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Research on the critical temperature of thermal decomposition for large cartridge emulsion explosives

Kai Wang, Sen Xu*, Dabin Liu, Gaowen Cai

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, China

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ABSTRACT

Emulsion explosives are one type of main industrial explosives. The emergence of the large cartridge emulsion explosives has brought new security incidents. The differential scanning calorimeter (DSC) and the accelerating rate calorimeter (ARC) were selected for the preliminary investigation of the thermal stability of emulsion explosives. The results showed that the initial thermal decomposition temperatures were in the range of 232–239 °C in nitrogen atmosphere (220–232 °C in oxygen atmosphere) in DSC measurements and 216 °C in ARC measurements. The slow cook-off experiments were carried out to investigate the critical temperature of the thermal decomposition (T_c) of the large cartridge emulsion explosives. The results indicated that the larger the diameter of the emulsion explosives, the smaller the T_c is. For the large cartridge emulsion explosives with diameter of 70 mm, the T_c was 170 °C at the heating rate of 3 °C h^{-1}. It is a dangerous temperature for the production of the large cartridge emulsion explosives and it should cause our attention.

1. Introduction

Emulsion explosives is widely used in the industry, which is manufactured by sensitization of emulsion matrix. Emulsion matrix is generally a high internal phase water-in-oil emulsion containing droplets of an oxidizer solution emulsified in the fuel. The preparation of emulsion explosives includes emulsification, sensitization and the packaging. (Mudene et al., 2010; Li et al., 2014; Nuntawong et al., 2013; Luo et al., 2012) With the development of application requirements, the variety of emulsion explosives has undergone major changes. Some large cartridge emulsion explosives have appeared, whose charge diameters are 35 mm, 70 mm and so on.

The emergence of new products has brought new security incidents. In March 24, 2014, a spontaneous combustion incident of large cartridge emulsion explosives occurred in China. The incident occurred at the entrepot storage in Dalian Antai Chemical Co., Ltd. During the investigation of the incident, it's found that the surface temperature of large cartridge emulsion explosives was high after the packaging. For large cartridge emulsion explosives sensitized under high temperature, the surface temperature could reach 90 °C sometimes. It's obvious that the internal temperature of the large cartridge emulsion explosives was higher.

In the large cartridge emulsion explosives, the heat generated by the thermal decomposition can't be promptly delivered to the surrounding environment. Under the above conditions, the temperature of emulsion explosives itself will rise (Wang et al., 2009; Roduit et al., 2005; Keller et al., 1997). As the temperature increases, the heat generated by the thermal decomposition is much higher than that transferred to the surrounding environment. When the temperature reaches a certain critical value, the temperature of the large cartridge emulsion explosives increase sharply, resulting in spontaneous combustion. The temperature is defined as the critical temperature of the thermal decomposition for large cartridge emulsion explosives (T_c).

The differential scanning calorimeter (DSC) (Berger and Wehrstedt, 2010) and the accelerating rate calorimeter (ARC) (Turcotte et al., 2003) were selected to investigate the thermal stability of emulsion explosives. The slow cook-off experiment was also carried out to investigate the T_c of the large cartridge emulsion explosives (Du et al., 2012; Gillard and Longuet, 2013). The finished product of large cartridge emulsion explosives was placed in the oven and was heated at a certain slow rate of temperature rise. The thermocouples were used to measure the temperature of the emulsion explosives and the surrounding environment.

* Corresponding author. Permanent address: No. 200, Xiaolingwei Road, Xuanwu District, Nanjing City, China.
E-mail address: xusen_345@sohu.com (S. Xu).

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2. Experimental

2.1. Experimental materials

The emulsion explosives was consisted of 71.5% ammonium nitrate, 7.4% sodium nitrate, 1.95% carbamide, 10.4% water, 2.3% emulsifier, 3.95% compound wax, 2.5% perlite. Two finished product of large cartridge emulsion explosives were used in the slow cook-off experiment, whose diameters were 35 mm and 70 mm, respectively.

2.2. Measurements by DSC

The DSC experiments were conducted on a DSC1, which is manufactured by Mettler Toledo Company in Switzerland. The samples were placed in the aluminum crucibles, and an empty crucible of the same type was used as a reference. The experiments were performed under dry nitrogen and oxygen atmosphere respectively with a flow rate of 40 ml min^{-1}. For the DSC tests, the samples were heated from 50 °C to 400 °C at 2, 5, 10 and 20 °C min^{-1}.

2.3. Adiabatic measurements by ARC

ARC, supplied by Thermal Hazard Technology in UK, was used to measure the thermal behavior under adiabatic condition. The ARC experiments were performed in Heat–Wait–Search model and the input data are listed in Table 1.

2.4. Slow cook-off experiments

The slow cook-off device is consisted of an incubator, heater, temperature controller, thermocouple, recorder and other components. The heating rate was 3 and 60 °C h^{-1} Fig. 1 is the diagram of the slow cook-off setup. The three samples tested in the slow cook-off experiment are listed as follows:

Sample 1: Emulsion explosives packed in a glass tube (diameter, 10 mm);
Sample 2: Large cartridge emulsion explosives (diameter, 35 mm);
Sample 3: Large cartridge emulsion explosives (diameter, 70 mm).

3. Results and discussions

3.1. Analysis of DSC measurements

DSC using various heating rates was applied to determine the thermal stabilities of the emulsion explosives. Fig. 2 demonstrates a comparison of the thermal curves of decomposition in nitrogen and oxygen atmosphere (Salzano and Basco, 2012) at four heating rates by DSC. Table 2 displays the parameters of their thermal decomposition.

As seen from Fig. 2 and Table 2, the peaks associated with the thermal decomposition of the emulsion explosives all moved up with increasing heating rates. The peak temperatures (T_{peak}) were in the range of 262–300 °C in nitrogen atmosphere at heating rates

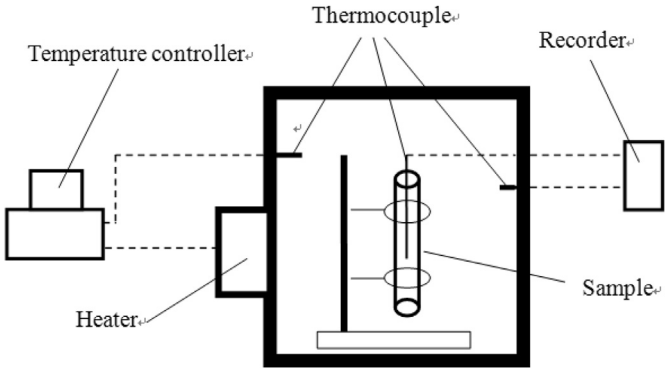

Fig. 1. The diagram of the slow cook-off setup.

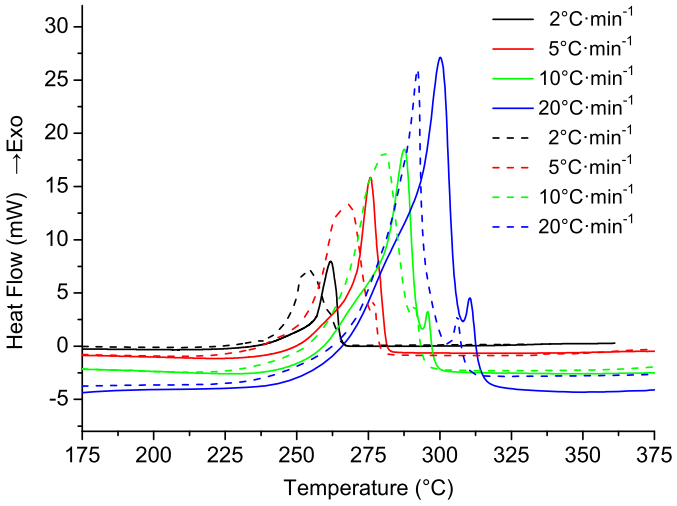

Fig. 2. Heat flow vs. temperature of the emulsion explosives at various heating rates by DSC tests (in nitrogen atmosphere – solid line, in oxygen atmosphere – dash line).

of 2, 5, 10 and 20 °C min^{-1}, whereas the peak temperatures of curves obtained in oxygen atmosphere were in the range of 254–292 °C. The initial thermal decomposition temperatures (T_{onset}) were in the range of 232–239 °C in nitrogen atmosphere and 220–232 °C in oxygen atmosphere. The peaks in oxygen moved up to the direction of low temperature compared to the peaks in nitrogen atmosphere in different heating rates. The curves of 10 and 20 °C min^{-1} in Fig. 2 showed a small shoulder peak, which demonstrated a multi-step reaction mechanism.

Emulsion explosives are closely zero-oxygen balanced explosives, but the decomposition enthalpy change (ΔHr) of thermal decomposition were still increased in oxygen atmosphere compared to that in nitrogen atmosphere. And the initial thermal decomposition temperatures in oxygen were much lower than that in nitrogen, which means that the emulsion explosives are more dangerous exposed in air.

The Kissinger and Ozawa method (Vyazovkin et al., 2011; Sovizi et al., 2009) were adopted in this paper to determine the apparent activation energy according to the data obtained from the DSC

Table 1
Input data of ARC test.

Sample	Sample mass (g)	Test-cell type	Bomb mass (g)	Temperature range (°C)	Heat gradient (°C)	Slope sensitivity (°C min^{-1})	Wait time (min)
Emulsion explosives	0.12	HC-MCQ	14.450	180–400	5	0.02	10