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3-Nitro-1,2,4-triazol-5-one (NTO) as a component of low sensitive explosive compositions

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A literature review of synthesis and crystallization methods and potential applications of 3-nitro-1,2,4-triazol-5-one (NTO) in low sensistive explosive compositions is done. The sense of research and designing insensitive munition is mentioned and examples of mass scale insensitive compositions are presented. Examples of synthesis and crystallization methods of NTO and their influence on the crystals morphology is presented.

1. Introduction

NTO (3-nitro-1,2,4-triazol-5-one), also called ONTA (oxynitrotriazolone), is an explosive with a sensitivity to mechanical stimuli comparable with that of TATB (1,3,5-triamino-2,4,6-trinitrobenzene), and much lower than the sensitivity of the most powerful explosives used nowadays – RDX (hexogen, cyclo-1,3,5-trimethylene-2,4,6-trinitroamine) and HMX (octogen, cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitroamine), and relatively high explosive parameters (comparable with RDX) [1]. Due to those properties, for many years it has been in the interest of research centres as a potential individual insensitive explosive or an ingredient of explosive compositions applied in the future in insensitive munition (IM). In addition, synthesis method of this matherial is quite simple and does not require harsh conditions.

A lot of recent publications [e.g. 2-12] about potentially low sensitive explosives and compositions show the ascending tendency to work with them. For example, in the US Army a research program called CLIMEx (Common Low-cost Insensitive Munition Explosive) was initiated in 2005. The main aim of this program is to choose an explosive that has apropriate properties and is cheap enough and easy to obtain to be used on mass scale instead of TNT (trotyl, 2,4,6-trinitrotoluene) in artillery munnition (cal. 155 mm). Similar projects were initiated in other NATO countries, for example in France and Germany [5-8].

2. Synthesis

NTO was synthesized for the first time by Manchot and Nolle in 1905, but its explosive properties were developed and described in the middle 1980s [13]. Synthesis method, worked out at Los Alamos National Laboratory, USA [14, 15], consists in condensation of solid semicarbazide hydrochloride with 90% formic acid at 90-100^{o}C and nitration of the obtained semi-product (fig. 1). With some slight modification, it is applied until now.

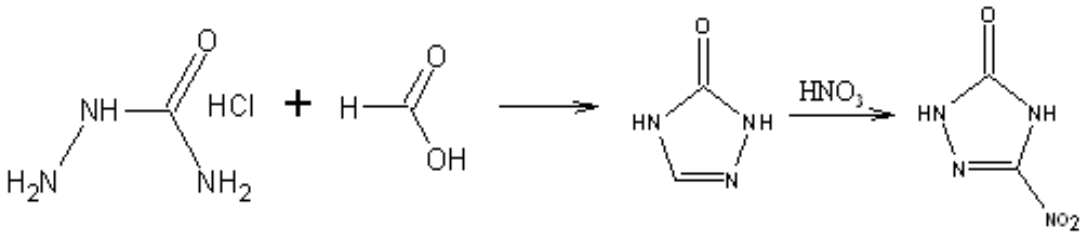

Fig. 1. NTO synthesis scheme [15]

The most efficient of the published synthesis methods was decribed in [13]: 34,5 ml of 88% formic acid was dropped into 33,45 g solid semicarbazide hydrochloride at room temperature. The resultant solution was heated to 65ºC while being constantly mixed, to form 1,2,4-triazol-5-one (TO). Then, the nitrating mixture consisted of 100 ml nitric acid and 20 ml of 98% sulphuric acid, was dropped during 1,5–2 hours. The temperature was maintained at 65°C. The mixture was then cooled and filtered, and the product was washed with water. NTO was recrystallized from hot water. Total yield was 77%. As shown, the two reactions can be combined in one pot, without isolation of the intermediate, which makes the synthesis shorter and more efficient. An additional merit is that the substrates are commercially available and inexpensive.

3. Crystallization

Being well soluble in water, at the beginning NTO was crystallized from it [15]. Unfortunately, it turned out that rising crystals are porous and plate-shaped with sharp edges. Coarse product has the same morphology, so crystallization from water can only be used to purify the product and not for obtaining good morphology. Round-shaped crystals are desirable because of their lower sensitivity to mechanical stimuli and better pourability of compositions containing those crystals, so a method enabling to obtain spherical crystals is needed.

In [16] Kim determined the solubility of NTO in NMP (N-methylpyrrolidone) and their mixtures. The solubility of NTO in water depends more on temperature than its solubility in NMP. Addition of water to NMP increases the extent to which the solubility of NTO depends on temperature. The author crystallized NTO from mixtures of those solvents by cooling solutions at different rates. The bigger the cooling rate was, the better was the morphology of the growing crystals. As NTO crystallizes from water/NMP mixtures in the form of spheres made of fine needle-like, concentric crystals, it is beneficial when the needles are as fine as possible. It is obtainable by rapid cooling, when a lot of crystallization seeds appear because of kinetic control of the process. Microscopic observation of crystal interiors confirms that they are always formed this way from the begining and then their diameter enlarges. The author indicated 10 K/min as the optimal cooling rate. Moreover, it was found that the content of water in the mixture with NMP influences the diameter and morphology of the particles [16-18]: the more water the mixture contains, the larger the needle-like crystals are, so the formed round particles are bigger, more porous and irregular in shape. However, the water/NMP mass ratio can not be less than 1, because if it is, an NTO-NMP complex is formed. If the ratio is greater than 4.8, the particles are irregular. The NTO/NMP ratio also influences the morphology of the crystallites: if it is greater

than 0.6, the growing particles are porous. A diffractometric analysis revealed that despite a different morphology, the product crystallized from water/NMP mixture has the same crystallogragrapihc structure as that crystallized from water. From among different mixtures (water/NMP in 1.0 to 8.0 ratio and NTO/NMP in 0.18 to 1.0 ratio) cooled at 10 K/min, the most advantageous morphology was observed with particles obtained from the mixture consisting of 6.4% NTO, 41.8% water and 41.8% NMP (water/NMP = 1.0, NTO/NMP = 0.39). Particles obtained by Kim et. al. had an average diameter of between 50 and 220 µm, which depended on the content of water in the mixture. NTO obtained in that way has high density: crystallized from a solution containing 12.5% NTO, 43.7% NMP and 43.8% water had a density of 1.927 g/cm^3, comparable to the density of real crystal, and low impact sensitivity – 46.5 J. The sensitivity of the product crystallized from water was 16.9 J.

4. Properties

Detonation parameters of NTO were measured in [1]. Particles of NTO crystallized from water with avarage size of crystals 130 µm were used. Detonation velocity in unconfined charge with a diameter of 30 mm and density of 1.80 g/cm^3 was 7860 m/s. In that conditions, critical diameter was defined as 16 mm. A similar result (14 mm) was obtained by the authors of [19]. Detonation pressure calculated from water test is 24.6 GPa and is comparable with the detonation pressure of Composition B (TNT/RDX 40/60).

5. Explosive compositions

A lot of explosive compositions containing NTO have been described. It is a material added both to melt-cast and plastic bonded explosives (PBX).

In the CLIMEx program, thanks to low sensitivity, IMX-101 composition containing 2,4-dinitroanisole (DNAN), nitroguanidine (NQ) and NTO, was indicated. Due to DNAN content, which is a meltable material, that composition can be elaborated by casting the same way as TNT. Sensitivity to mechanical, thermal and explosive stimuli is much lower than the sensitivity of Comp. B and pure TNT and RDX. Holding in a raised temperature (60^{o}C or 70^{o}C) for several months leads to a vital rise of sensitivity of IMX-101 to mechanical and thermal stimuli [3]. A secondary aim of the CLIMEx program was to choose a material or composition to displace Composition B from use in mortar shells (cal. 120, 81 and 60 mm). For this aim, the IMX-104 composition containing DNAN, NTO and RDX apeared to be the most suitable. Both mentioned materials were tested to mechanical and thermal sensitivity and passed the tests favourably (fast and slow cook-off test, bullet and fragment impact tests, gap test). Detonation parameters were not measured [9]. Another explosive composition containing DNAN instead of TNT and also NTO and HMX as energetic components, is PAX-48. Like IMX-104, it also meets the requirements for explosives for low sensitive munnition. Both materials are much less sensitive to mechanical and explosive stimuli than Comp. B, but have slightly lower detonation performance. The authors of [4] determined experimentally and calculated in CHEETAH 5.0 code the velocity and the pressure of detonation for compositions, presenting the results as a rate to Comp. B

parameters. The detonation velocity is about 90% of the dentonation velocity of Comp. B, while the detonation pressure is about 80%.

In the French Nexter Munition centre in 2006 experiments aiming at working out an insensitive explosive composition for mass scale were started. As the most suitable for the large-calibre munition (155 mm), the XF®13333 composition was selected. The composition contains 48±2% NTO, 31±2% TNT, 7.5±2% wax, 13.5±2% Al powder. When the density is 1.75g/cm^3, the detonation velocity is 6976 m/s and the detonation pressure is 210 kbar. Impact and friction sensitivity (50% of "go" reactions) is 160 N and 48 J respectively. Artillery munition LU211 filled with this composition meets the requirements for IM determined in STANAG 4439 and is produced in France on mass scale [5]. Among several cmpositions containing NTO and RDX, the best ones turned out to be the XP3264® containong 33% RDX, 49% NTO, 14% Al, 4% wax, with detonation velocity 7921 m/s and detonation pressure 285 kbar when the density is 1.82 g/cm^3. The friction sensitivity is lower than 353 N, the impact sensitivity is 30% of „go" for a force 50 J. The critical diameter of an unconfined charge is 5-10 mm. In tests to detonation transfer (gap test) and the bullet impact, munition cal. 40 mm ends by burning of explosive material. The composition is too sensitive to heating (both in slow and fast cook-off test it undergoes a deflagration of the explosive). Because of this, it does not meet the requirements from STANAG 4439, but it is still much safer than the traditionally used munition of this caliber. From the 2009, XP3264® is produced on mass scale and used for medium-caliber bullets [6].

Experiments to design an explosive for insensitive munition, not containing TNT, are carried out also in Military University of Technology. As a TNT replacement in melt-cast composition, DNAN was examined. It is a material with the melting point at 86.9°C and 94.5°C (depending on the crystal form), less toxic than TNT and insensitive to mechanical stimuli (impact sensitivity is lower than 200 J, friction sensitivity is lower than 360 N). In addition, in the melted DNAN, about 30% RDX can be dissolved. Addition of RDX lowers the melting point of DNAN by a few Celsius degrees. Compositions containing 40% DNAN, 20% RDX, 40% NTO, with NTO crystals with size 125-160 µm and 250-300 µm were examined. Crystal fractions was determined on the basis of viscosity measurements and sedimentation rate of NTO in temperature of working process (90-95°C). It was discovered that compositions are less sensitive to impact (25 J regardless of NTO crystal size) than pure RDX and NTO, and moreover have higher detonation velocity than pure TNT (7040 m/s and 6730 m/s respectively). Described compositions melt at about 80°C and start to decompose at about 180°C, which supplied safe margin during casting charges [20].

6. Summary

Research on low sensitive explosives is conducted in most countries participating in any military operations. The main trend is to replace TNT, which is thought to be too sensitive and toxic for humans. Nevertheless, its explosive properties are sufficient for most applications. Compositions presented in this review are less senitive to mechanical and thermal stimuli than TNT or Composition B, but also much more expensive.

NTO seems to be a good candidate for a component of low sensitive explosive compositions, but optimization of the crystallization method is needed.

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