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*Research paper*

## Regularities of Spheroidization of HMX Extracted from Solid Propellant Disposal Products

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**Abstract:** Nitramines of high quality for manufacturing high-energy composites, such as octogen (HMX) and hexogen, have received much attention by researchers worldwide. Mixed formulations containing fillers in the form of spheroidal dispersed particles of explosives are homogenized at lower energy consumption. They are characterized by stable rheological characteristics, which guarantee the quality of the products obtained on the basis thereof. Methods for obtaining spherical nitramine particles by means of ultrasonic and hydromechanical rounding using commercial HMX were evaluated. It was found that under similar conditions, rounding by the hydromechanical process in a vortex device is more efficient and less energy-consuming than that of the ultrasonic method. It was confirmed that spheroidization of commercial HMX in an aqueous dimethyl sulfoxide (DMSO) medium by hydromechanical rounding occurs due to erosion of crystals of large size (70  $\mu\text{m}$  or more). Based on the experimental results with spheroidization of commercial nitramine, the mass fraction content below 50  $\mu\text{m}$  *versus* time was plotted for hydromechanical rounding. The method of hydromechanical rounding in aqueous DMSO to obtain spheroidized HMX, extracted from solid propellant using DMSO, was found to be the most suitable. Spheroidized modified HMX with specific characteristics (density and crystals of near-spherical shape) was obtained, which could be used for the manufacture of high-energy composites.

**Keywords:** solid propellant, octogen, spheroidization, dimethyl sulfoxide

## 1 Introduction

Powdered products of high-energy fillers (octogen (HMX) and hexogen (RDX)) with a near-spherical shape have been used for the production of high-energy composites (HECs). HMX crystals of the orthorhombic monoclinic  $\beta$  modification can be obtained both in an elongated rod-like form and in an isometric, or a rather spherical, form. The elongated rod-like form reduces the physical and mechanical properties of HMX-based composites. Hence the requirement for obtaining the  $\beta$  modification of HMX with a certain particle size distribution and spheroidal shape.

At present, the Ukraine has no production of nitramines (HMX and RDX), the main components of many high energy compositions. The deficiency of the above nitramines may be solved by applying recovery resources obtained with special technology for the disposal of solid propellant and ammunition [1-3] that are unusable as intended. The solid propellant was a polybutadiene-based polymeric binder filled with an oxidizer (ammonium perchlorate), as well as energetic additives (HMX and aluminium) and process additives. There are a number of methods for the disposal of solid propellant and ammunition while simultaneously recovering the required solid propellant components in order to subsequently use them as a raw material base for producing new HECs. The hydromechanical method is one of the most efficient methods, and consists of hydrodynamic extraction of the solid propellant fragments and subsequent shredding [1]. However, the above mentioned technology only allows technical-grade nitramines to be obtained, which do not meet the quality requirements of the commercial product, in terms of the crystal form and particle size.

According to one source [4], spheroidal RDX particles were obtained by machining crystals of the commercial product in a saturated acetone solution with subsequent etching in ethyl acetate. Transparent spheroidal hexogen particles with smooth surfaces were thus obtained. Nitramine crystals with near-isometric form can be produced by recrystallization from organic solvents [5-9]. Spherical crystals of energetic materials are reported [10-12] to be obtained in various ways:

- by hydromechanical rounding in a specially designed beaker, and
- using ultrasonic treatment of the HMX crystals.

The purpose of the present work was to determine the optimum parameters for obtaining spherical HMX (nitramine) from both commercial nitramine and nitramine extracted from the polymer matrix of a solid propellant, using ultrasonic and hydromechanical rounding methods.

## 2 Experimental

### 2.1 Preparation of spherical HMX

At the initial stage of these studies, the spherical products obtained using ultrasonic rounding (method 1) and hydromechanical rounding (method 2) of commercial nitramine was evaluated. In order to compare these two methods under the same conditions, the spheroidization of commercial nitramine was performed for 1 h in an aqueous medium using both the ultrasonic (method 1) and hydromechanical rounding processes (methods 1 and 2 respectively):

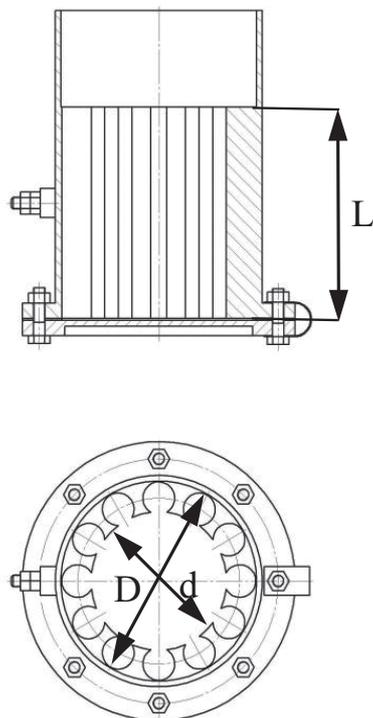
#### *(a) Method 1*

The ultrasonic impact on commercial nitramine was studied using a BANDELIN SONOREX ultrasonic bath. A glass beaker, fitted with a mechanical stirrer, was placed in a BANDELIN SONOREX ultrasonic bath filled with distilled water. Commercial nitramine and water were added to the beaker in a mass ratio of 1:4. Stirring with a mechanical stirrer (0.785 m/s) and ultrasonic treatment (radiation frequency 35 kHz) were applied. The suspension was stirred with simultaneous exposure to ultrasonic radiation for 1 h. Upon completion of the spheroidization process, the nitramine crystals were filtered off, washed on the filter with ethyl alcohol, dried and weighed. The specific features of this method are that a suspension of the commercial nitramine is mixed with a mechanical stirrer in a working liquid in a beaker placed in an ultrasonic bath using water as the working fluid. Mixing is only required to maintain the solid phase in suspension in the working fluid and is not critical for spheroidization. The spherical nitramine obtained was analyzed for its crystal shape using a Leica DMILM microscope. Its fractional composition was determined by wet sieving in ethyl alcohol, and the density was determined by the pycnometer method.

#### *(b) Method 2*

Weighed quantities of commercial nitramine and water in a mass ratio of 1:5 were placed into a beaker (Figure 1) fitted with a propeller-stirrer. Mixing was performed with a hydromechanical stirrer (3.14-4.45 m/s) for 1 h. Upon completion of the spheroidization process the nitramine crystals were filtered off, washed on the filter with ethyl alcohol, dried and weighed. In addition, a modified method 2 was employed which involved hydromechanical spheroidization of the nitramine in aqueous DMSO.

The hydromechanical rounding method was implemented using a specially designed beaker complete with a stirrer, which is shown in Figure 1 (the stirrer is not shown).



**Figure 1.** The beaker for hydromechanical rounding of the nitramine

$L$  is the height of the beaker surface,  $D$  is the outer diameter of the beaker,  $d$  is the inner diameter of the beaker; the ratio of the geometrical parameters of the beaker used in the experiments was as follows:  $D = 50$  mm,  $D/d = 1.4$ ;  $L/D = 1.1$ . The fluid within the beaker was circulated by stirrer rotation, while rotational movement of the liquid occurs in the central channel, which, due to viscous friction, initiates eddy current in the peripheral channels. The spherical nitramine obtained was analyzed for crystal shape using a Leica DMILM microscope. Its fractional composition was determined by wet sieving in ethyl alcohol, and the density was determined by the pycnometer method.

## 2.2 Extraction and spheroidization of HMX

In the second phase of the study, the spheroidization of nitramine extracted from the polymer matrix (PM) of a solid propellant was performed. The nitramine was extracted from the solid propellant polymer matrix using dimethyl sulfoxide (DMSO) [1, 2, 5], followed by separation of the extract from the refined PM crumb and precipitation of the nitramine by adding the extract

solution to water, which does not dissolve the nitramine. The resulting product was filtered off, washed on the filter with ethyl alcohol, dried at room temperature and weighed. After this, the nitramine was crystallized from DMSO by adding water as a precipitating agent. The modified nitramine obtained was filtered off, washed on the filter with ethyl alcohol, dried at room temperature and weighed. Subsequently, the hydromechanical rounding method was applied to one sample of the obtained nitramine. The spherical nitramine obtained was analyzed for its crystal shape using a Leica DMILM microscope. Its fractional composition was determined by wet sieving in ethyl alcohol, and the density was determined by the pycnometer method.

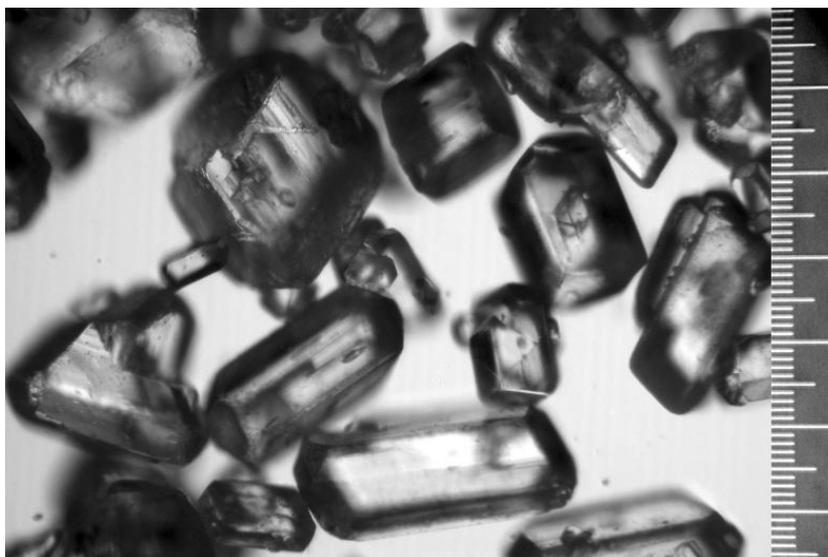
### 3 Results and Discussion

#### 3.1 Physicochemical characteristics of commercial and recrystallized HMX

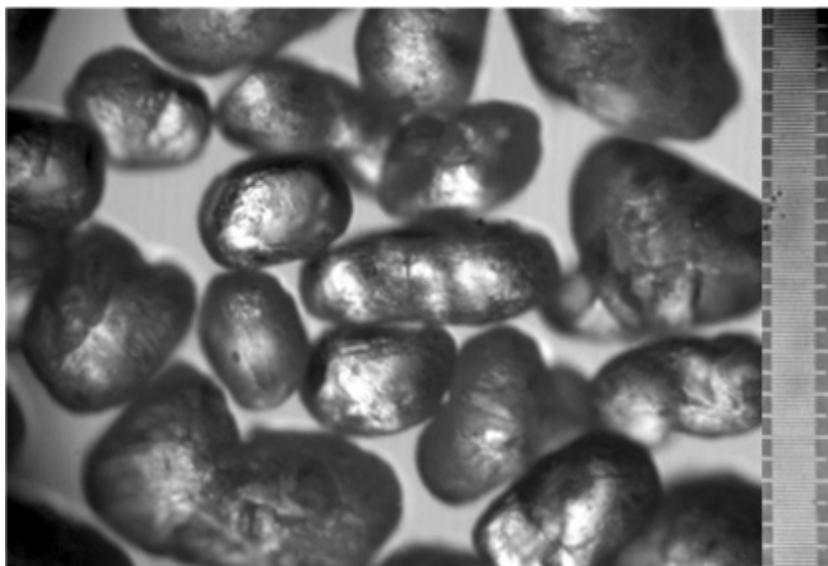
Table 1 shows the comparative physicochemical characteristics of commercial HMX before and after its spheroidization using the ultrasonic and hydromechanical rounding methods. Figures 2 and 3 show images of screened commercial HMX after 1 h of spheroidization using the ultrasonic the hydromechanical rounding method, respectively.

**Table 1.** The comparative physicochemical characteristics of commercial HMX before and after its spheroidization using the ultrasonic and hydromechanical rounding methods

Parameter	HMX sample		
	original commercial	obtained by ultrasonic method	obtained by hydromechanical rounding
Crystal form ( $\beta$ -form)	isometric and rod-like	isometric and rod-like	near-spherical
Crystalline density [g/cm <sup>3</sup> ]	1.90	1.90	1.91
Particle size distribution [ $\mu$ m]	Content [%]		
$\geq 700$	1.2	0.0	0.0
250-700	34.7	33.5	22.0
100-250	43.9	43.2	46.6
<b><math>\leq 100</math>, including:</b>	<b>20.2</b>	<b>23.3</b>	<b>31.2</b>
– 100-50	7.7	9.6	13.7
– $\leq 50$	12.5	13.7	17.5



**Figure 2.** The image of screened commercial nitramine after 1 h of spheroidization using the ultrasonic method (spacing between minimum graduation marks is 10  $\mu\text{m}$ ; working fluid was water)



**Figure 3.** The image of screened commercial nitramine after 1 h of spheroidization using the hydromechanical rounding method (spacing between minimum graduation marks is 10  $\mu\text{m}$ ; working fluid was water)

Based on the data obtained on spheroidization of commercial nitramine under similar conditions (spheroidization time was 1 h, working fluid was water), method 2, hydromechanical rounding, was more effective than method 1 (ultrasonic rounding) where only a slight spheroidization of the largest crystals of the commercial nitramine occurred (Figures 2 and 3). Moreover, in addition to ultrasonic treatment, method 1 also uses mechanical stirring to maintain the crystals in suspension, which consumes more energy than method 2. Therefore, method 1 is hardly practicable for spheroidization of a nitramine under the given conditions.

### 3.2 Spheroidization of commercial nitramine

On the basis of the tests performed, the preliminary conclusions made were that, with the present designs of the beaker and the stirrer, and the ratio of liquid and solid phases, the most intensive process of hydromechanical rounding of the nitramine occurred when the mechanical stirrer speed was 4.45 m/s and higher. Considering that the crystallization and collection of the modified nitramine from a solid propellant polymer matrix takes place in aqueous DMSO, it was decided that the subsequent spheroidization using the hydromechanical rounding method (method 2) should be performed in aqueous DMSO (at a ratio of 1:1), *i.e.* modified method 2.

The circle form-factor using the ImageJ program (the circular form-factor of the spheroidal particle is 1) was determined for comparison between the samples of commercial nitramine after spheroidization in aqueous DMSO (fraction 150-350  $\mu\text{m}$ ) and the same fraction of the screened original commercial nitramine. The minimum, average and maximum values of the circular form-factor of the commercial nitramine before and after spheroidization in aqueous DMSO are shown in Table 2.

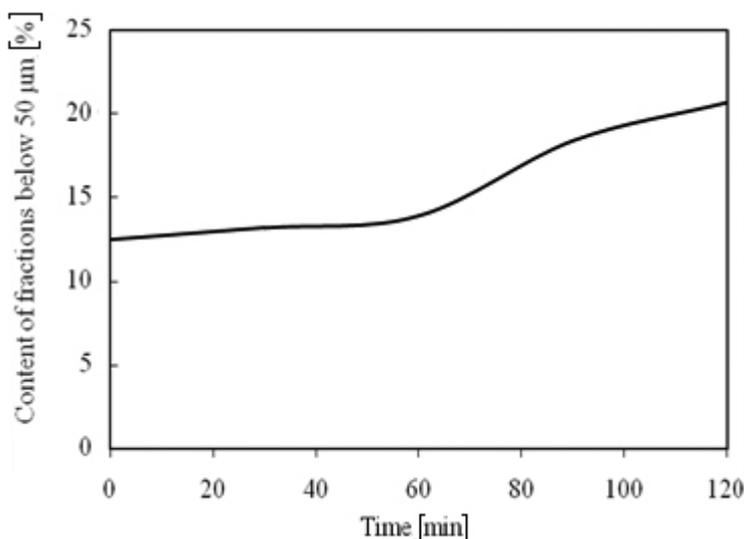
**Table 2.** Minimum, average and maximum values of the circular form-factor of the commercial nitramine before and after spheroidization in aqueous DMSO

Fraction 150-350 $\mu\text{m}$ , commercial nitramine	Number of particles	Circular form-factor		
		minimum	average	maximum
before spheroidization	53	0.430	0.677	0.870
after spheroidization	42	0.665	0.804	0.908

Thus, after spheroidization of commercial nitramine, the average circular form-factor increases by 18.8% and reaches a value of 0.804 when the process was performed using hydromechanical rounding in aqueous DMSO (at a ratio of 1:1), with a duration of 2 h and a mechanical stirrer rotation speed of 4.45 m/s.

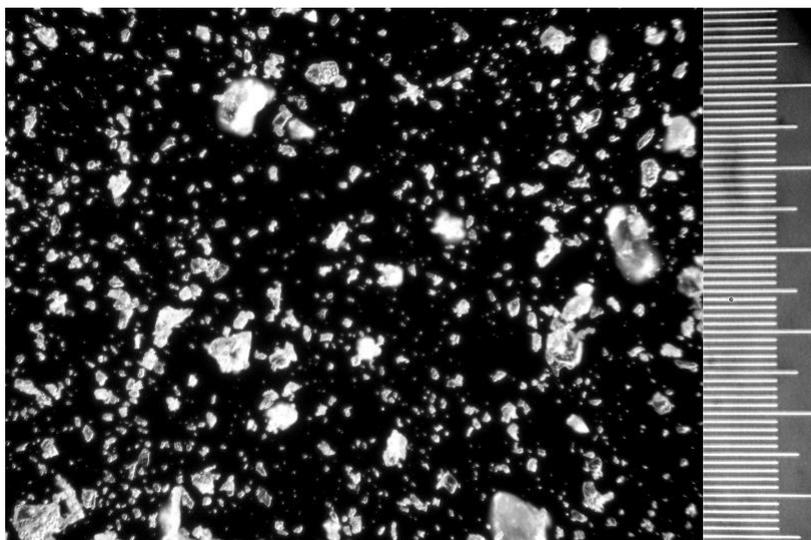
### 3.3 Received and created fractions below 50 $\mu\text{m}$

As previously noted, the fraction below 50  $\mu\text{m}$  was a quantitative measure of the intensity of the hydromechanical rounding process due to mechanical erosion. During the first 60 min 11.2% fraction below 50  $\mu\text{m}$  was observed, and with increased duration of hydromechanical rounding of commercial nitramine of 80-120 min, the volume increment of the fraction below 50  $\mu\text{m}$  increased by 40-65.6 %, respectively. Therefore, if the spheroidization of the nitramine needs to be intensified, then the process should be run for at least 80 min. The fraction below 50  $\mu\text{m}$  was a measure of the intensity of spheroidization when using hydromechanical rounding. Figure 4 shows the fraction below 50  $\mu\text{m}$  *versus* time for hydromechanical rounding of commercial nitramine in aqueous DMSO.

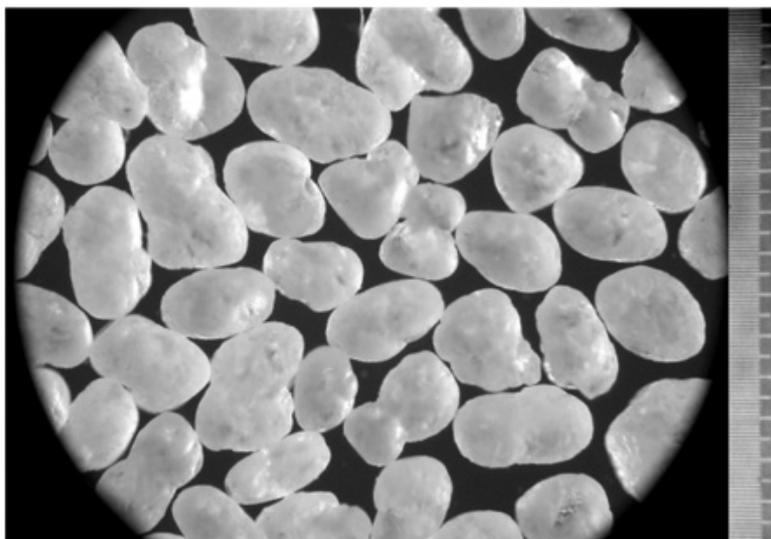


**Figure 4.** The fraction below 50  $\mu\text{m}$  *versus* time for hydromechanical rounding of commercial nitramine in aqueous DMSO

The image of the fraction below 50  $\mu\text{m}$ , shown in Figure 5, proves that the process of hydromechanical rounding of commercial nitramine progressed by mechanical erosion of larger fractions with the formation of fragments. Figure 6 shows the image of screened commercial nitramine after 2 h of spheroidization using the hydromechanical rounding method. As can be seen from Figure 6, the crystals of the commercial nitramine (fraction 150-350  $\mu\text{m}$ ), obtained by the hydromechanical rounding method in aqueous DMSO, have a near-spherical form and may be recommended for the rounding of modified nitramine obtained by extraction from a solid propellant polymer matrix.

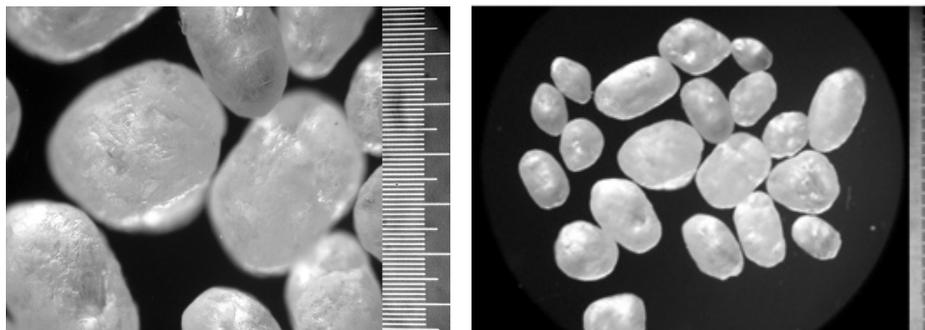


**Figure 5.** The image of crystals of commercial nitramine obtained by hydromechanical rounding (spacing between minimum graduation marks is 10  $\mu\text{m}$ , fraction below 50  $\mu\text{m}$ )



**Figure 6.** The image of screened commercial nitramine after 2 h of spheroidization using the hydromechanical rounding method in aqueous DMSO (spacing between minimum graduation marks is 10  $\mu\text{m}$ ; fraction 150-350  $\mu\text{m}$ )

Figure 7 shows images of the screened modified nitramine obtained by extraction from a solid propellant polymer matrix after 2 h of spheroidization using the hydromechanical rounding method in aqueous DMSO (spacing between minimum graduation marks is 10  $\mu\text{m}$ ; fraction 150-350  $\mu\text{m}$ ).



**Figure 7.** The images of modified nitramine obtained by extraction from a solid propellant polymer matrix after 2 h of spheroidization using the hydromechanical rounding method in aqueous DMSO (spacing between minimum graduation marks is 10  $\mu\text{m}$ ; fraction 150-350  $\mu\text{m}$ )

As a result of spheroidization (Figure 7), the crystals of the modified nitramine extracted from a solid propellant polymer matrix were obtained with specific characteristics (density and crystals of near-spherical shape). The fine fraction of modified nitramine obtained by extraction from the solid propellant polymer matrix (less than 50  $\mu\text{m}$ ), which is formed in the process of spheroidization, can be included, after screening, in active substance compositions for the production of non-electrical initiation systems without additional crystallization, or returned to the crystallization process in aqueous DMSO solution followed by spheroidization.

Thus, the hydromechanical rounding method is useful for improving not only the shape of the nitramine crystals obtained, but also the particle size distribution. In order to estimate the applicability of spheroidized modified nitramine as a component in solid propellants, it would be necessary to continue work on the production and testing of trial batches of high-energy composites using this methodology.

## 4 Conclusions

1. The methods for obtaining spherical nitramine by means of ultrasonic and hydromechanical rounding methods using a commercial product were examined. It was determined that the hydromechanical rounding method in a vortex device is more efficient and less energy-intensive than the ultrasonic method.
2. Based on the experimental results, the circular form-factor of commercial nitramine before and after spheroidization in aqueous DMSO was determined and the fraction below 50  $\mu\text{m}$  versus time was plotted for hydromechanical rounding.
3. Based on the results obtained during hydromechanical rounding of commercial nitramine in aqueous DMSO, experiments were conducted on the spheroidization of nitramine recovered by extraction from a solid propellant polymer matrix. Spheroidized modified HMX with specific characteristics (density and crystals of near-spherical shape) was produced, which could be used for the manufacture of high-energy composites.

## References

- [1] Zabelin, L.V.; Gafiyatulin, R.V.; Ponik, A.N.; Meleshko, V.Yu. *Fundamentals of Industrial Technology for the Disposal of Large Solid Propellant Charges*. (in Russian) Nedra-Biznescentr, Moscow, **2004**, 226.
- [2] Shiman, L.N.; Ustimenko, E.B.; Golinko, V.I.; Sobolev, V.V. *Safety of Processes for the Production and Use of Emulsion Explosives with Components of Utilized Weapons. Monograph*. (in Russian) Lira, Dnipropetrovsk, **2013**, 526.
- [3] Cheltonov, M.M.; Oparin, S.A.; Matrosov, A.S.; Kirichenko, A.L. Extraction of High-energy Components from Products of Recovery of Solid Propellant using Dimethyl Sulfoxide. (in Russian) *Voprosy Khimii i Khimicheskoi Tekhnologii* **2020**, 2: 141-147.
- [4] Zhilin, V.F.; Zbarsky, V.L.; Yudin, N.V. *Insensitive Explosives: Tutorial*. (in Russian) RKhTU named after D.I. Mendeleev, Moscow, **2008**, 160.
- [5] Ahmedshina, V.A.; Bazotov, V.Ja. *Crystallization of Energy-Saturated Compounds from Solutions: A Training Manual*. (in Russian) KNITU, Kazan, **2012**, 124.
- [6] Kim, K.J.; Kim, H.S.; Sim, J.S. Solubilities of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in  $\gamma$ -Butyrolactone + Water, Dimethylsulfoxide + Water, and *N*-Methyl pyrrolidone + Water. *J. Chem. Eng. Data* **2013**, 58(9): 2410-2413.
- [7] Svensson, L.; Nyqvist, J.; Westlin, L. Crystallization of HMX from  $\gamma$ -Butyrolactone. *J. Hazard. Mater.* **1986**, 13: 103-108.
- [8] Meulenbrugge, J.J.; Van der Steen, A.C.; Van der Heijden, A.E. Crystallization of

- Energetic Materials, the Effect on Stability, Sensitivity and Processing Properties. *Proc. Symp. (Int.) on Energetic Materials Technology*, Phoenix, Arizona, USA, **1995**.
- [9] Krober, H.; Teipel, U. Crystallization of Insensitive HMX. *Propellants Explos. Pyrotech.* **2008**, *33*(1): 33-36.
- [10] Teplov, G.V.; Lapina, Yu.T.; Aponyakina, S.N.; Zolotukhina, I.I.; Belyaev, V.N. *Method for Spheroidizing Cyclic Nitramine Crystals*. Patent RU 2674970, **2018**.
- [11] Lavertu, R.R.; Godbout, A. *Process for Spheroidization of RDX Crystals*. Patent US 4065529, **1977**.
- [12] Lasota, J.; Chylek, Z.; Trzciński, W.A. Methods for Preparing Spheroidal Particles of 3-Nitro-1,2,4-triazol-5-one (NTO). *Cent. Eur. J. Energ. Mater.* **2015**, *12*(4): 769-783.

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