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Cause analysis of spontaneous combustion in an ammonium nitrate emulsion explosive

Sen Xu [a, b, *], Liu Tan [a], Jing-ping Liu [a, b], Xiang Chen [c], Wei Jiang [a], Yuan Chen [a], Da-bin Liu [a]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, Jiangsu, China
[b] National Quality Supervision and Inspection Center for Industrial Explosive Materials, Nanjing, 210094, Jiangsu, China
[c] Shanghai Entry-Exit Inspection and Quarantine Bureau, Shanghai, 200135, China

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ABSTRACT

Emulsion explosives (EE) have been widely used in the mining industry for their comparatively high detonation performance and exceptionally good safety characteristics. However, an accidental spontaneous burning of an emulsion explosive occurred in March 24, 2014. The investigation of the accident showed that the reaction between crystalloid sodium nitrite and ammonium nitrate (AN) was likely the cause of the spontaneous burning. To investigate the stability of the EE mixed with crystalloid sodium nitrite, AN, crystalloid Sodium nitrite, and EE, were analyzed by differential scanning calorimeter (DSC), accelerating rate calorimeter (ARC) and Dewar test. The results indicated that crystalloid sodium nitrite could decrease the onset decomposition temperature of AN and EE and the induced thermal runaway is the reason for the accident.

1. Introduction

Emulsion explosives have been widely used in the mining industry for their comparatively high detonation performance and exceptionally good safety characteristics (Silva et al., 2006; Anshits and Anshits, 2005; Deribas et al., 2003). Emulsion explosives comprise a class of foamed water-in-oil solutions. The basic oxidizer used in emulsion explosives is ammonium nitrate (AN). Sodium nitrate and calcium nitrate are frequently added to modify properties of the oxidizer solution. The fuel phase consists of various kinds of mineral oil, wax, and polymer in some cases.

Ammonium nitrate emulsion (ANE) is extremely insensitive to initiation. In order to become detonable and be utilized as explosives, ANE needs to be sensitized. The most common sensitization methods involve introducing low-density material with voids into the ANE. The voids provide hot spots at which the explosion may nucleate (Mader, 1965; Sychev, 1985). Sensitization can be obtained either by distributing material of a hollow or porous nature throughout the ANE or by generating gas bubbles in-situ via chemical reaction. The use of chemical reaction to produce voids within ANE is often referred to as chemical gassing and this process has emerged as one of the most efficient and cost-effective means of ANE sensitization. Sodium nitrite is the most common chemical sensitizer (Lu, 2008). Chemical gassing of an ANE proceeds by addition of a concentrated sodium nitrite solution to the ANE, where sodium nitrate reacts with AN in the oxidizer solution and produces nitrogen gas via a nitrosation mechanism (Ngai et al., 1997; Bryant and Wililams, 1988).

To ensure the safety of the production process, studies with various methods have been carried out on the safety of ANEs and emulsion explosives (Olson, 1997; Lightfoot, 2008). Olson (1997) showed that an increase in initial temperature in an ANE lowers the minimum burning pressure but raises the linear burning rate. Lightfoot (2008) indicated that emulsion explosive cartridges physically sensitized by the presence of voids can be initiated by high velocity bullet or sabot. Turcotte et al., (2010) reported that the presence of sodium nitrate may have a significant effect on the minimum burning pressure of ANEs. Medvedev et al., (2008) reported that detonation of an emulsion explosive based on a water solution of ammonium nitrate with filler in the form of hollow micro-balloons follows the "hot spot" mechanism.

Although EE have a number of valuable properties, they show

* Corresponding author. School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, Jiangsu, China.
E-mail address: xusen_345@sohu.com (S. Xu).

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good explosive parameters and are insensitive to thermal and mechanical stimuli. There have been several explosion accidents over the last few years with multiple fatalities (Moreton et al., 1996; Peter, 2009). Recently, an accident took place in March 24, 2014, in Dalian Antai Chemical Factory, China. This time, an unexpected spontaneous combustion of emulsion explosive occurred in the interim storage, approximately 12 h after the production. Almost 12,384 kg of emulsion explosive cartridges were burned off in two hours. In the consequential field investigation, it was detected that crystalloid sodium nitrite was built up on the sensitizer sprayer nozzle (Fig. 1) because of loose connection. The accident investigation concluded that the reaction between the crystalloid sodium nitrite and the AN in the emulsion explosive caused the spontaneous burning. The accident investigation concluded that the reaction between the crystalloid sodium nitrite and the AN in the emulsion explosive caused the spontaneous burning. During the investigation, the thermal runaway mechanism of the mixture of the emulsion explosive and crystalloid sodium nitrite was studied by analyzing ammonium nitrate (AN) and emulsion explosive with crystalloid sodium nitrate using differential scanning calorimeter (DSC), accelerating rate calorimeter (ARC) and Dewar test.

2. Experiment

2.1. Materials

Samples of AN and crystalloid sodium nitrite were obtained from Kailong Chemical (China) and Huarui Chemical (China) without further processing in the experiments. The EE (74% AN, 10% sodium nitrate, 10% water and 6% oil phase, sensitized by chemical gassing) used in the experiment was from the Dalian Antai Chemical Factory.

2.2. Test methods

The DSC thermal analysis was used to study the thermal stability. The thermal stability of samples can be determined from the onset temperature in the DSC curves (Whiting et al., 1988; Egorov, 1994). However, due to the complexity of the EE composition and the small sample size, DSC does not accurately reflect the thermal decomposition characteristics of emulsion explosive. Moreover, EE that stacked in the warehouse are similar to a thermally insulated system, because of the poor thermal conductivity. Therefore, ARC and large-scale adiabatic heating test were used to study the thermal decomposition characteristics of EE under adiabatic condition. In order to simulate the scenario in the accident, a small amount of crystalloid sodium nitrite was added into the EE. Dewar test was used to study the effect of crystalloid sodium nitrite on the thermal decomposition of the emulsion explosive as well as AN.

2.2.1. DSC thermal analysis

Dynamic scanning experiments were performed on a Mettler DSC 1 instrument. The samples of 1–2 mg were heated from 25 °C to 400 °C in sealed crucibles. For the purpose of better thermal equilibrium, two different heating rates (β), 2 °C/min and 20 °C/min, were chosen. The reaction was studied in nitrogen atmosphere with a constant flow rate of 30 ml/min. The mass of each component is listed in Table 1.

2.2.2. ARC and large-scale adiabatic heating test

In this study, an adiabatic calorimeter was used. This instrument was used for acquiring thermodynamic and kinetic information for runaway reactions in order to evaluate thermal hazards associated with the reactive material (Fu et al., 2003; Sun et al., 2001). The main components and the detailed description of principle of ARC can be found elsewhere (Townsend and Tou, 1980). The tested conditions were listed as follows:

Detection sensitivity: 0.02 °C/min
Test mode: H–W–S (heat–wait–seek)
Temperature range: 0–500 °C
Pressure range 0–20 MPa
Bombs: Ti-LCQ
Sample mass: the mass of each component is listed in Table 2.

It is well known that the heat accumulation has an important influence on thermal stability of energetic materials. In the accident, the mass of the stack is 12,384 kg. To better understand the thermal decomposition characteristics of the emulsion explosive in large scale, the large-scale adiabatic heating test was carried out. In these series of experiments, a portion of an emulsion explosive cartridge, 505± 2 g (500 g AN+5 g crystalloid Sodium nitrite or 500g EE+5 g crystalloid sodium nitrite), was cured in a glass container with an inner diameter of 7 cm and height of 12 cm. The ends of the tube were sealed using Teflon disks and capped with threaded stainless steel covers. Type-K thermocouple was direct inserted at the centre of the samples to gain for internal

Table 1
Composition of samples for the DSC measurements.

Sample	AN/mg	Sodium nitrite/mg	Total mass/mg
1#	1.49	0	1.49
2#	0.75	0.70	1.45

Fig. 1. Scene picture in sensitization process with a close-up of the sensitizer sprayer nozzle.