

Supramolecular Structure Influence on Ammonium Nitrate Explosive Properties

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Abstract. The ideas regarding the mechanisms of ammonium nitrate (AN) explosive properties occurrence are systematized. It is shown that the AN explosion specific TNT equivalent varies within 0.45–4.0 depending on the accompanying factors set. The AN behavior in the presence of ammonium sulfate and moisture impurities was simulated. It is emphasized that ammonium sulfate can increase the AN explosive properties by releasing a large amount of ammonia in micropores during decomposition, which exacerbates the initiating shock wave pulse as in the Oppau incident case. The moisture role in increasing the AN explosive properties was determined based on the mechanism of wedging water molecules into the crystal lattice: this becomes a dipole barrier that weakens the Coulomb repulsion between nitrate ions, allowing them to come closer together to the point of forming a peroxide bridge under shock wave conditions. Schemes of the AN supramolecular structure for the stable state and for the explosive transformations initiation moment are described with the determination of the detonation susceptibility index K_D based on the "melting ease" index. It was established that the scheme "linear cluster based on nitro basis" gives the detonation tendency index $K_D > 1$, which does not correspond to reality; and for rhombic lattices – $K_D < 1$, which indicates the explosive properties absence. Under the conditions of crystal structure destruction to dimers with a clustering scheme by nitro groups "head-to-head", $K_D > 1$ was obtained, which determines significant explosive properties. The rearrangements model in AN under the shock wave action was developed: the head-to-head AN molecules reorientation of nitrate groups; intermolecular interaction with the nitrogen of a neighboring molecule; nitrate complex formation; the emergence of a bimolecular transition state formation with a peroxide linkage; and dimerization-induced decomposition with the NO_2 release and reactive oxygen species, which together initiate the explosion.

1 Introduction

Ammonium nitrate (AN) is both a common nitrogen fertilizer and a raw material for the many explosives production. It is difficult to initiate an explosion of this substance in its chemically pure form, although in practice explosions of it and its mixtures for agricultural purposes (FGAN) is observed under conditions of fire or other explosion. It is difficult to initiate an explosion of this substance in its chemically pure form, although in practice explosions of it and its mixtures for agricultural purposes (FGAN) is observed under conditions of fire or other explosion. Determining the causes and physicochemical mechanisms of such processes initiation is an important task.

Known factors that increase the ability of AN to explosive transformations include: the impact of a powerful shock wave, finely dispersed state, caking, supramolecular structure degradation, significant changes in storage temperatures, and the fire temperature impact [1]. But a clear physicochemical model of these processes development not yet developed. For such analysis, it is possible to apply methods for modeling supramolecular structures that arise at the combustion initiation moment in the form of cooperative rearrangement [2].

Thus, the current scientific concept on this issue has no basis for assessing the explosion probability in the event of a fire or ammunition entering an AN storage location. Accordingly, at

not explode, the most reliable method for extinguishing fires and preventing explosions is flooding with large volumes of water containing surfactants to accelerate penetration and cooling of the porous granules, along with a fire retardant to inhibit peroxide rearrangement [46].

The developed approaches are of interest for understanding the mechanisms behind the AN's explosive properties formation, their deliberate enhancement or complete elimination, and for predicting the probability and consequences of explosions involving AN or its mixtures.

5 Conclusion

Analysis of FGAN explosion cases revealed that the specific TNT equivalent ranges from 0.45 to 4.0. This wide variation is attributed to the fact that impurity types and content, AN degradation levels, mass accumulation, and initiation mechanisms collectively shape the resulting explosive properties. It is argued that among typical FGAN mixtures containing ammonium sulfate or calcium carbonate, the latter is safer as it binds decomposition products, whereas ammonium sulfate merely mechanically obstructs the cooperative explosive process of supramolecular restructuring. A model was developed suggesting that ammonium sulfate can enhance the mixture's explosive properties: its decomposition starting at 100 °C releases more ammonia than AN, generating counter micro-shock waves within micropores as an avalanche-like process. This intensifies the impact on AN and initiates its explosive decomposition, as potentially occurred during the Oppau incident. The enhancement of AN explosive properties at approximately 2 % moisture is explained by water molecules wedging into the crystal lattice, acting as a dipole barrier that weakens Coulombic repulsion between nitrate ions and allows them to converge. Under shock-wave conditions, this facilitates the association of AN molecules via nitro groups, transforming the complex into a peroxide bridge. For such crystal disruption, calculated for an 8-vertex crystal basis, one water molecule per two bases (1.4 %) is sufficient. Supramolecular modeling of AN: for the "linear cluster based on a nitro-basis" scheme, the detonation susceptibility index was 7.48–32.1 ($K_D > 1$), indicating extreme explosive properties inconsistent with empirical data. Correlation was achieved for orthorhombic lattices ($K_D = 0.7$); however, upon crystal structure collapse into dimers, K_D rises to 2.81, reflecting significant explosive potential. This model predicts that shock-wave pressures reorient AN molecules into a "head-to-head" oxygen configuration, leading to dimerization-induced decomposition via a bimolecular transition state with peroxide linkage" (N-O-O-N), which possesses a significantly lower activation energy. This mechanism explains the release of NO_2 and the active oxygen species formation, which collectively initiate detonation.

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