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Methods for Preparing Spheroidal Particles of 3-Nitro-1,2,4-triazol-5-one (NTO) *)

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Abstract: This paper presents an overview of methods for recrystallizing 3-nitro-1,2,4-triazol-5-one (NTO), with particular emphasis on methods for obtaining spheroidal particles with low porosity. The effects of selected solvents and surfactants on the recrystallization results was checked. Products in the form of spheroidal particles were obtained for some selected solvent-surfactant systems. The bulk density, surface area, size distribution, and sensitivity to friction and impact were tested for the spherical NTO samples and thermal analysis was also performed.

Keywords: NTO, recrystallization, properties

1 Introduction

The basic solvent used for purification and recrystallization of NTO is water. However, this generates crystals with unfavourable morphology – porous and plate-like, with sharp edges. Thus crystallization from water can only be used to purify the product, not for obtaining good morphology. Round-shaped crystals are desirable because of their lower sensitivity to mechanical stimuli, and better pourability of compositions containing this type of crystal. Consequently a method that enables spherical crystals to be obtained is required.

In paper [1], Chapman has described methods for the recrystallization of

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NTO from water, N-methyl-2-pyrrolidinone (NMP) and a mixture of water and NMP. The most irregular crystals were obtained by cooling a water solution. As a result of pouring a solution of NTO in NMP into the water containing ice, very porous agglomerates, with a diameter of 15-100 μm, were formed from single crystals with size 2-10 μm. When a solution of NTO in a mixture of water and NMP was cooled, spheroidal crystals (or agglomerates of very small crystals) with high porosity and a diameter of 10-30 μm were formed. The grain size depended on the ratio of water/NTO in NMP solution.

Collignon [2] described a way for obtaining spheroidal NTO as a result of crystallization from alcohols or their admixtures with water. The alcohols which were studied in this process contained from 1 to 4 carbon atoms in the aliphatic chain. A solution of NTO in the alcohol was heated from 40 °C to a temperature near the boiling point of the alcohol, and was then subjected to rapid cooling (6-20 °C/min) with stirring. After bringing the suspension of NTO in the alcohol to a temperature of +5-10 °C, the spheroidal product was filtered off.

The authors of paper [3] announced a method of crystallization from water with the addition of a surfactant (perfluorinated salts of aliphatic compounds) and methylcellulose, as a way of obtaining spheroidal NTO. This involved heating a solution to a temperature above 60 °C, followed by rapid cooling (6-20 °C/min).

The authors of paper [4] determined the solubility of NTO in mixtures of water and NMP in different ratios. They then recrystallized NTO from these mixtures by cooling the solutions at different rates. It was found that faster cooling rates gave better morphology. As NTO crystallizes from the water/NMP mixture in the form of spheroids made from fine, concentric needles; needles as fine as possible were the most favourable. Such an effect can be achieved by cooling the solution at a fast rate. At this stage, crystallization nuclei are formed in a large quantity, and the growth of the crystals is delayed (it is a kinetic control of crystal growth, not a thermodynamic one). The authors selected a cooling rate of 10 °C/min as being optimal. Moreover, it was found that the water quantity in the mixture with NMP influenced the diameter and the morphology of the recrystallized NTO [4, 5]. The larger the water quantity is, the larger the crystals from which the granules are formed are. As a result, the recrystallized product is porous and irregular in shape. However, the mass ratio of water/NMP cannot be lower than 1, because a complex of NTO-NMP is then formed. On the other hand, when this ratio is over about 4.8, the crystallites formed are irregular in shape. The mass ratio of NTO/NMP also influences the morphology of the NTO crystallites. If it is too high (over 0.6), the NTO particles are porous and can be seriously deformed (with cracks and fissures). It was shown by diffractometric analysis, that particles recrystallized from water/NMP mixtures have an identical

crystallographic structure to those recrystallized from water, in spite of there being large differences in the morphology of both products.

The fact that spheroidal NTO with the appropriate morphology is formed only during recrystallization from a water/NMP mixture was confirmed by the authors of papers [6-7]. The authors of [6] also tried to recrystallize the material from other solvents, such as aliphatic alcohols and their admixtures with water. It turned out that none of the solvents allows NTO with the required morphology to be obtained. The products of recrystallization from alcohols were identified only as partly rounded granules. In paper [7], NTO was recrystallized from a water-NMP mixture (H2O/NMP = 60/40 v/v, cooling rate 1 K/min). The NTO particles obtained were spherical with diameters in the range 50-500 μm. This NTO was added to the formulations containing DNAN (2,4-dinitroanisole) or TNT with RDX.

The aim of the present work was to study the possibility of obtaining spheroidal crystals of NTO by saturating its liquid solutions in common solvents or their admixtures on addition of surfactants. The crystals obtained should have a high density (no pores inside or on the surface of the crystals).

2 Research on NTO Recrystallization

2.1 Materials used in the experiments

During the experiments, NTO was obtained by nitration of 1,2,4-triazol-5-one (TO) with a nitrating mixture composed of $HNO_3/H_2SO_4/H_2O$ (60/20/20 by weight) at a temperature of 55-65 °C. For the crystal shape optimization research, NTO recrystallized from water was used. The decomposition temperature of this NTO was 267 °C. Water and N-methylpyrrolidinone (NMP) were used as the solvents. Surfactants and other compounds or mixtures of macromolecular compounds with functional groups (mainly hydroxyl, for their hydrophilic properties), *e.g.*, polyols, esters of fatty acids, and a number of polyoxyethyleneglycol octadecyl ethers, were used.

2.2 Description of the recrystallization methods

The basic research on NTO recrystallization utilised a 500 cm^3 round-bottomed flask equipped with a stirrer and a temperature sensor, and a water bath. For the cooling of the system, an ice-water bath or a glycerine bath at a temperature of about −20 °C, were used. In each experiment, 100 g of solvent (or mixture of solvents), with the addition of 0.001-0.5 g of surfactant, was used. The mass of NTO was in the range of 6-14 g.

In the second part of the research, the scale was increased. The experiments utilised a round-bottomed reactor of capacity 1 dm^3 (5-times increase in solvent mass), and in a reactor of capacity 4 dm^3 (25- and 34-times increase in relation to the basic solvent mass). To achieve efficient cooling of larger volumes of the NTO solution, an alcohol bath with the addition of solid CO_2 was used (−60 °C). In the research described, a variety of cooling rates in the range of 5-10 °C/min were applied. The cooling rate was controlled by varying the depth of immersion of the flask in the cooling bath.

The NTO, surfactant and solvent (or a mixture of solvents) were placed in the flask. The mixture obtained was heated to a temperature of about 80 °C, and then cooled with a cooling bath. The set cooling rate was maintained. When the temperature was about 20 °C, the cooling rate was usually decreased to below 5 °C/min for the range of solution temperatures from 20 to 5 °C. At lower temperatures, this parameter was no longer controlled. The suspension obtained was conditioned at a temperature range of 0 to −5 °C. The amount of product was determined by mass, and the morphology was characterized by observation with an optical microscope (USB Microscope BRESSER, Nikon Eclipse E200) and by means of scanning electron microscopy (SEM, apparatus Gemini LEO 1530).

2.3 Selecting the conditions for recrystallization

In the literature, water and NMP mixtures are described as the most suitable solvent systems for the spheroidization of NTO crystals, as a result of rapid cooling of the ternary systems (NTO/NMP/H_2O) with different compositions. In the present research, water or NMP mixed with water were used. Some surfactants were added to the solvent systems H_2O/NMP or H_2O.

Initially, the influence of the composition of the solvent mixture on the yield and shape of the NTO crystals generated was investigated. The yield was determined as the ratio of the filtered and dried recrystallization product to the initial mass of NTO submitted to the process.

A selection of the result is presented in Tables 1-2.

Table 1. The results of NTO recrystallizations (initial mass 9 g) in the system H_2O/surfactant (mass ratio 100/0.1 g/g)

Surfactant (type) / mass, [g]	Cooling rate [°C/min], $T_{in} \rightarrow T_{fin}$ *	Recrystallization yield, [%]	Description of the product
None	10 *80→0.5 °C*	65	transparent, cubic crystals
	5 *80→0.5 °C*		transparent, cuboidal crystals
n-Hexadecyltrimethylammonium bromide (4NBr) / 0.1	10 *80→0.5 °C*	75	agglomerates of fine, cubic crystals
	5 *80→0.5 °C*		fine dendrites, highly porous on the surface
Betaine / 0.1	10 *80→0.5 °C*	75	transparent, cubic crystals
	5 *80→0.5 °C*		transparent, cubic crystals
Brij 72 / 0.1	10 *80→0.5 °C*	75	agglomerates of cubic crystals
	5 *80→0.5 °C*		agglomerates of cubic crystals
Polyvinyl- alcohol (PVA) / 0.1	10 *80→0.5 °C*	60	fine agglomerates of irregular-shaped crystals
	5 *80→0.5 °C*		fine agglomerates of irregular-shaped crystals
Aluminium stearate / 0.1	10 *80→0.5 °C*	70	transparent, cubic crystals
	5 *80→0.5 °C*		transparent, cubic crystals
Zinc stearate / 0.1	10 *80→0.5 °C*	75	transparent, cubic crystals
	5 *80→0.5 °C*		transparent, cubic crystals

* T_{in} – the initial temperature of the system, before commencing cooling;
T_{fin} – the final temperature of the system, after termination of the cooling stage.

Table 2. The results of NTO recrystallization (initial mass 9 g) in the system H_2O/NMP/surfactant

Surfactant / mass [g]	Composition of the mixture H_2O/NMP [g/g]	Cooling rate [°C/min], $T_{in} \rightarrow T_{fin}$	Recrystallization yield, [%]	Description of the product
None	90/10	10 *80→0.5°C*	70	fine agglomerates of plates
		5 *80→0.5°C*		fine agglomerates of plates
n-Hexadecyltrimethylammonium bromide (4NBr)/ 0.1	90/10	10 80→0.5°C	70	very fine agglomerates
	80/20	10 *80→0.5°C*		very fine, spherical agglomerates
		5 *80→0.5°C*		very fine agglomerates
Brij 72 / 0.1	90/10	10 *80→0.5°C*	75	agglomerates of plates with a smooth surface
PVA / 0.1	80/20	10 *80→0.5°C*	45	various sizes, spheroidal crystals with a smooth surface
		5 *80→0.5°C*		irregular-shaped crystals, a few spheroidal ones
Aluminium stearate / 1	90/10	10 *80→0.5°C*	80	agglomerates with shapes similar to spherical
		5 *80→0.5°C*		irregular agglomerates of fine crystals
Zinc stearate / 0.2	90/10	8 *60→0.5°C*	75	diverse agglomerates of plates
		2 *80→0.5°C*		diverse agglomerates of large crystals
Sodium stearate / 0.5	90/10	8 60→0.5°C	70	irregular agglomerates of plates
		2 60→0.5°C		agglomerates with shapes similar to spherical, formed from plates
Sodium stearate / 0.2	90/10	2 60→0.5°C		agglomerates with shapes similar to spherical, formed from plates

The use of the water as a single solvent, despite the addition of surfactants, gave no essential improvement in the morphology of the crystals obtained. The use of water and NMP mixtures in different mass ratios enabled spheroidal crystals to be obtained in only a few systems – with the addition of Brij 72 (polyethyleneglycol octadecyl ether) and polyvinyl alcohol (PVA). The products obtained from the solvent mixtures containing Brij 72 are formed by needles or rods arising radially from a common centre. This causes their surface to be highly developed. Adding small amounts of PVA to the solution gave a product with potentially advantageous crystal morphology. The addition of other surfactants, both in larger and smaller amounts, to the mixture of NMP and water, did not favourably influence the structure of the crystals generated.

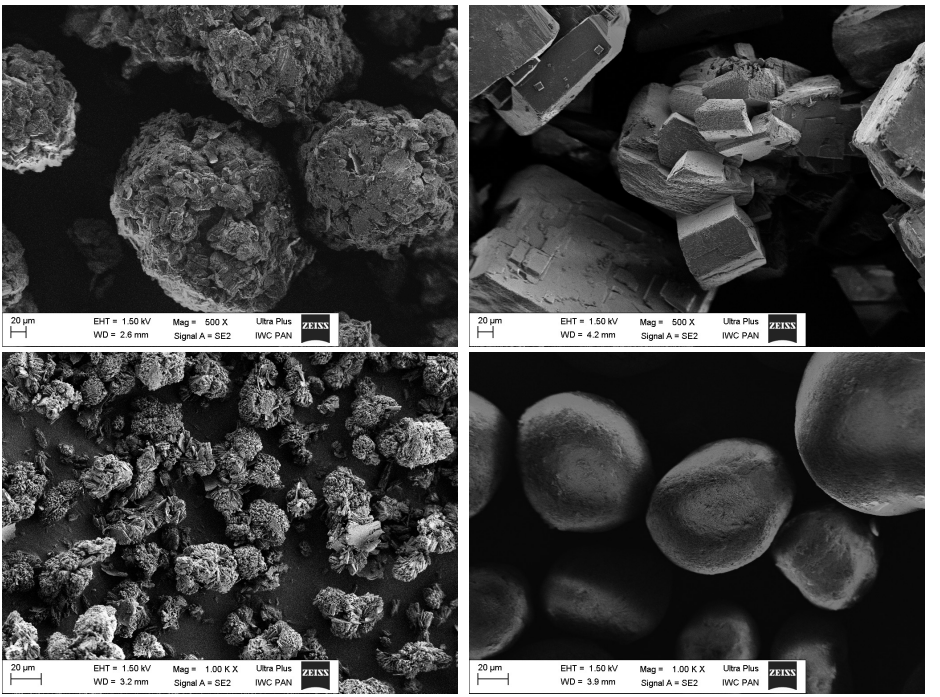

Figure 1. SEM images of some examples of NTO recrystallized under different conditions:
(A) from the mixture H_2O/4NBr (100/0.1), cooling rate 10 °C/min;
(B) from the mixture H_2O/Brij 72 (100/0.1), cooling rate 10 °C/min;
(C) from the mixture H_2O/NMP/4NBr (80/20/0.1), cooling rate 10 °C/min;
(D) from the mixture H_2O/NMP/PVA (80/20/0.1), cooling rate 10 °C/min.

Table 3. The results of NTO recrystallization in the H_2O/NMP/PVA system (PVA mass 0.1 g)

Composition of the mixture H_2O/NMP, [g/g]	NTO mass [g]	Cooling rate [°C /min], $T_{in} \rightarrow T_{fin}$	Recrystallization yield, [%]	Description of the product
90/10	9	10 *80→0.5°C*	50	spheroidal crystals and some fine, irregular agglomerates
		5 *80→0.5°C*		different sizes, irregular agglomerates
80/20	7	5 *80→0.5°C*	25	spheroidal, and a few fine, irregular crystals
	8	7 80→0.5°C	40	different sizes, spheroidal crystals
		5 *80→0.5°C*		different sizes, spheroidal crystals
	9	10 *80→0.5°C*	45	different sizes, spheroidal, smooth crystals
		7.5 *80→0.5°C*		different sizes, spheroidal, smooth crystals
		5 *80→0.5°C*		irregular crystals, with a few spheroidal ones
70/30	9	10 *80→-8°C*	45	fine, irregular crystals
		5 *80→0-8°C*		irregular crystals, with a few spheroidal ones
	10	10 *80→0.5°C*	30	fine crystals with shapes similar to spherical
	11	10 *80→0.5°C*	70	fine and very fine spherical crystals

The products of recrystallization were initially analysed by optical microscopy. The objectives of the evaluation were the morphology and size of the crystallites. Some examples of the SEM images of some of the recrystallization products are shown in Figure 1. The products shown in Figures 1(A, B, C) are characterized by highly developed surfaces, fissures and inner pores; the crystals were polycrystalline and visibly irregular in structure with sharp edges. The product shown in Figure 1(D) has a spheroidal shape and seems to be less porous than the others.

For further optimization, a mixture of H_2O/NMP and PVA was selected.

A dependence of the morphology of the product on the mass ratio of the solvents, the NTO concentration and the cooling rate was observed (Table 3). When the ratio of H_2O/NMP was equal to 90/10, not all of the crystals were spheroidal in shape. The products were not highly homogeneous until the ratio 80/20 was used. Cooling at a rate greater than 5 °C/min leads to a product with a spherical shape and a smooth surface. As a result of the slower saturation, fine crystals, forming irregular agglomerates, precipitated. Moreover, using higher concentrations of NTO (more than 12 g per 100 g of solvent mixture) lead to some fine, irregular non-spheroidal crystals being obtained.

The next step of our research was to determine the lowest possible concentration of PVA in the solution, for which it is possible to obtain a product with desirable morphology (Table 4). The minimum amount of PVA that seriously influenced the shape and surface of the crystals generated in the system NTO/H_2O/NMP 9/80/20 was about 0.008 g per 100 g of solvent mixture. The product obtained in this way had a suitable morphology. What is more, thanks to using a minute amount of PVA, the crystals do not agglomerate (do not stick together), and the surfactant, as a potential impurity, is not a significant part of the product. A comparison of the yields of the products obtained revealed a tendency to retain more than a half of the introduced NTO, which means limited precipitation of the product in the systems with higher concentrations of PVA (more than 0.01 g per 100 g of solvent mixture).

Table 4. The results of NTO recrystallization (initial mass 9 g) in the system H_2O/NMP 80/20 with the addition of PVA; cooling rate 10 °C/min

PVA mass [g]	Recrystallization yield, [%]	Description of the product
0.0027	70	agglomerates of irregular crystals
0.0055	75	agglomerates of irregular crystals
0.0078	75	different sizes of spheroidal crystals
0.1	45	different sizes of spheroidal crystals
0.2	45	agglomerates of different sizes of spheroidal crystals

Using the small scale experimental system (100 g of solvent with the addition of PVA), the influence of changes in the solution compositions on the recrystallization product, obtained with a cooling rate 5-10 °C /min, was verified. The more saturated NTO solutions were becoming cloudy during rapid cooling (the product was appearing) at a temperature above 20 °C. At the other extreme, with the lowest concentrations of NTO, NTO did not precipitate even

after cooling to −5 °C. It was observed that crystals with a desirable morphology were obtained when the system NTO/H_2O/NMP/PVA, with a mass composition 9-10/80/20/0.008-0.1, was used, and the cooling rate was greater than 5 °C /min. Under these conditions, the product starts to precipitate when the temperature is about 5-15 °C. On the basis of the foregoing experiments, further experiments connected with scaling up the process for the system NTO/H_2O/NMP/PVA with a mass composition 10/80/20/0.008 were chosen.

2.4 Modification of the conditions and scale-up of the process

The scale of the recrystallization process was gradually enlarged in the next step of the investigation. In effect, the scale of a 4 dm^3 reactor was reached. For efficient external cooling of such a large system, a bath with ethyl alcohol and solid CO_2 was used (temperature about −60 °C). When enlarging the scale, there was a clear tendency for the temperature at which the initial cloudiness was noticed (the beginning of crystallization) to decrease, even to a temperature near 0 °C (in the 4 dm^3 reactor). In order to prevent excessive cooling of the solution, the system was conditioned at a temperature of about 0 °C, at which, after about 3 min, crystallization of the NTO began. As a result of some introduced modifications, the process at the larger scale was realised as follows: into the 4 dm^3 reactor, equipped with an efficient stirrer, temperature sensor, reversible cooler and heating bath, were added water (2720 g) and NMP (680 g). Next, when the stirring had been turned on, PVA (0.275 g) and NTO (340 g) were added. After intensifying the mixing, the suspension was heated to 80 °C, and then the intensive cooling was commenced. At the beginning, the cooling rate could reach more than 10 °C/min; however when the temperature of the solution had decreased, this value had also decreased, reaching 5-6 °C/min when the system temperature was about 20 °C. The contents of the reactor were cooled to 0-2 °C, and then maintained at that temperature until the moment when crystallization began (visible cloudiness of the solution). After a further 15 min of mixing, the recrystallized product was filtered off on a Büchner funnel with suction and washed with one portion of cold water. After drying, about 260 g of NTO (about 75% yield) was obtained.

3 Characterization of Spheroidal-shaped NTO

3.1 Microscopic analysis

The analysis of microscope photographs convinced us that the most promising recrystallized product was the NTO obtained from the mixture NTO/H_2O/NMP/

PVA (10/80/20/0.008). Hereafter it is labelled NTO-B. This product is shown in Figures 2 and 3. The SEM images clearly show the regular surface formed by crystallites which are oriented in such a way as to form a spherical shape, without inner voids. Further experiments confirmed that in addition to the complicated structure, the spheroidal polycrystals of NTO obtained retained a high density, were thermally stable and exhibited low sensitivity to mechanical stimuli.

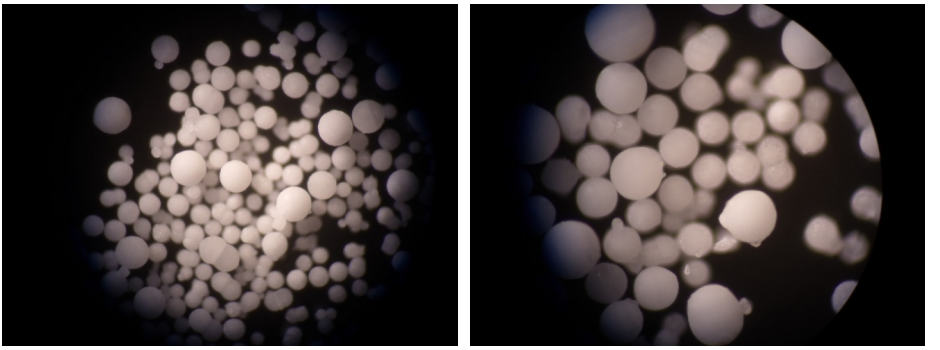

Figure 2. Images of NTO recrystallized from the mixture NTO/H_2O/NMP/PVA (10/80/20/0.008). Scale – about 3400 mL of solution (reactor 4 dm^3). Optical microscope (reflected light).

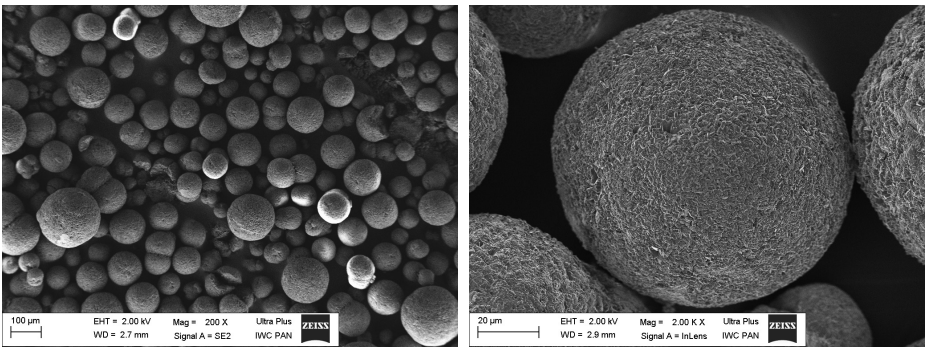

Figure 3. SEM images of the product recrystallized from the mixture NTO/H_2O/NMP/PVA (10/80/20/0.008). Scale – about 3400 mL of solution (reactor 4 dm^3)

3.2 Size distribution and specific area

The size distribution was determined for a sample of NTO-B. To determine the size distribution, photographs from the optical microscopy and a counting computer algorithm were used, and gave an estimate of the grain size distribution. The

number and mass distribution of the tested sample NTO-B is shown in Figure 4.

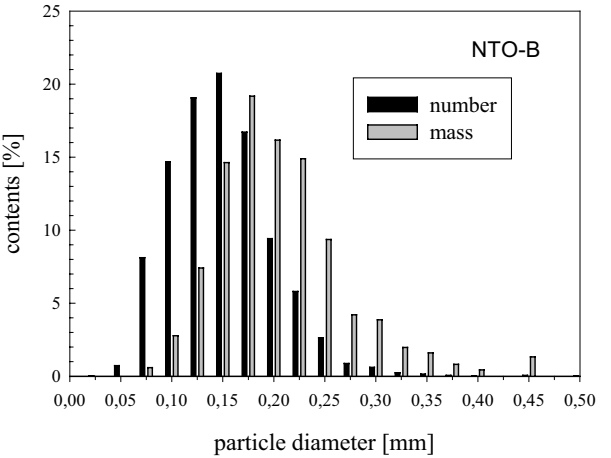

Figure 4. Size distribution of NTO-B particles, crystallized from the mixture NTO/H_2O/NMP/PVA (10/80/20/0.008).

The specific area and porosity of the NTO were obtained using the device ASAP 2020 from the company Micromeritics. Purification of the samples consisted of heating them at a rate of 10 °C/min to 50 °C, and then maintaining this temperature for 6 hours. The samples were then cooled to ambient temperature. Both the processes of heating and cooling were carried out in a vacuum (pressure about 0.7 Pa). After purification, vials containing the test substance were filled with analytical grade nitrogen.

The process for measuring the specific area of all of the samples was identical and was carried out as follows: a vial with a prepared sample was placed in the analytical port, and a measurement of the free space was done by means of helium of purity 6.0. For each sample, 15 measurement in the range of P/P_0 from 0.02 to 0.3 in intervals of 0.02 were obtained (P/P_0 is the ratio of the current pressure P to the pressure at saturation at the temperature of liquid nitrogen P_0: for Kr – P_0 = 0.3 kPa).

NTO-B, and also NTO-S produced in Scandinavia and NTO-W (recrystallised in water) were investigated. The results are shown in Table 5.

The specific areas of the tested powders of NTO is very small. NTO-S has a specific area comparable with that of the NTO recrystallized from water (NTO-W). Although the specific area of NTO-B is nearly an order of magnitude higher, it is still small, taking into consideration the polycrystalline character of these particles.

Table 5. Values of the specific area of the NTO samples

Sample	Specific area BET, [m^2/g]	Correlation factor
NTO-B	0.226	0.99993
NTO-S	0.032	0.99962
NTO-W	0.044	0.99968

3.3 Thermal stability

An investigation of the thermal stability according to PN-V-04011-21 [8] was carried out using a Labsys TG/DTA/DSC analyzer, working in the conjugated system mode TG/DTA (thermogravimetry and differential thermal analysis). The masses of the samples were 3-5 mg. The material was heated at 5 °C/min to 400 °C, in open aluminium oxide crucibles of volume 100 μL, in an atmosphere of nitrogen (flow rate 50 mL/min). An illustrative result of such a measurement, as a plot of the DTA signal and the proportional mass changes against temperature, for a sample of NTO recrystallized in the 4 dm^3 reactor (NTO-B) is shown in Figure 5.

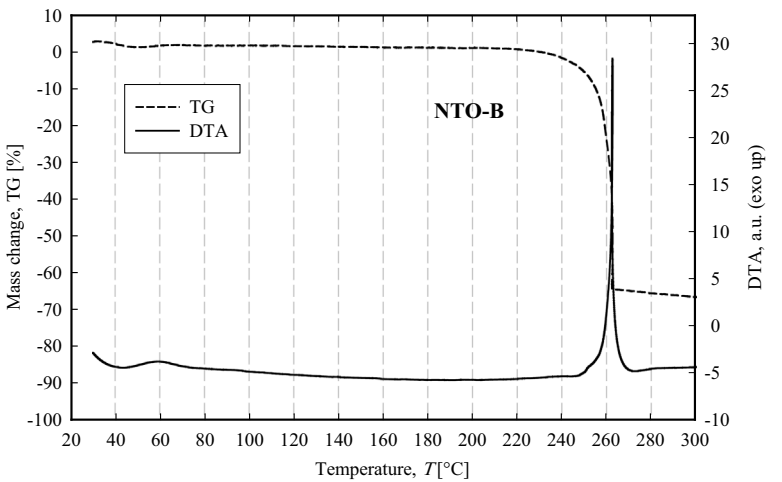

Figure 5. DTA/TG curves for a sample of NTO crystallized from the mixture NTO/H_2O/NMP/PVA (10/80/20/0.008).

In the analysed temperature range, NTO does not undergo any visible changes, apart from decomposition. Decomposition of the sample starts at 259.5 °C, and the maximum rate is achieved at 262.7 °C. The decomposition is accompanied by a loss of about 66% in mass.

3.4 Bulk density and sensitivity

The bulk density of NTO-B was determined by the method described in the standard PN-V-04011-11 [9], using a measuring cylinder of volume 43.34 cm^3. The shaken density was determined after 5-minute vibration of the sample on a sieve shaker. Each measurement was performed three times and the density was calculated as the ratio of an average mass of NTO sample to the measured volume. The loose bulk density of NTO-B was 0.996 g/cm^3, and the shaken one was 1.160 g/cm^3. For comparison, the loose bulk density of NTO-S was 0.960 g/cm^3, and the shaken bulk density was 1.072 g/cm^3.

The friction sensitivity of the NTO samples was determined on a Peters apparatus. Measurements were commenced at a load of 353 N – the highest value used when secondary explosives are investigated. The experiments were performed by reducing the load to a level at which only negative results in 10 trials were observed (without any reaction) [10]. This value was recognized as the minimum friction sensitivity for the tested explosive. The minimum sensitivities of the NTO-B and NTO-S samples were higher than 353 N.

The impact sensitivity of the NTO samples was investigated by means of a massive hammer according to standard PN-EN 13631-4 [11]. The investigation consisted in hitting a sample of the explosive with a hammer dropping from specific heights. The lowest drop height (H) was determined, at which there was at least one explosion in six subsequent trials (*the minimum sensitivity*) and the kinetic energy of the dropping hammer corresponding to this height was calculated. The weight of the hammer was 5 kg, and the mass of the explosive sample was about 0.02 g. The minimum impact sensitivity of the tested NTO samples were as follows: NTO-B – 13 J, NTO-S – 6 J, NTO-W – 7 J.

4 Conclusions

Recrystallized NTO with desirable properties and appropriate particle morphology was obtained as a result of these investigations. Using the proposed system, NTO/H_2O/NMP/PVA, and by saturating the solution as a result of intensive cooling, spheroidal particles with poorly developed surfaces (lack of significant porosity) were obtained. Despite the polycrystalline structure, the granules of NTO gave a relatively high bulk density (more than 1 g/cm^3) due to their shape and size (the diameter of most particles ranged from 100 to 250 μm). The recrystallization product was also characterized by good resistance to mechanical stimuli, such as friction (353 N) and impact (minimum sensitivity equal to 13 J).

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