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Effect of urea on detonation characteristics and thermal stability of ammonium nitrate

Liu Tan [a], Liang-hong Xia [a], Qiu-jie Wu [a, b], Sen Xu [a, b, *], 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

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ABSTRACT

A study has examined the effect of urea on the thermal stability and detonation characteristics of ammonium nitrate (AN). The thermal decomposition temperature and surface morphology of samples were investigated by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). For further research on the thermal sensitivity and shock sensitivity of the samples, the Koenen test and UN gap test were conducted. The results indicate that urea can substantially increase the thermal stability of AN (the greatest exothermic peak is increased by more than 100 °C) and reduce the thermal sensitivity of AN. However, AN-50wt. % urea mixtures can still produce a steady detonation in the UN gap test. Urea cannot reduce the ability to propagate a detonation. Possible explanations for these results are discussed.

1. Introduction

Ammonium nitrate (AN) is one of the most important ammonium compounds in the chemical industry and agriculture. It has been widely used in nitrogen fertilizers and civil explosives (Kirk, 1922; Ullmann, 1989; Lu et al., 1994). AN has many advantage: for example, it is inexpensive, releases almost 100% gaseous products and has a positive oxygen balance (Shalini and Pragnesh, 2013; Oommen and Jain, 1999; Atsumi et al., 2007). However, the applications of AN are limited by phase transition, hygroscopicity and unlawful use (Lu et al., 1994; Michael et al., 1997; C. Sjolin, 1971; Anuj et al., 2009; Wu et al., 2008). On the other hand, the knowledge of preparing explosives from AN and the common availability of ingredients are used by offenders and terrorists (Klimova et al., 2011; Trevor, 2009; Foulger and Hubbard, 1995). There has been a growing demand for detailed information on its detonation characteristics.

There have been several attempts to solve these problems and improve the explosion characteristics of AN (Tang et al., 2003; Jimmie et al., 2002; Theodor et al., 1999). These studies sought to use additives to improve the thermal stability of AN. One hypothesis is that diluting AN with a chemically inert material or the incorporation of small amounts of a material that increases the chemical reaction zone could diminish the explosivity of AN. However, whether the AN-additive mixtures exhibit explosivity or not needs to be confirmed. We chose urea for our studies because it is often used for fertilizer, and thus the safety performance of AN-urea mixtures is important for industrial production, transportation and use. In this paper, the thermal stability and detonation characteristics of AN-urea mixtures were studied, with an emphasis being placed on analyzing whether increasing thermal stability could suppress the detonation of AN.

2. Experimental

All the reagents were of technical grade and used as obtained without further purification. AN was mixed with different proportions of urea by ball mill at a speed of 120 r/min for 0.5 h and stored in a desiccator before use.

2.1. Test methods

DSC thermal analysis is used to study the thermal stability. The onset temperature and exothermic maximum in the DSC curves can indicate the thermal stability of AN-urea mixtures (Whiting et al., 1988; Egorov, 1994). A shift from the exothermic maximum peak of the mixture from the value for AN to lower temperatures is

* 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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interpreted as destabilization, while a shift to higher temperatures is considered to indicate stabilization (Jimmie et al., 2002). Considering experimental errors, only shifts of 10 °C or greater are considered significant. According to "The United Nations proposals on the transport of dangerous goods-Testing and Standards Manual" (the fifth revised edition), the Koenen test is used to measure the sensitivity of solid substances to intense heat with varied confinement. The UN gap test is used to measure the ability of a substance under confinement in a steel tube to propagate a detonation by subjecting it to the detonation from a booster charge (United Nations, 2009a, 2009b).

2.1.1. DSC thermal analysis

The thermal stability of AN-urea mixtures was studied using a DSC 1 instrument. AN-urea mixtures of 1–2 mg were heated from 25 °C to 400 °C in a sealed crucible at a scan rate of 10 °C min^{-1}. The reaction was studied in nitrogen atmospheres with a constant flow rate of 30 ml min^{-1}. The water content of the mixtures was identified using a Sartorius-MA35, and the moisture was maintained at approximately 0.06% to ensure the consistency of the experiment. All samples were dried in a vacuum desiccator before use.

2.1.2. The Koenen test

Fig. 1 shows the specific experimental apparatus. The samples were placed in a specified sample tube fitted with a 1.0 mm diameter orifice at one end. The tube was exposed to direct flame heating at a rate of 3.3 ± 0.3 K s^{-1} and heated for 5 min or until an earlier event occurred (United Nations, 2009a, 2009b).

2.1.3. The UN gap test

Fig. 2 shows the test schematic diagram. The test pipe was made of steel deep, with an inner diameter of 40 mm and an outer diameter of 48 ± 2 mm, and the total length of the tube was 400 mm. One hundred 60 g of booster explosive (PETN and TNT 50/50, diameter 50 ± 1 mm, density 1.60 g/cm^3) was used for the donor charge and was initiated with a no. 8 electric detonator. The edge length of the witness plate was 150 ± 10 mm, and the thickness was 3.2 ± 0.2 mm (United Nations, 2009a, 2009b).

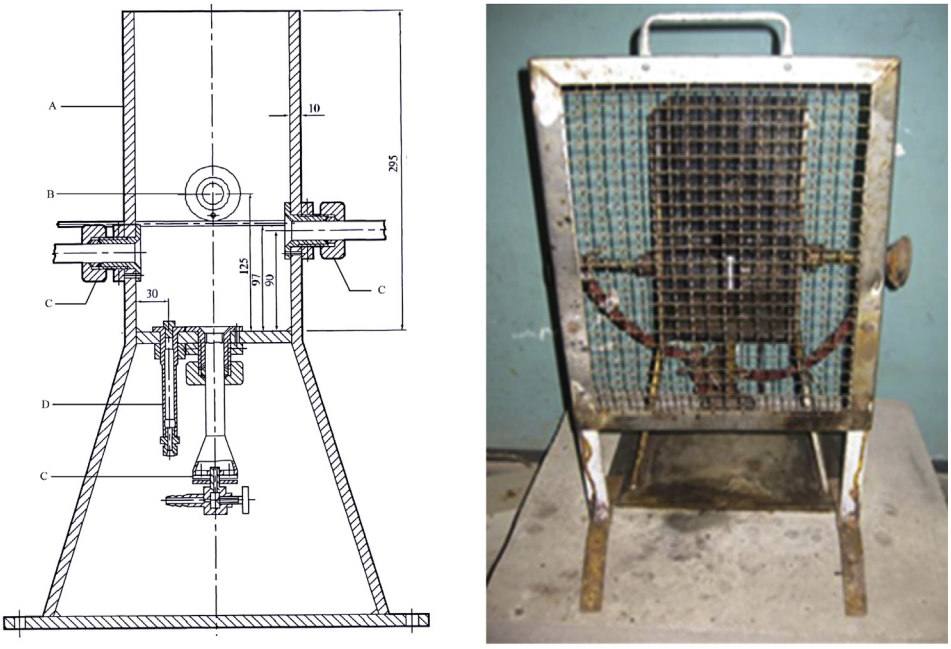
3. Results and discussion

3.1. DSC thermal analysis results

The DSC curve of AN is presented in Fig. 3. AN shows four endothermic peaks and one exothermic peak. The third endothermic peak is the phase change peak, and the fourth, at approximately 169 °C, is the melting point of AN. Solid AN dissociates into ammonia and nitric acid as the temperature rises (Reaction (1)). The observed exothermic peak was approximately 113 °C wide and had an exothermic maximum of 284.83 °C. As shown in Table 1, the urea had little effect on the phase transition route and the melting point. Fig. 4 shows the DSC curves of AN-urea mixtures. The onset temperature of AN-5wt. % urea is increased from 203.50 °C to 284.83 °C, and the exothermic maximum peak is increased from 284.83 °C to 358.50 °C. As the urea is increased to 10wt%, the exothermic maximum peak is observed at 385.27 °C. Thus, urea substantially stabilized the thermal stability of AN. Meanwhile, the heat fluxes of the samples increase slowly with increasing temperature, and the onset reaction temperature is much higher than for pure AN. This result shows that the first step in the decomposition reaction of AN has been greatly delayed.

The thermal decomposition of AN is initiated by an endothermic proton transfer reaction, as shown in reaction (1). NH_3 is subsequently oxidized by the decomposition products of HNO_3 according to reaction (2). NO_2 is the main catalyst in the AN autocatalytic decomposition reaction (Lu et al., 1994; Shalini and Pragnesh, 2013; Oommen and Jain, 1999; Kazuomi et al., 2013; Richard and Zhang, 2009).

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \quad (1)$$



(A) Steel plate; (B) sample tube; (C) Burner; (D) Ignition source

Fig. 1. Experimental apparatus of the Koenen Test.