal data from ARC, and the thermo kinetics of the tip mixture consisting of barium nitrate ($Ba(NO_3)_2$), potassium nitrate (KNO_3), Aluminum (Al 666) (it is an extra fine quality of aluminum with particle size (<45 μm), and apparent density 0.070–0.125 gm/cc) and dextrin with particle sizes of 17 μm reported. The objective is to throw light on the behavior of these samples under adiabatic conditions; i.e., under conditions of bulk storage, handling, and transportation. Such a study of these fireworks mixtures has not been attempted before.

2. Materials

The chemicals used in this study were of commercial grade and obtained from a fireworks chemical manufacturing company situated in southern Tamil Nadu, India. The purity and assay of the chemicals were $Ba(NO_3)_2$ – 92%, KNO_3 – 91.6%, Al – 99.1%, and dextrin – 92%. The pyrotechnic compositions were mixed using a wooden spatula in a non-flammable container, and each time a sample size of 1 g was prepared. The sample was then stored in an airtight container and kept away from light and moisture.

2.1. Flowerpot tip composition

Flowerpot is a non cracking type of fireworks, which on ignition emits a colorful flame. It consists of two types of mixtures called the inner mixture and tip mixture. The present study deals with the exothermic hazards of the tip mixture and its effect due to water addition. The wet mixtures often get involved in accidents. Flowerpot tip composition is used to coat on the ignition part of the flowerpot. During the tip manufacture, the mixtures get wet with water added. The water uptake varies with the particle size of the chemicals so that a consistency is obtained to enable applying the paste on the tip for easy ignition (Lee, Lin, Huang, Chen, & Ch'en, 1991). The composition of tip mixtures used for ARC testing is given in Table 1. The compositions were finalized based on the data collected from several fireworks industries. The composition was found to differ ±4% from industry to industry.

3. Methods

3.1. Differential Scanning Calorimeter (DSC)

TA instruments, DSC Q-200 model was used to study thermal stability of various pyrotechnic compositions. DSC consisted of a sample chamber of 250 μL capacity. A 2 mg of the sample was taken in an aluminum pan. The pan was sealed with an aluminum lid and placed in the sample thermocouple of the DSC chamber. It was heated at constant rate of 10 °C/min to an end temperature of 350 °C. An online PC continuously monitored the thermal changes and stored the data (Hou et al., 2009; Roy et al., 2010; Simoes, Rodriguez Perez, De Saja, & Constantino, 2010). The data could be later analyzed using the general utility analysis software supplied by the instrument manufacturer. From the heat flow curves, onset temperature, peak temperature and heat of reaction were

Table 1
Composition of flowerpot tip mixture.

S. No	Chemicals	Flowerpot tip mixture in %
1	Barium nitrate	28.57
2	Potassium nitrate	28.57
3	Aluminum (666)	17.85
4	Dextrin	25