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Review on Non-explosive and Irrestorable Ammonium Nitrate

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Abstract: The criteria for an ideal desensitizing AN and thermal decomposition mechanism of AN are introduced. At the same time, some viewpoints on the selection of desensitizing additives and testing for detonability of desensitized AN mixtures are presented.

Key words: inorganic chemistry; ammonium nitrate (AN); non-explosivity; irrestorability; desensitizing additives; review

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1 Introduction

Ammonium nitrate (AN) is one of the most useful ammonium compounds. It has extensive use in the area of nitrogen fertilizers and explosives. It can provide ammonia and nitrate ion which is vital to some plants. AN serves as an excellent oxidizing agent and finds its application as the principal component of commercial explosive[1-7]. For example, the explosive ANFO (ammonium nitrate fuel oil), which is a stoichiometrically balanced mixture of approximately 94.5% AN and 5.5% hydrocarbon material acting as fuel oil, is a high order explosive capable of detonation in response to a shockwave that passes through a block of the high explosive material, releasing considerable amounts of energy. Both fuel oil and fertilizer-grade AN are readily available and relatively accessible products thereby making them excellent raw materials for producing illegal bombings for terrorists. Therefore in order to prevent the misuse of AN in improvised explosives, much research aimed at desensitizing fertilizer-grade AN was done. For example, a variety of additives have been proposed which could inert AN formulations to detonation or severely curtail their explosive performance. No additive however, has been shown to be capable of rendering the desensitized fertilizer-grade AN mixtures non-detonable under all circumstances when the additive is present at a concentration of approximately 20% or less by weight.

This paper introduce the method and composition for desensitizing AN, which have no negative environmental impact and undetectable and non-emulsified or difficult to separate from AN.

2 Criteria of desensitizing AN

The criteria of desensitizing AN are described as follows:

(1) The ideal desensitizing method have effects on preventing detonation when the desensitized AN is intimately mixed with hydrocarbon material acts as fuel oil in the large-scale explosivity device, even when detonated with a 8# detonator or a powerful booster charge.

(2) The ideal desensitizing additives which retard AN decomposition may increase the reaction zone of the composition to the point that a detonation cannot be propagated [1,6].

(3) The ideal desensitized fertilizer-grade AN has no adverse environmental impact in any way and is undetectable or difficult to separate from AN. Also, the desensitized substance is still usable as fertilizer.

(4) The efficacy of the ideal desensitizing method

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does not degrade with time owing to evaporation of the desensitizing materials or reversion to thermodynamically preferred (more explosive) morphologies[1].

(5) The ideal desensitizing method retains safety in manufacturing, distribution, or legitimate end use[1].

(6) Addition of the ideal desensitizing ingredient imposes no cost on the production, distribution and application. And its use is acceptable to the public owing to no perceived or real negative consequences.

3 Thermal decomposition mechanism of AN

The thermal decomposition of AN is initiated by an endothermic reaction as shown in reaction (1). Studies have shown that the decomposition of AN operates by an ionic mechanism in the temperature range 200 ~ 300 ℃. Furthermore, most decomposition mechanisms for AN assume first the production of ammonia and nitric acid and subsequent oxidation of NH_3 by the decomposition products of HNO_3[8~11].

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

Recently, rapid heating and immediate analysis of the decomposition products of AN using rapid scan FTIR spectroscopy clearly indicates the formation of HNO_3 as an intermediate[8]. Apart from N_2O and H_2O, NO_2 is also formed during the decomposition[8,9]. Since HNO_3 is formed only at high temperature during the decomposition of AN, the reaction (2) mode of decomposition of HNO_3 was thought to be more realistic [9].

$$2\ HNO_3 \rightleftharpoons 2NO_2 + H_2O + \frac{1}{2}O_2 \quad (2)$$

NO_2 formed can subsequently oxidize NH_3 as reaction (3) in the temperature range 342 ~ 387 ℃.

$$4\ NH_3 + 5NO_2 \longrightarrow N_2O + 2N_2 + 6H_2O + 3NO \quad (3)$$

However, Brower et al. [11] decomposed AN in a sealed capillary and examined the products using IR spectroscopy. NO_2 was not observed under the conditions. They assumed that at high temperature a hemolytic mechanism for the decomposition of HNO_3 is more likely. The observed activation energy changes continuously from 118 $kJ \cdot mol^{-1}$ at low temperature to 193 $kJ \cdot mol^{-1}$ at high temperature which is nearly equal to the N—O bond energy in nitric acid [2,10]. As a result, water and ammonia strongly inhibit the ionic reaction at low temperature, but the effect fades away at high temperature. In this mode, the decomposition proceeds through the formation of nitramide. Above 290℃, a free-radical decomposition mechanism dominates and homolysis of HNO_3 is the rate-controlling step. The reactions have been proposed as follows [6,10]:

$$NH_4^+\ NO_3^- \rightleftharpoons NH_3 + HONO_2 \quad (4)$$

$$HONO_2 + HA \xrightleftharpoons{-A} H_2NO_2^+ \rightarrow NO_2^+ + H_2O \quad (5)$$

Where, HA = NH_4^+, H_3O^+, HNO_3

$$NO_2^+ + NH_3 \rightarrow [NH_3NO_2^+] \rightarrow N_2O + H_3O^+ \quad (6)$$

$$NH_4NO_3 \rightleftharpoons N_2O + 2\ H_2O \quad (7)$$

According to the mechanism above-mentioned, at low temperature, ionic decomposition pathway for AN suggests acidic additives destabilized while basic additives stabilize thermal decomposition. A large number of experimental results indicate that the improvement on the thermal stability of AN could lead to reduce detonability.

4 Research and testing needed

4.1 The selection of desensitizing additives

In principle, the desensitization can be done in some general ways as follows:

(1) The selected additives exhibit the following properties: substantially water soluble, substantially hydrocarbon insoluble, which are undetectable or difficult to separate from AN.

(2) The thermal decomposition of AN was reduced by adding the selected additives acting as the chemical reaction suppressants.

(3) The detonation process was catalytically interfered with combination AN and the selected additives, as fire retardants are commonly added to textiles and polymer to reduce their potential to burn.

(4) Diluting AN with the selected additives will take energy from the chemical reaction possibly leading to failure of a detonation or to a lower explosive yield [1].

(5) The selected additives have the properties of flame-retardant agents which are highly water soluble.

(6) The selected additives may contain hydrated crystals because water can reduce or eliminate the detonation potential of AN at the water concentration of approximately 10%.

(7) The selected additive has a property of break-e-

mulsifier which is highly water soluble, thus emulsion explosives in terrorist bombs cannot be formulated.

Unfortunately, the desensitizing methods above-mentioned do not materially degrade the performance of the explosive under all circumstances. According to the literature[1], it is likely that mixtures exist with a diluent concentration of 50 percent or more that are nondetonable under most circumstances. However, unless the diluent were an equivalent agricultural fertilizer, up to two times as much product would have to be used to yield the same agriculture benefit to farmers. Therefore, fundamental research is needed to better understand how nonideal explosive (ANFO) react and might be desensitized or rendered inert. In addition, improved computer codes that accurately simulate the chemical reaction mechanisms of AN would be particularly useful. Furthermore, new ideals for desensitizing AN should be pursued and tested using standard test protocols that also must be developed. This work should be coordinated with current work funded by government agencies.

4.2 Testing for detonability of desensitized AN mixtures

Small-scale tests currently are used by industry to assess the detonability of explosive mixtures. In addition, it will be necessary to have a standard test protocol to evaluate the detonability of any proposed, desensitized AN mixtures, whether they are based on AN or other ingredients likely to apply in large-scale bombings.

Because the behavior of a nonideal explosive (ANFO) does not scale linearly with the mass of the explosive mixture [12], thus, even if tests on a smaller charge mass indicate that a mixture will not detonate, a large charge of the desensitized AN mixtures can in fact detonate[1]. In addition, the critical diameter of a cylindrical charge of a nonideal explosive that will detonate may be relatively large (about 50mm or more). Therefore, it is important, in assessing the detonability of a candidate desensitized AN mixtures, to determine critical diameter using large-scale testing of some of the best formulations. Thus the charge size of a candidate desensitized AN mixtures should be larger than the critical diameter. A suitable container must also be used to ensure adequate confinement.

5 Conclusions

High concentrations of desensitizing agents may not be practicable owing to both their cost and their negative effect on the intended purpose as a fertilizer.

The selected additives should be considered include: (1) the properties of any proposed desensitizing additives being undetectable or difficult to separate from the desensitized AN mixtures; (2) the properties of the desensitizing AN being non-emulsifiable; (3) safety in AN manufacturing, distribution, or legitimate end use; (4) no additional cost imposed on the farmers; (5) no adverse impact on the fertilizer itself, the plant material or the environment when introducing desensitizing additives.

In addition, standard test protocols for evaluating the detonatability of fertilizer-grade AN should be developed by the government agencies.

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非爆炸且不可还原硝酸铵的研究综述

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摘要: 综述了非爆炸且不可还原硝酸铵的研究现状, 提出了钝化硝酸铵的要求并介绍了硝酸铵的热分解机理。同时, 对如何选择钝化剂以及钝化后的硝酸铵的爆炸性测试提出了见解。

关键词: 无机化学; 硝酸铵; 非爆炸性; 不可还原性; 钝化剂; 综述
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