



Researches on New Crystalline Form of Some Insensitive High Explosives in PBX

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Abstract: In this paper, the results of researches on crystallization of insensitive high explosives were described. 3-Nitro-1,2,4-triazol-5-one (NTO) and nitroguanidine (NQ) were selected. The laboratory methods of preparation were presented. The influence of different solvents and other parameters on crystallization process was investigated. The results of the particle size distribution in the crystals obtained were presented. The suitability of NTO and NQ for their application in plastic bonded explosives (PBX) was checked.

Keywords: NTO, NQ, PBX

Introduction

In recent years, the interest in insensitive high explosive compositions has been growing. A major component of usable form, which decides on explosive properties, is the explosive itself. Common explosives like hexogen (RDX), octogen (HMX), pentrit (PETN), used to be considered

adequate for all weapon applications, but because of a number of accidents involving initiation of munitions by external stimuli, these explosives have become less attractive. So there is much research worldwide to obtain explosives that have high performance coupled with low sensitivity. The increase of resistance to mechanical, electrical and thermal impact, without worsening other parameters, is realized by the addition of such explosives like 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ) or 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).

The researches of NTO and NQ were begun, because these materials are relatively inexpensive and easy to synthesize [1, 2]. The important problem is to obtain the suitable form of crystals of these materials. This crystalline form should provide an effective utilization of NTO and NQ as an individual explosives or components of explosive mixtures.

In the literature, various crystallization methods of 3-nitro-1,2,4-triazol-5-one and nitroguanidine are presented. The researches on NTO crystallization are described in [3-5] and chosen methods of NQ crystallization are shown in [6-8].

The main purpose of this work was to check a suitability of obtained crystalline forms of NTO and NQ to their application in plastic bonded explosives. Some explosive properties of the samples were investigated.

Properties of 3-nitro-1,2,4-triazol-5-one and nitroguanidine

Nowadays the interest in 3-nitro-1,2,4-triazol-5-one is growing due to its performance and low sensitivity to mechanical stresses. In the future, NTO might become substitute of RDX in mixtures about lower sensitivity to external impacts.

NTO is a crystalline substance with high density and velocity of detonation (VOD). The crystal density and VOD of NTO are equal to those of RDX, whereas it is far less sensitive than RDX and HMX. Calculated and measured detonation velocities of NTO are presented in [9]. The melting point of this explosive is 260 °C with decomposition [10]. NTO exists in two crystalline forms α ($\rho_0 = 1.92 \text{ g/cm}^3$) and β ($\rho_0 = 1.92 \text{ g/cm}^3$) [11]. The α form of NTO is characterized by high density and low sensitivity to mechanical stimuli. The impact sensitivity of NTO is 291 cm (H_{50}) and

RDX is 22 cm (H_{50}) for the same conditions [12]. The sensitivity of NTO in the comparison with hexogen, trinitrotoluene and other explosives are also presented in [13, 14].

3-Nitro-1,2,4-triazol-5-one is soluble in water and organic solvents like: methanol, ethanol and *N*-methyl-2-pyrrolidone. It can be crystallized from these solvents. The solubility of NTO in different solvents is described in [15].

Nitroguanidine like NTO is of low sensitivity to mechanical impacts. The sensitivity to friction of NQ is 353 N and the sensitivity to impact is 49 N m [16]. In the last century NQ was used as the component of propellants. Bulk density of NQ is about 0.2 g/cm³, therefore this compound did not find any practical applications as an individual explosive or a component of explosive mixtures.

In the paper [17], the influence of NQ additive on the sensitivity to mechanical stimuli for PBX containing HMX is shown.

Nitroguanidine is white crystalline substance, it exists in two tautomeric forms α (thin needles) – Figure 1 and β (elongated plates) – Figure 2 [18]. The water solubility of these forms is different. The solubility of nitroguanidine in common organic solvents like: acetone, methyl and ethyl alcohols, ethyl acetate, ether, carbon tetrachloride, toluene, is limited. The melting point of nitroguanidine is 246 °C [5].

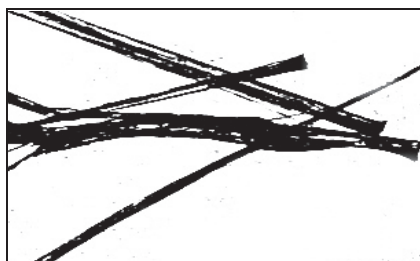


Figure 1. The α crystalline form of NQ.

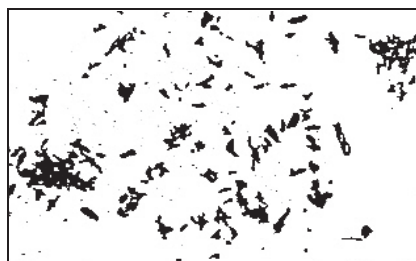


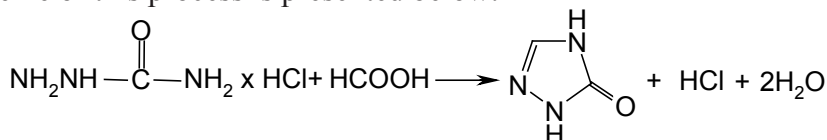
Figure 2. The β crystalline form of NQ.

Synthesis of 3-nitro-1,2,4-triazol-5-one and nitroguanidine

In order to obtain NTO and NQ a lot of syntheses were made. On

the basis of these reactions the optimal parameters of the process were determined. During the selection of reaction parameters we paid attention to the reduction of costs. The optimal methods of NTO and NQ preparation are shown below.

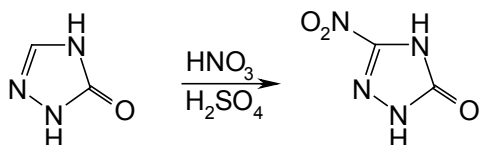
3-Nitro-1,2,4-triazol-5-one was obtained in a two-stage reaction. The scheme of this process is presented below:



The synthetic preparation of triazolone (TO) by the condensation of semicarbazide hydrochloride with formic acid.

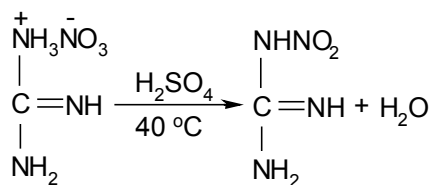
For the synthesis 85% formic acid was used and the molar ratio, semicarbazide/HCOOH was 1/2. The reaction mixture was stirred at 85-90 °C for 8 hours. Then the solution was cooled to 5 °C, and neutralized with 10% Na₂CO₃. Next, the precipitated triazolone was filtered and washed with cold water. In the second stage, the crude product with melting point of 234 °C was nitrated.

The nitration of triazolone with the nitrating acid:



The mixture of 65% HNO₃ and 100% H₂SO₄ in the volume ratio of 85 to 15 was used. The triazolone was dosed to nitrating acid at 5-10 °C, then the mixture was stirred at 65 °C for 2 hours. Next, the mix was cooled to 20 °C, and the precipitated product was filtered, washed with ice-cold water and dried. The crude NTO was obtained with melting point 267-269 °C and overall yield ~ 70%.

The nitroguanidine was obtained in a single-stage reaction. The scheme of this process is presented below [3]:



Guanidine nitrate was dozed to 96% sulfuric acid and the mixture was stirred. The temperature of reaction did not exceed 40 °C. The stirring was continued until crystals were dissolved. After that, the solution was poured into ice water and precipitate of NQ was filtered and washed with water. Then NQ was poured into water with ammonia additive in order to remove residual acids from the product. The nitroguanidine was filtered again and crystallized. The yield of the reaction was 85%.

Crystallization of 3-nitro-1,2,4-triazol-5-one and nitroguanidine

In order to obtain desirable crystalline form of these materials a lot of crystallization tests were carried out. During the tests different parameters were changed, for example: solvents, mass ratio of compound, stirring time and cooling rate.

The different solvents and their mixtures were used. The following solvents were checked: ethylene glycol, dimethylsulfoxide, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, ethyl alcohol.

The best of crystallization methods are presented below.

Crystallization of NTO from C₂H₅OH/H₂O mixture

The mixture of ethyl alcohol with water was used as solvent to crystallization of NTO. The volume ratio of these compounds was 9/1. NTO was mixed with the solvent in volume ratio 1/12.5. Next, the mixture was gradually heated to 65 °C and stirred 600 rpm. The nuclei of crystallization (crystals of NTO) were added at the beginning of cooling. The mixture was gradually cooled to 20 °C with a cooling rate 3 °C /min. The precipitated product was filtered, washed with acetone and dried.

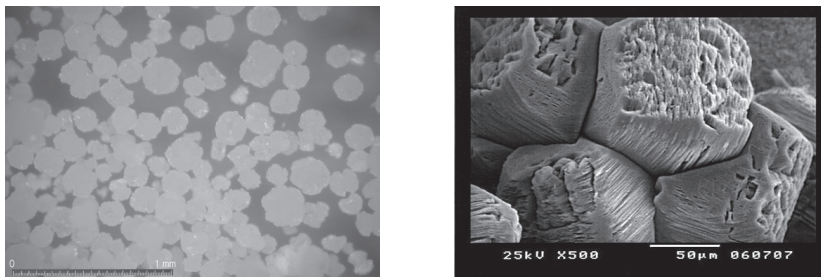


Figure 3. Crystals of NTO after crystallization from C_2H_5OH/H_2O .

The spherical crystals of NTO (Figure 3), with grain size 80-300 μm were obtained. The grain size analysis of NTO is presented in Figure 4. After crystallization, bulk density of NTO was 0.80 g/cm^3 and tap bulk density was 0.96 g/cm^3 .

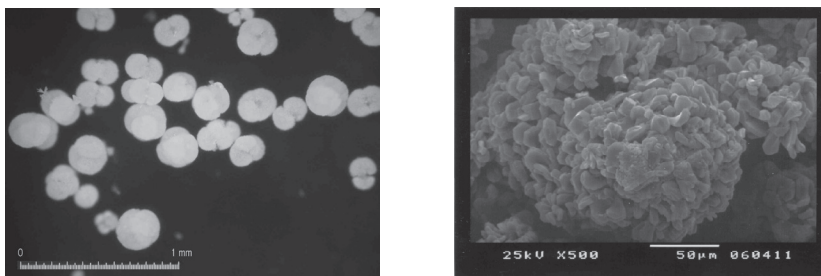


Figure 4. Particle size distribution of NTO after crystallization from C_2H_5OH/H_2O .

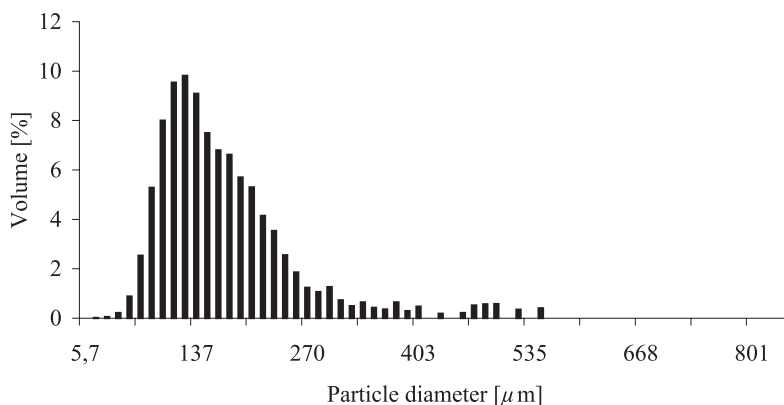


Figure 5. Crystals of NQ after crystallization from *N*-methyl-2-pyrrolidone.

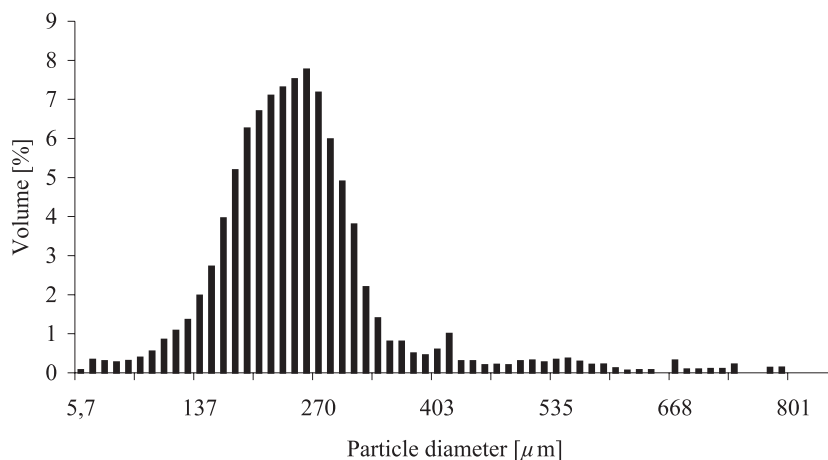


Figure 6. Particle size distribution of NQ after crystallization from *N*-methyl-2-pyrrolidone.

Crystallization of NQ from *N*-methyl-2-pyrrolidone

The mixture consisted of nitroguanidine and NMP (weight ratio 1/4.5) and about 30 ppm nickel nitrate, was gradually heated to 95 °C. The mixture was stirred 800 rpm. Then the solution was cooled by the addition of acetone. When the whole acetone was added, stirring was held for ten minutes. Next, the nitroguanidine was filtered, washed with acetone and dried. The crystals of NQ are presented in Figure 5, and particle size distribution of product is shown in Figure 6. Bulk density of nitroguanidine after crystallization was 0.65 g/cm³ and tap bulk density 0.85 g/cm³. The grain size of NQ crystals was about 130350 μm.

PBX based on 3-nitro-1,2,4-triazol-5-one and nitroguanidine

The samples of plastic bonded explosives based on NTO and NQ were obtained. The samples consisted of 84% high explosive and 16% of binder. The high explosives included RDX/NTO or RDX/NQ mixtures. The content of the mixture of high explosive was the same, whereas the mass ratio of RDX/insensitive additive was changed. The binder consisted of butadiene-styrene-copolymer, which was plasticized by the dioctyl adipate. The

content of the polymer in the binder was 33%. In order to obtain PBX samples, the wet RDX was mixed with the binder, and then the PBX was dried. Next, insensitive additive (NQ or NTO) was mixed with the PBX. The mixing was performed in kneader.

The parameters of hexogen, which was used were as follows: grain size about 10-150 μm and tap bulk density 0.9 g/cm^3 . NTO and NQ were synthesized and crystallized according to methods, which are described above.

Detonation velocities (VOD) for the plastic bonded explosives were measured. The explosive mixtures were placed into a plastic tube of 35 mm inside diameter. VOD was determined by short circuit sensor method. The working capacity of PBX was measured in Trauzl block test and ballistic mortar test.

The results of investigation for PBX containing NTO and NQ are presented in Table 1 and Table 2.

Table 1. The results of investigation for PBX containing NTO

Content 84% Explosive 16% Binder	0% NTO 100% RDX	20% NTO 80% RDX	40% NTO 60% RDX	60% NTO 40% RDX	80% NTO 20% RDX
Density [g/cm^3]	1.42	1.45	1.46	1.49	1.52
Detonation velocity [m/s]	7300	7200	7000	6800	Not detonated
Trauzl block test [cm^3]	390	378	348	305	248
Balistic mortar test [%]	84	62	57	46	36

The increase of NTO content causes the increase of samples density and simultaneously the decrease of detonation velocity. For the PBX containing NQ (up to 60%) the increase of density is observed. In case of NQ as well as NTO it is connected with the grain size of the components. For the samples above 60% of NQ content, the density decreases. The detonation velocity of PBX containing above 40% of NQ considerably decreases, because NQ is of low density and high critical diameter. The

drop of measured values, which was observed in Trauzl block test and ballistic mortar test, results from small volume of samples applied to these tests. The underwater test or cylinder tests are better for determination of working capacity of these explosives.

Table 2. The results of investigation for PBX containing NQ

Content 84% Explosive 16% Binder	0% NTO 100% RDX	20% NTO 80% RDX	40% NTO 60% RDX	60% NTO 40% RDX	80% NTO 20% RDX
Density [g/cm ³]	1.43	1.45	1.48	1.47	1.41
Detonation velocity [m/s]	7300	7400	7300	6000	Not detonated
Trauzl block test [cm ³]	390	363	298	252	230
Balistic mortar test [%]	84	65	62	52	40

Summary

Researches on crystallization of 3-nitro-1,2,4-triazol-5-one and nitroguanidine were carried out.

In the case of NTO, the best method which was described by other authors reference, led to spherical agglomerates of this explosive.

After many experiments we obtained compact spherical crystals of NTO, when the mixture of ethanol/water in volume ratio 9/1 was used as solvent to crystallization. The grain size of NTO was about 80-300 μm . The bulk density of NTO was 0.80 g/cm³ and tap bulk density was 0.96 g/cm³. The method of crystallization is easy and inexpensive. The positive result can be obtained when the crystallization parameters are obeyed.

The spherical crystals of NQ after crystallization from *N*-methyl-2-pyrrolidone were made. In the case of NQ, the crystals were spherical agglomerates, but their structure was compact. The obtained crystalline form was suitable for the preparation of PBX with NQ additive. The grain size of these explosive was about 130-350 μm .

The improvement of bulk density and tap bulk density of NQ was

achieved. The results are shown below:

- ✘ tap bulk density of NQ after crystallization from water – 0.24 g/cm³,
- ✘ tap bulk density of NQ after crystallization from NMP – 0.85 g/cm³.

Scaling up the NQ crystallization was carried out. The results obtained in these experiments were in agreement with the previous study reference.

The plastic bonded explosives containing NTO and NQ were obtained. The crystalline form and grain size of these explosives enable practical utilization.

For the PBX containing up to 40% of NTO and NQ the slight decrease of detonation velocity was observed. The decrease of working capacity measured in Trauzl block test and ballistic mortar test was higher than the corresponding decrease of detonation velocity. It results presumably from the fact that the samples used in these tests are small, and tested explosives are of high critical diameters.

Acknowledgements

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