Preparation and study of some characteristics of spherical gunpowder based on nitrocellulose and DINA

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ABSTRACT

This article presents the results of research on the selection of components, recipes, method and technological regime for the production of spherical gunpowders based on nitrocellulose (grade Pi-BA) and ethylene glycol-N-nitramine dinitrate (DINA), as well as the results of studying some of their characteristics. In these gunpowders, DINA plays the role of an energetic plasticizer with a content in the range of 8.2 - 39.4% by mass. The selected technological regime allows to obtain spherical gunpowders with high yield on a laboratory scale (over 95% for particle sizes less than 1 mm and over 90% for particle sizes in the range of 0.2 - 0.8 mm). The obtained samples of spherical gunpowders have a density in the range of 1.60 - 1.62 g/cm^3 and a bulk density in the range of 0.98 - 1.02 g/cm^3, which well meets the requirements commonly applied to these criteria for military-use spherical gunpowders. The introduction of DINA has slight effect on the auto-ignition temperature of the obtained samples. Theoretical calculations of some energetic characteristics using the REALWIN program also show the potential of using DINA to replace nitroglycerin as a second energetic component in the development of high-energy spherical gunpowder.

Keywords: Spherical gunpowder; Nitrocellulose; Ethylene glycol-N-nitramine dinitrate; DINA; Nitroglycerin; Energetic plasticizer.

1. INTRODUCTION

In recent years, spherical gunpowders (SPGP) have displaced several brands of pyroxylin and ballistite gunpowders in various types of barrel weapon systems, such as military, hunting, and sporting firearms, as well as mortars and small-caliber artillery. This is due to the many advantages of SPGP over these classic nitrocellulose-based gunpowders, both in terms of technological characteristics and specific physico-chemical and ballistic properties [1, 2]. Currently, the most commonly used for military purposes are double-base SPGP based on nitrocellulose (NC) and nitroglycerin (NGC), in which NGC plays the role of an energetic plasticizer. However, with an increase in NGC content, the combustion temperature of gunpowder rapidly increases, leading to an increase in the erosion effect of gunpowder gases on the barrel bore. In addition, NGC has moderate thermodynamic compatibility with NC and in practice is often used for plasticizing NC with a moderate nitrogen content and low viscosity (colloxylin). An increase in the NGC content negatively affects the physical and chemical stability of gunpowder. NGC also has a high sensitivity to mechanical impacts, which causes an explosion hazard in the manufacture of composites based on it. All these problems limit the possibility of obtaining high-energy SPGP based on NC and NGC. Therefore, one of the actual tasks is to study the possibility of using new energetic plasticizers to replace NGC in the production of various types of gunpowders, including SPGP. Until now, many energetic plasticizers for NC have been synthesized and studied, but among them only DINA is produced on an industrial scale for adding to the composition of some brands of tubular ballistite powder and solid rocket propellants [3, 4]. In addition, there is little information about the application of DINA in SPGP. This problem is the focus of our work.

2. MATERIALS AND METHODS

2.1. Materials

The object of the study is samples of SPGP based on NC and DINA, the choice of their initial components (NC grade), recipes, method and technological regime of production, as well as some important properties. The initial components were NC grades Pi-BA (from factory Z) and DINA (from Institute of Propellant and Explosive), the main technical characteristics of which are shown in tables 1 and 2. Diphenylamine (DPA) was added as a chemical resistance stabilizer. Sodium sulfate (Na_2SO_4), gum arabic, and ethyl acetate (ETA) are used as technological auxiliary substances in the process of manufacturing SPGP samples.

Table 1. *Technical characteristics of NC grade Pi-BA.*

	Specifications	Value
1	Appearance	White powder
2	Nitrogen content, %	13.2
3	Solubility in alcohol-ether solvent, %	26.8
4	Solubility in ethyl alcohol, %	2.2
5	Viscosity, ^{o}E	6.9
6	Mass fraction of ash, %	0.12
7	Alkalinity, %	0.03
8	Chemical stability at 132°C, ml NO/g	1.97
9	Moisture, %	33

Table 2. *Technical characteristics of DINA.*

	Specifications	Value
1	Appearance	White crystal
2	Melting point, ^{o}C	51.0
3	Chemical stability (Abel test at 82^{o}C), min.	35
4	Alkalinity, %	0.15

2.2. Methods

Samples of SPGP based on NC and DINA were prepared by an emulsion method on a laboratory scale using a special device consisting of the following parts: an IKA stirring device with a blade stirrer and the ability to adjust the rotation speed in the range of 50 - 2000 rpm, a thermostatic bath, a 500 ml three-neck flask, and a setup for distilling ETA. The main stages and the corresponding technological regime of SPGP preparation are described in section 3.1. The obtained samples were washed several times with warm and cold water, then sieved through sieves with mesh sizes of 1.0 mm, 0.8 mm, and 0.2 mm.

The shape and surface morphology of SPGP particles are studied using a Nikon-YS100 optical microscope. The density and bulk density of SPGP samples are determined by methods according to TCVN/QS 1995:2008 [5].

The auto-ignition temperature of SPGP samples is determined using a DT-400 complex setup with a temperature increase rate of 20 °C/min.

The heat of combustion, combustion temperature and gunpowder force are calculated theoretically based on the principle of maximum entropy using the REALWIN program.

3. RESULTS AND DISCUSSION

3.1. Selection of components, composition, method, and technological regime for the production of SPGP based on NC and DINA

The structure and properties of SPGP are largely determined by the nature of the initial components, composition and manufacturing method, as well as the technological regime used. DINA is not only a good plasticizer for NC with different nitrogen contents but also a powerful explosive comparable to hexogen [3, 4]. Moreover, compared to NGC, DINA plasticizes NC with high nitrogen content much better [3]. This opens up the possibility of obtaining high-energy SPGP, which includes NC with high nitrogen content as a polymer and energetic component, and DINA as an energetic plasticizer. In this work, NC of the Pi-BA grade and DINA with technical characteristics presented in tables 1 and 2 were selected, and the recipes of the prepared samples of SPGP based on them are presented in table 3. For all recipes, the content of DPA is fixed at 1.5% by mass.

Table 3. *Recipes of prepared samples of SPGP in this work.*

№	Recipe		
	NC, % mass.	**DINA, %mass.**	**DPA, %mass.**
1	98,5	0	1,5
2	90,3	8,2	1,5
3	83,7	14,8	1,5
4	73,9	24,6	1,5
5	59,1	39,4	1,5

From a technological point of view, DINA is highly soluble in ETA and poorly soluble in water [3, 6], which makes it possible to produce SPGP based on NC and DINA using the emulsion method commonly used in industrial and laboratory conditions, where water is used as the dispersion medium and ETA as the solvent for making gunpowder lacquer. Therefore, this method was chosen in this work to obtain SPGP. The technological process consists of the following main stages: 1 - Dissolving NC and DINA in ETA (preparation of gunpowder lacquer); 2 - Dispersing the gunpowder lacquer in water and stabilizing the formed emulsion; 3 - Dehydration (removal of water inside the gunpowder lacquer droplets); 4 - Removal of the solvent (ETA); 5 - Washing and sieving the obtained SPGP particles. It is clear that the process of making SPGP is complex and multi-stage, with many factors affecting the structure and properties of the finished gunpowder. This, on the one hand, provides a wide opportunity to regulate the characteristics of SPGP, but on the other hand, complicates the search for the optimal technological regime. In this work, the choice of the applied regime is based on the study of available information on the technology of obtaining double-base SPGP based on NC and NGC, which is presented in some scientific and technical literature [1, 2, 7], in patents [8, 9], as well as in the technological regulations [10]. This is quite reasonable due to the lack of open information on SPGP based on NC and DINA, as well as the similarity of these SPGP types in terms of processing plasticized NC. Table 4 presents the main parameters of the technological regime for the production of SPGP within the framework of this work. This regime allowed obtaining spherical gunpowder with a high yield: over 95% for particles smaller than 1 mm and over 90% for particles in the range of (0.2 - 0.8) mm. This product yield is well comparable to the yield in the production of SPGP based on NC and NGC on both laboratory and industrial scales.

***Table 4**. Main parameters of the technological regime for the production of SPGP samples*

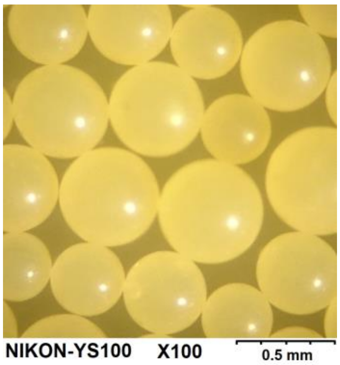
Stage	Technological regime	Value
Dissolving NC and DINA in ETA (preparation of gunpowder lacquer)	ETA module (MD_{ETA})	3,2
	Gradually increasing the temperature from room temperature to 68 °C at a rate of 1 °C/min and regulating the stirrer rotation speed within the range of (300 - 400) rpm.	
Dispersing the gunpowder lacquer in water (Formation of gunpowder lacquer emulsion)	Water module (MD_{water})	7
	Temperature, °C	67 - 68
	Stirrer rotation speed, rpm	600
Stabilizing the formed emulsion	Temperature, °C	67 - 68
	Amount of gum arabica introduced into the system (% by mass relative to the water content in the system)	4
Preliminary stage of solvent removal	Temperature, °C	72 - 74
	Amount of ETA removed (ratio to initial amount)	1/3
Dehydration	Amount of Na_2SO_4 introduced into the system (% by mass relative to the water content in the system)	6
	Temperature, °C	71 - 73
	Duration, min	45
Main stage of solvent (ETA) removal, consisting of 3 steps:	1- In the temperature range of 73 °C to 76 °C: removal of 1/3 of the initial amount of ETA	
	2 - In the temperature range of 77 °C to 83 °C: removal of 1/4 of the initial amount of ETA	
	3- In the temperature range of 84 °C to 98 °C: removal of the remaining ETA	
Washing and sieving	Washing with water to clean the obtained SPGP from technological impurities, as well as sieving to determine the yield by particle size.	
Remark: In the case of producing single-base SPGP (sample 1), dehydration was carried out immediately after stabilizing the formed gunpowder lacquer emulsion, i.e., without the preliminary stage of solvent removal. During the first stage of the main solvent removal process in the range of 73 °C to 76 °C, an amount of ETA equal to 2/3 of the initial amount was distilled off.		

3.2. Physical and morphological characteristics of the obtained SPGP samples

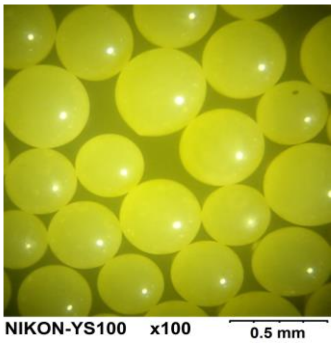
In this work, we studied some important physical and structural characteristics of the obtained SPGP samples, such as shape, color, surface character of particles, as well as their density and bulk density. The study results are presented in figure 1 and table 5.

As can be seen, the spherical shape is preferred for the vast majority of the obtained particles (figures 1-a, 1-b, 1-c, 1-d, 1-e), except for large particles in the range of 0.8 - 1 mm (figure 1-f). This indicates that the selected technological regime provides a good balance of tensile and compressive forces acting on the particles of the gunpowder lacquer, as well as the optimal character of their deformation during the production process of SPGP. The larger the particle size, the more difficult it is to form and maintain their spherical shape.

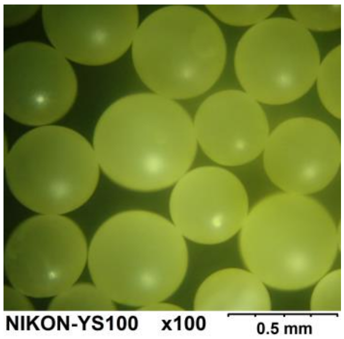
In this work, it was also observed that the introduction of DINA into the SPGP composition leads to a change in their color: from yellowish (in single-base SPGP – sample 1) to green (samples 2, 3, 4, 5). Moreover, the higher the DINA content, the deeper the green color of the obtained SPGP samples. The introduction of DINA also leads to an increase in the glossiness and transparency of the SPGP particles, which is associated with the effectiveness of DINA's plasticizing action on NC.



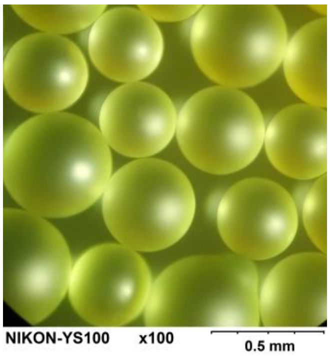
(a) Sample 1



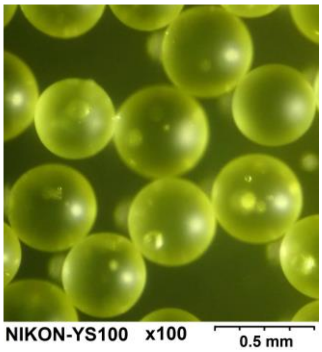
(b) Sample 2



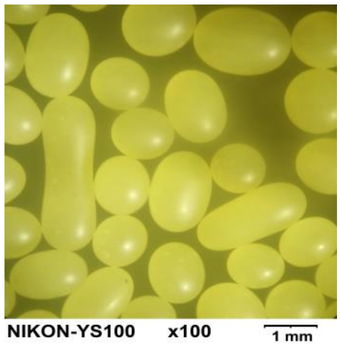
(c) Sample 3



(d) Sample 4



(e) Sample 5



(f) Fraction with particle size of 0.8 - 1.0 mm

Figure 1. *Photographs of the obtained SPGP samples taken using an optical microscope.*

The density of gunpowder has a significant influence on several of its important properties, such as physical-mechanical strength, burning rate, ballistic characteristics, and physico-chemical stability. As is known, the density of SPGP largely depends on the density and content of its components, as well as the morphological structure of the particles. In turn, the particle structure of SPGP is greatly influenced by the technological regime of manufacture (especially the dehydration and ETA removal regimes). As seen in table 5, all samples of the obtained SPGP have high density (within the range of 1.58 - 1.62 g/cm^3), indicating the correct choice of the technological regime in this work. All samples containing DINA (sample 2 – 5) have a higher density compared to the single-base SPGP sample (sample 1). Probably, this is due to DINA's ability to plasticize NC, which facilitates the compaction of structures within the SPGP particles during the manufacturing process. It is also necessary to consider the fact that DINA has a higher density than NC. However, in samples 2 - 5, obtained under a similar technological regime, only a slight increase in density was observed with an increase in DINA content from 8.2% to 39.4%.

Table 5. *Density and bulk density of obtained SPGP samples.*

SPGP sample	Density, g/cm^3	Bulk density, g/cm^3
Sample 1 (0% DINA)	1.58	0.98
Sample 2 (8.2% DINA)	1.60	0.98
Sample 3 (14.8% DINA)	1.61	1.02
Sample 4 (24.6% DINA)	1.62	1.00
Sample 5 (39.4% DINA)	1.62	0.99

As seen in table 5, all obtained samples of SPGP have a high bulk density (within the range of 0.98 - 1.02 g/cm^3). However, with an increase in DINA content, this parameter changes irregularly. As is known, the bulk density of SPGP depends on many factors, not only on the density of the gunpowder itself but also on the surface texture of the particles, their shape, and the character of their size distribution. The relationship between these factors determines the character of the change in the bulk density of the obtained SPGP samples.

3.3. Energetic characteristics of the obtained SPGP samples and their thermal sensitivity

In this work, theoretical calculations of some energetic characteristics of SPGP samples with selected recipes were carried out using the REALWIN program, as well as comparative samples in which NGC was used instead of DINA. The calculation results are presented in table 6.

Table 6. *Energetic characteristics of SPGP samples containing DINA according to selected formulations, and comparative SPGP samples containing NGC.*

Sample	Recipe			Heat of combustion, kJ/kg	Combustion temperature, K	Gunpowder force, kJ/kg
	NC	DINA	DPA			
1	98,5	0	1,5	4697,1	3197	1055,5
2	90,3	8,2	1,5	4754,5	3236	1074,0
3	83,7	14,8	1,5	4800,1	3267	1088,7
4	73,9	24,6	1,5	4866,8	3313	1110,6
5	59,1	39,4	1,5	4965,9	3380	1143,8
	NC	**NGC**	**DPA**			
S2	90,3	8,2	1,5	4915,3	3345	1089,0
S3	83,7	14,8	1,5	5091,1	3465	1114,1
S4	73,9	24,6	1,5	5345,8	3639	1148,2
S5	59,1	39,4	1,5	5716,3	3891	1192,1

As seen in table 6, the introduction of DINA or NGC leads to an increase in the energetic characteristics of SPGP. Interestingly, compared to samples containing NGC (samples S2, S3, S4, S5), the samples in which DINA is used instead of NGC (samples 2, 3, 4, 5) have similar gunpowder force (only slightly lower), but significantly lower heat of combustion and combustion temperature. In other words, using DINA as an energetic plasticizer instead of NGC allows maintaining the gunpowder force at the same level while significantly reducing the heat of combustion and combustion temperature. This phenomenon can be explained by the fact that the DINA-containing SPGP samples burn with the formation of lighter gunpowder gases compared to the NGC-containing samples. A significant reduction in combustion temperature while maintaining the required gunpowder force is a beneficial effect, that allows reducing thermal-erosion action of gunpowder gases on the barrel bore, which plays a key role in the development of high-energy SPGP for weapon systems with rifled barrels. All of the above indicates the potential of using DINA as a second energetic component to replace NGC.

Table 7. *Auto-ignition temperature obtained SPGP samples.*

SPGP Sample	Auto-ignition temperature, °C
Sample 1 (0% DINA)	185.0
Sample 2 (8.2% DINA)	184.9
Sample 3 (14.8% DINA)	184.9
Sample 4 (24.6% DINA)	184.1
Sample 5 (39.4% DINA)	182.2

In this work, the thermal sensitivity of the obtained SPGP samples was evaluated by determining their auto-ignition temperature. The measurement results are presented in table 7, which shows that the introduction of DINA has slight effect on this parameter. The introduction of 39.4% DINA leads to a decrease in the auto-ignition temperature of SPGP by only 1.5% (from 185 °C to 182.2 °C).

4. CONCLUSIONS

In this work, based on the study of available literature data, the selection of initial components, recipes, as well as the method and technological regime for the production of SPGP based on NC and DINA, in which the DINA content varies in the range of 8.2 - 39.4% by mass, was carried out. The selected technological regime allows to obtain SPGP with a high yield on a laboratory scale (more than 95% for particle sizes less than 1 mm and more than 90% for particle sizes in the range of 0.2 - 0.8 mm) and with the spherical shape being the preferred particle form. The obtained SPGP samples have a density in the range of 1.60 - 1.62 g/cm^3 and a bulk density in the range of 0.98 - 1.02 g/cm^3, which well meets the requirements for these criteria for military-grade SPGP. The introduction of DINA has slight effect on the auto-ignition temperature of SPGP but significantly improves its energetic characteristics. Compared to NGC, the prospects of DINA lie in the fact that its use makes it possible to obtain a high-energy SPGP with a slight increase in combustion temperature and, as a result, to reduce the erosive effect of gunpowder gases on the barrel bore.

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TÓM TẮT

Chế tạo và khảo sát một số đặc trưng của thuốc phóng cầu trên cơ sở nitroxenlulo và DINA

Bài báo trình bày kết quả nghiên cứu lựa chọn thành phần, phương pháp, chế độ công nghệ chế tạo và khảo sát một số đặc trưng của các mẫu thuốc phóng cầu trên cơ sở nitroxenlulo (mác Pi-BA) và etylen glycol-N-nitramin dinitrat (DINA), trong đó, DINA đóng vai trò chất hóa dẻo năng lượng với hàm lượng thay đổi trong khoảng 8,2 - 39,4%. Chế độ công nghệ áp dụng trong nghiên cứu này cho phép thu được thuốc phóng cầu với hiệu suất cao ở quy mô phòng thí nghiệm (trên 95% cho dải cỡ hạt dưới 1 mm và trên 90% cho dải cỡ hạt trong khoảng 0,2 - 0,8 mm). Các mẫu thuốc phóng cầu chế tạo được có mật độ trong khoảng 1,60 - 1,62 g/cm^3 và mật độ đong trong khoảng 0,98 - 1,02 g/cm^3, đảm bảo tốt yêu cầu thường áp dụng đối với các chỉ tiêu này của các loại thuốc phóng cầu quân dụng. Thêm DINA vào thành phần chỉ ảnh hưởng nhẹ đến nhiệt độ bùng cháy của các mẫu thuốc phóng cầu. Tính toán lý thuyết một số đặc trưng năng lượng bằng phần mềm REALWIN cũng cho thấy triển vọng sử dụng DINA để thay thế nitroglyxerin làm cấu tử năng lượng thứ hai khi phát triển các loại thuốc phóng cầu năng lượng cao.

Từ khoá: Thuốc phóng cầu; Nitroxenlulo; Etylen glycol-N-nitramin dinitrat; DINA; Nitroglyxerin; Chất hóa dẻo năng lượng.