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Morphological Features of the Nanoporous Structure in the Ammonium Nitrate Granules at the Final Drying Stage in Multistage Devices

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The article investigates the morphological features of the nanoporous structure in the ammonium nitrate granules obtained by the humidification method, followed by heat treatment, including final drying. The necessity to improve the basic scheme is substantiated using the “humidification-heat treatment” scheme in vortex granulators towards obtaining a developed network of nanopores. A comparative analysis regarding the morphology of the initial granules in ordinary ammonium nitrate, ammonium nitrate after heat treatment, ammonium nitrate after the “humidification-heat treatment” stages in a vortex granulator and ammonium nitrate after the “humidification-heat treatment-final drying” stages in a multistage shelf device is carried out. The obtained data form the basis to create an engineering calculation method for multistage dryers with vertical sectioning of the workspace included to units for producing 3D nanostructured layers on the surface and inside the ammonium nitrate granules.

Keywords: 3D nanostructured porous layer, Multistage shelf dryer, Morphology.

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1. INTRODUCTION

The most cost-effective way is to use ammonium nitrate granules as a component of industrial explosives [1, 2]. An ordinary ammonium nitrate (mineral fertilizer) and ammonium nitrate with increased porosity (porous ammonium nitrate – PAN) [3] can be used to prepare a mixture of ammonium nitrate with diesel distillate (ANFO) [4].

The ordinary ammonium nitrate can be prepared to be used as a component of an industrial explosive using the following operations:

– the crushing of granules;

– removal of the shell (powder from various inert substances), which reduces the caking of the granules.

All these operations are aimed at increasing the volume of gaps and cracks after mechanical destruction of the original granules. In this case, despite the high absorptivity, the retentivity does not fit the minimum standard indicator. Therefore, ANFO based on the ordinary ammonium nitrate should be prepared directly at the blasting places and stored for a short time (due to the intensive draining of diesel distillate).

It is more successfully to use PAN in the technology for obtaining ANFO. Granules with a developed porous structure can reliably hold diesel distillate during transportation to the place of blasting and storing the industrial explosives.

Researchers face the task to investigate new methods for producing PAN with a developed nanoporous structure, which will provide the necessary standard indicators of granules for their successful use as ANFO components.

2. OBJECTIVATION OF THE POROUS AMMONIUM NITRATE PRODUCTION METHOD

PAN can be obtained directly during the formation of granules (product manufacturing) or by physical and thermal effects on the already formed ammonium nitrate granules to change its structure and create the so-called “mechanical” pores [5]. The first group of methods requires various additives to intensify the pore formation process. The necessity to introduce these additives is the reason to increase the cost of the finished product. The second group of methods allows to obtain a developed porous structure without the pore-forming additives. A brief description of the PAN obtaining methods within the presented classification is shown in Table 1. The first six methods to produce PAN are given according to [6]. The Chemical Engineering Department of Sumy State University proposes the seventh method [7].

The article proposes a more cost-effective group of methods of physical and thermal effects on ordinary ammonium nitrate granules.

Method 6 from Table 1 was used as a basic variant. However, the research part shows that as a result of heat treatment, only “mechanical” pores are formed in the micrometer range that do not reliably retain diesel distillate during transportation and long-term storage. Therefore, the authors [6] propose to produce PAN industrial explosives directly at the blasting place, which is not always advisable.

An improved scheme for producing PAN (method 7 in Table 1) enables to obtain pores in the nanometer range, which positively affects the retentivity of the granules. However, this method provides destruction of the ordinary ammonium nitrate granules due to the high value of the final humidity.

PAN granules with excess final humidity are characterized by the following properties [8]:

– insufficiently developed nanoporous structure;

– many "mechanical" pores that have a straight configuration;

– weak core of the granule (as a result of a significant number of "mechanical" pores);

– many rectilinear macropores in the nanoporous structure of the granule.

Table 1 – PAN production methods [6, 7]

No	A method to obtain granules	The structure of granules
1	Prilling of a "dry" melt and cooling of granules in a monotonic mode	Spherical bodies with a smooth surface and a shrink shell in a dense crystalline array
2	Prilling of a "dry" melt, foaming of droplets with poroform and cooling in a monotonic mode	Spherical bodies with a smooth surface and closed gas inclusions in a dense crystalline array
3	Prilling of a "wet" melt and cooling with drying in a staged mode	Rounded bodies with a rough surface and cavity in a loose crystalline array
4	The formation of granules by spraying melt on the seeding agent (granulation)	Rounded bodies with a rough surface and homogeneous granular structure in the array
5	The formation of granules with additives of iron salts, followed by surface-active reagents in a drum	Rounded bodies with such formations as flakes on the surface and a granular structure of the body
6	Heat treatment – "porization" of finished granules according to paragraphs 1, 2, 5 with phase transitions	It fits the original ammonium nitrate, but is saturated with cracks on the surface and inside the granule
7	Humidification followed by heat treatment (drying) with phase transitions	The core of the granule fits the initial ammonium nitrate, the surface and nearsurface layers of the granule form a combination of nanopores of various sizes, depths and configurations

Table 2 – Modification of the ammonium nitrate [9]

Modification	Temperature variation range for various modifications, °C	Type of symmetry	Change in volume, %
I	169.6-125.2	Cubic	– 2.13
II	125.2-84.2	Tetragonal	– 1.33
III	84.2-32.3	Rhombic monoclinic	+ 0.8
IV	32.3-(– 17)	Rhombic bipyramidal	– 3.3
V	(– 17)-(– 50)	Tetragonal	+ 1.65

It is explained by the high intensity of moisture removal when the drying velocity increases (heating of the material and the first drying period in accordance with accepted terminology).

Here one should consider the regarding ammonium nitrate modifications (Table 2). Solid ammonium nitrate in the temperature range from – 17 to 169.6 °C has five crystalline modifications, each of which has a strictly defined temperature range [9].

In terms of the production and storage conditions, the polymorphic transformations of ammonium nitrate can adversely affect its physical and mechanical properties. The transition from one modification to another (polymorphic transition) is accompanied by a change in the crystal structure and volume of the crystal grid. Transitions from one modification to another are reversible and proceed with breakage of the structure, which negatively affects the strength of the granule with an increase in the transitions' number. The preservation of the initial flowability of ammonium nitrate granules under long-term storage conditions significantly depends on the frequency of $\mathrm{III} \leftrightarrow \mathrm{IV}$ conversion, proceeding at 32.3 °C with a decrease in the specific volume by 3.7 %. The strongest granules will be produced if the modification transformations of ammonium nitrate proceed with minimal volume and structural changes, i.e. without significant deformation of its crystals. This condition will be observed when the sequentially flowing chain of transformations $\mathrm{II} \rightarrow \mathrm{III} \rightarrow \mathrm{IV}$ is replaced with the transformation $\mathrm{II} \rightarrow \mathrm{IV}$. The transformation $\mathrm{II} \rightarrow \mathrm{IV}$ is stabilized with a decrease in the residual moisture content in PAN.

The balanced temperatures of the modification transformations of ammonium nitrate can be changed by increasing the amount of moisture in the granule, which will affect the polymorphic transitions kinetics. According to [9], so far as the water content increases from 0.5 to 3.4 %, the $\mathrm{IV} \rightarrow \mathrm{III}$ transition temperature decreases from 48 to 37 °C. With an increase in water content from 0.03 to 0.5 %, the $\mathrm{I} \rightarrow \mathrm{III}$ transition temperature decreases from 125 to 120 °C. This fact justifies the need to carry out not only the heat treatment process of the granules, but also their preliminary humidification. However, moisture does not change the nature of the modification transitions.

The final value of the absorptivity can be increased due to more intensive drying under falling velocity. It is possible to carry out this process with prolonged drying in a drying agent's vortex stream only with a decrease in the strength index of the granules [8].

One should also note that ammonium nitrate is highly hygroscopic, that is one of the reasons for its caking. In the open air, it quickly becomes wet, then spreads out and loses its crystalline form. Therefore, the final drying stage, in addition to the possibility to obtain a developed nanoporous structure, can increase the storage period of PAN granules keeping their normative indicators.

An additional drying stage under the falling velocity mode in the active (but less turbulized) hydrodynamic mode will allow us to achieve the necessary changes in the nanoporous structure of the granules.

Thus, the finally improved scheme for PAN production with the final drying stage is illustrated in Fig. 1. This scheme was first proposed in [10], where it was the first time the granule samples after final drying were studied.

The aim of the article is to assess the effect of the drying stage in PAN granules on their nanoporous structure based on the results of studying the PAN morphological features.

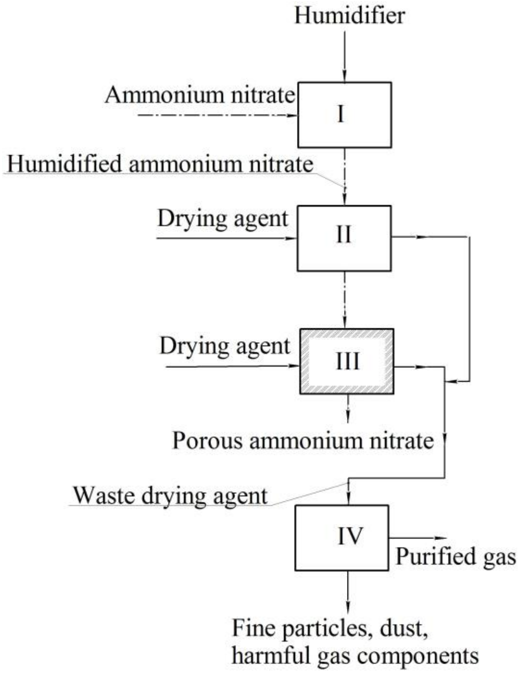


Fig. 1 – Scheme of PAN production: 1 – humidification of ordinary ammonium nitrate granules; 2 – granulation-drying; 3 – final drying; 4 – purification of exhaust gases

3. DESCRIPTION OF OBJECT AND METHODS OF RESEARCH

A scheme of an experimental unit for studying the drying process of granules in gravitational shelf dryers is presented in [10]. The experimental unit provides three stages of final drying.

The morphology of the NH_4NO_3 granules surface was studied by scanning electron microscopy using the device FEI Nova NanoSEM 650.

Other devices and equipment:

– thermocouple TC10-C, recording potentiometer KSP-3 – to measure the temperature in the heater;

– thermal imager Fluke Ti25, pyrometer Victor 305B – to measure the temperature in the granulator's workspace;

– multimeter DT-838 – to measure humidity of granules and air.

FTIR spectra were obtained by ATR technique using Nicolet iS50 FT-IR spectrometer (by Thermo Scientific) in the range from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} (no. of scans: 32) (sensitivity for finding peaks was 95 %).

Four samples were prepared for research:

– the original granules of ordinary ammonium nitrate;

– granules of ammonium nitrate after heat treatment;

– granules of ammonium nitrate after the "humidification-heat treatment" stages in a vortex granulator;

– granules of ammonium nitrate after the "humidification-heat treatment" stages in a vortex granulator and the "final drying" stage in a multistage shelf device.

A thin film of an electrically conductive substance (carbon) was sprayed onto the surface of the samples to carry out the research.

4. RESULTS AND DISCUSSION

The initial granule structure of ordinary ammonium nitrate is shown in Fig. 2.

A complete surface without a developed network of pores is peculiar for the sample. The surface structure is characterized by "mechanical" pores in the micrometer range. These pores arose directly upon production of the granules due to temperature stresses and mechanical effect on the packed granules during their transportation from the production place. Such granules can be used as an ANFO component without prior preparation. The absorptivity of the sample is quite high due to the large "mechanical" pores. The retentivity of the sample does not meet the standard indicator. The reason is that the diesel distillate easily leaves the granule (it flows from faults on its surface influenced by the gravity).

A sample of ordinary ammonium nitrate granules after heat treatment ("porization") is shown in Fig. 3.

The formation of new "mechanical" pores in the micrometer range, appeared due to temperature stresses in the granule after an additional heat treatment cycle, is peculiar for the sample. Such granules have a high absorptivity. As for the retentivity in relation to the diesel distillate, it is sufficient to obtain an effective ANFO without its subsequent long-term storage and transportation.

The PAN granule sample obtained by the humidification method in a vortex granulator with subsequent heat treatment in the workspace of the same device is shown in Fig. 4. In addition to "mechanical" pores (their number is not greatly increased in comparison with the initial ordinary ammonium nitrate sample), "modifica-

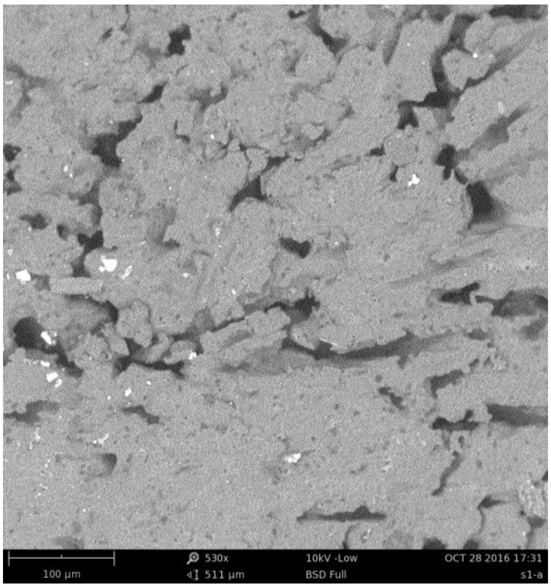


Fig. 2 – The initial granule structure of ordinary ammonium nitrate

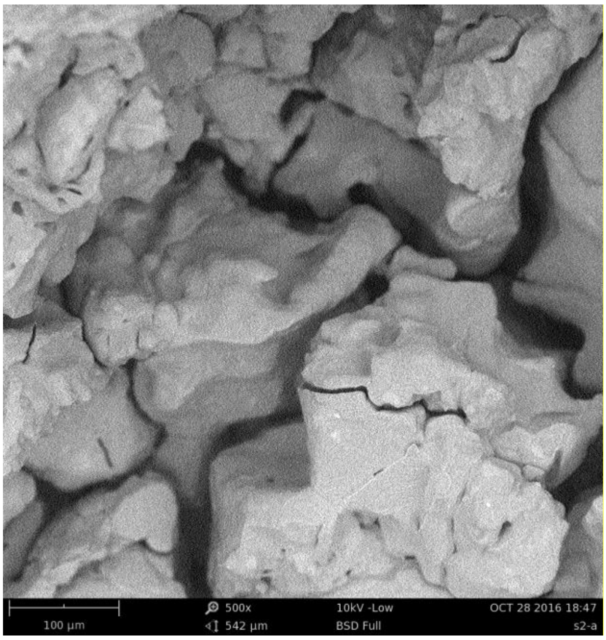


Fig. 3 – The structure of the ammonium nitrate granules after heat treatment ("porization")

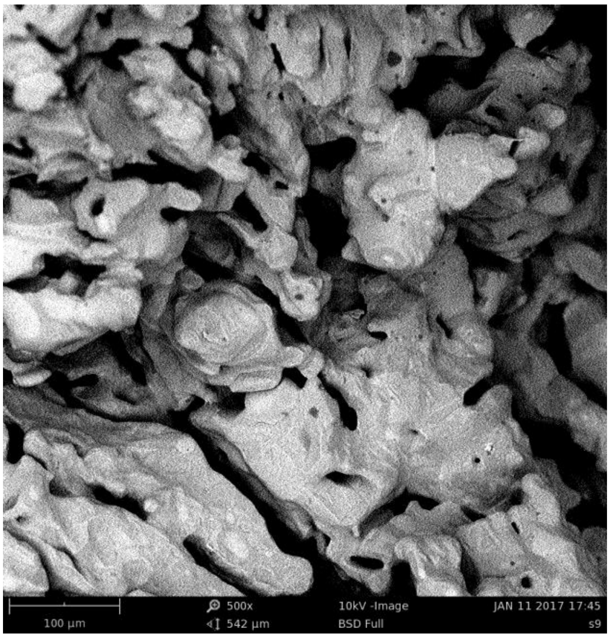


Fig. 4 – PAN granule sample obtained by humidification in a vortex granulator with subsequent heat treatment in the workspace of the same device

tion" pores of nanometer size are also present in the surface structure. The presence of these pores increases the retentivity of the PAN granules and provides the storage and transportation of ANFO to the blasting place. However, the presence of moisture in the granule leads to an undesirable change in the polymorphic transformations chain. A sequentially flowing chain of transformations II → III → IV replaces the transformation II → IV (the advantages of such a chain are described above). The granule becomes more porous and can be destroyed even due to a small external physical impact.

A PAN sample after the final drying stage in a multistage shelf device is shown in Fig. 5.

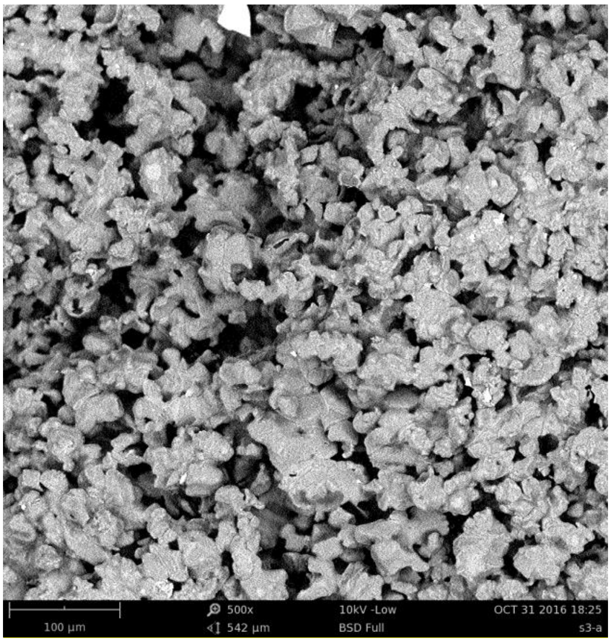


Fig. 5 – PAN granules after the "humidification-heat treatment" stages in a vortex granulator and the "final drying" stage in a multistage shelf device

The sample is characterized by an extensive network of deep curved (tortuous) mesopores of a "modification" nature and their uniform distribution over the entire surface of the granule. In this case, each pore is physically separated from the other and there are practically no united pores in the surface structure. Such a PAN sample (among other inherent advantages in the previous sample) can be successfully stored together with a diesel distillate in the pores due to a slight increase of the granules retentivity.

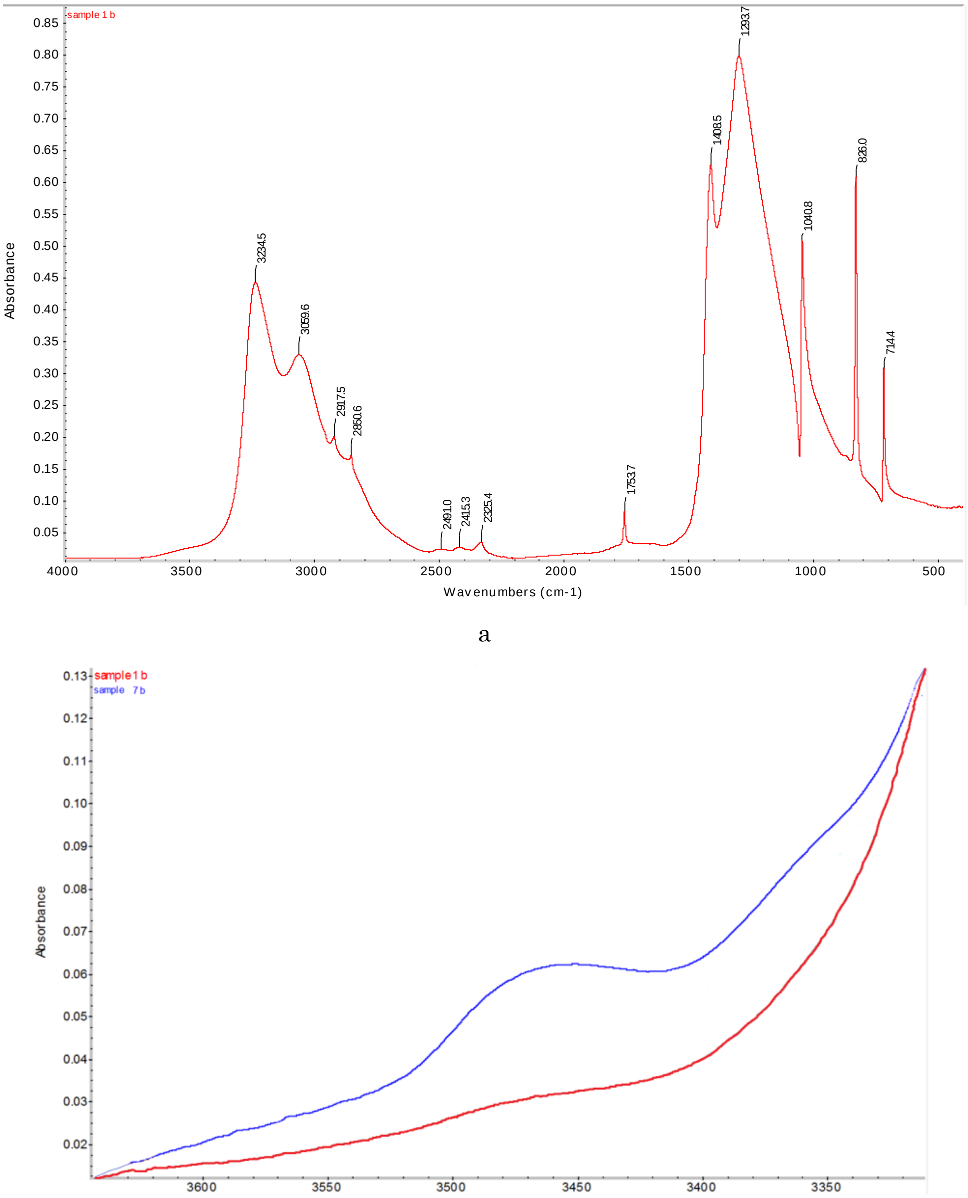
Sectioning of the dryer's workspace allows to carry out the final drying stage in the "soft" mode. At the same time, at each dryer's stage there are conditions, which ensure the minimum temperature stresses in the granule.

One should note that as time goes by, granules influenced by diesel distillate, begin to loosen and soften. Therefore, it is not recommended to store PAN granules together with diesel distillate for a long time.

During the PAN obtaining process by the method of physical and thermal effects on the ordinary ammonium nitrate granule, it is important to ensure the constancy of the sample phase composition. The results of studies of FTIR spectra regarding the PAN granules for the last sample show that new phases are not formed during the implementation of the described method (Fig. 6a). The presence of some splashes of intensity (as, for example, shown in Fig. 6b) relates to the presence of moisture in the ammonium nitrate sample and to an increase in the heat treatment time due to the use of a multistage dryer.

5. CONCLUSIONS AND RECOMMENDATIONS

Studies regarding the nanoporous structure morphology of PAN granules demonstrate that the final drying stage can improve product quality indicators. Although the PAN production technology using the final drying stage increases the cost of production (compared



a

b

Fig. 6 – FTIR spectra of PAN granule after the "humidification-heat treatment" stages in a vortex granulator and "final drying" stage in a multistage shelf device (a), an example of the comparative description of the FTIR spectra part of the initial granule (sample 1b) and PAN granules after the "humidification-heat treatment" stages in a vortex granulator and the "final drying" stage in a multistage shelf device (sample 7b, area between wavenumbers 3390 and 3540 cm $^{-1}$) (b)

with the basic scheme for PAS production in a vortex granulator), the cost for storing granules can be reduced. Besides, due to the compactness of the multistage dryer, it seems possible to create mobile eco-friendly installations to obtain PAN [11].

Samples of PAN granules after final drying are characterized by a developed network of nanopores with various configurations. Nanopores do not only absorb diesel distillate but also successfully retain it in the granules. Thanks to the improved technology, the granules undergo a polymorphic transformation, which does not affect the granule's strength. Moreover, the granule's low moisture content allows it to be stored for a long time without loss of strength and specific (absorptivity and retentivity) properties. Compared with the "porization" process, the proposed technology has several advantages, including:

– minimal destruction of the granules;

– minimal formation of "mechanical" micropores with an emphasis on the "modification" nanopores formation;

– the shape of the nanopores allows increasing the retentivity of the granules.

The objective of further research is to study the dependence of the final drying time effect on nanopores' structure and the quality indicators of PAN granules.

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Морфологічні особливості нанопористої структури гранул аміачної селітри на стадії фінального сушіння в багатоступеневих апаратах

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Стаття присвячена вивченню морфологічних особливостей нанопористої структури гранул аміачної селітри, яка отримана методом зволоження з наступною термообробкою, в тому числі фінальним сушінням. Представлено обґрунтування необхідності удосконалення базової схеми з використанням методу “зволоження-термічна обробка” в вихрових грануляторах з точки зору отримання розвиненої мережі нанопор. Проведено порівняльний аналіз морфології вихідних гранул рядової аміачної селітри, аміачної селітри після термообробки, аміачної селітри після стадій “зволоження-термічна обробка” в вихровому грануляторі та аміачної селітри після стадій “зволоження-термічна обробка-фінальна сушка” в багатоступінчастому поличному апараті. Результати, які представлені в даній статті, будуть використані в якості одного із етапів інженерного розрахунку багатоступеневих поличних сушарок в складі технологічних ліній для отримання 3D наноструктурних шарів на поверхні і всередині гранули аміачної селітри.

Ключові слова: 3D наноструктурований пористий шар, Багатоступенева полична сушарка, Морфологія.