Abstract: The process of obtaining NK and NMg-fertilizers of various compositions from carbamide and fine-crystalline potassium sulfate or carbamide and caustic magnesite powder has been optimized. The commodity properties (qualitative composition, absorbability, strength) of the obtained granulated NK and NMg fertilizers have been studied. By the methods of X-ray phase analysis and IR spectroscopy, the possibility of undesirable chemical reactions during the fusion of potassium sulfate or magnesia oxide with carbamide in fertilizer mixture melt has been investigated.

Key words: prilled carbamide, complex fertilizers, consumer qualities, carbamide melt, fine-crystalline products.

Introduction

Currently, at the enterprises of the nitric industry of the Russian Federation producing granular carbamide by prilling smethod (spraying melt in the granulation tower) a product with insufficient mechanical strength of granules is produced, which leads to the formation of a significant fraction (2-5% mass) of the substandard product returned to the beginning of the process (into carbamide melt). As a result, the cost of carbamide commodity increases. In addition, while storing, transporting and reloading carbamide due to mechanical destruction of carbamide granules, its consumer qualities decrease. The problem is aggravated by the fact that recently the market of prilled carbamide has been decreasing [1].

Materials and Methods

At the same time, substandard fractions of carbamide with a high nitrogen content are most expedient to be used as a nitrogen containing component of complex fertilizers that are most popular among consumers. The second component of fertilizers may be substandard fine-crystalline products containing potassium and magnesium components in the form assimilated by plants which are in demand as individual fertilizers due to the extremely low particle size.

On the base of availability, harmlessness and satisfaction of the declared characteristics of the final product a fine-crystalline, technical K₂SO₄, can be used as the potassium-containing component of NK fertilizer and magnesite caustic powder with 85 mass % MgO can be used as magnesium containing component of NK fertilizer. However, a mechanical mixture of nutrient components will not have properties of the required product, so for their processing, a technology of fusing unconsolidated fractions of carbamide with pulverized K₂SO₄ and MgO has been proposed. Understanding the physicochemical regularities of the processes proceeding in carbamide melt is very important for the successful implementation of this technology. Thus, while obtaining mixed complex fertilizers, it should be taken into account that some initial salts and final products cannot be mixed, since they may cause undesirable chemical processes that result loss of nutrients and deterioration of the physical properties of fertilizers [2].

There is a reservation that the issue of fertilizer antagonism has been insufficiently studied, but the possibility of mixing K₂SO₄ and carbamide is...
indicated [3]. The authors note the formation of alkali (alkaline-earth) sulfates and carbamide of complex compounds in water solutions \( \text{MSO}_2\cdot\text{CO(NH}_2\text{)}_2\), \( \text{MgSO}_4\cdot\text{CO(NH}_2\text{)}_2\), \( \text{MgSO}_4\cdot 2\text{CO(NH}_2\text{)}_2\), \( \text{MSO}_4\cdot 4\text{CO(NH}_2\text{)}_2\), \( \text{MgSO}_4\cdot 6\text{CO(NH}_2\text{)}_2\) [4-5]. It can be assumed that such compounds are formed even during the interaction of molten carbamide with dissolved \( \text{K}_2\text{SO}_4\) in it. The suspension \( \text{MgO}\) in water has a slightly alkaline reaction, therefore, hydrolysis of carbamide is possible with the final product of alkaline hydrolysis being corresponding to carbonate and ammonia [6]:

\[
2\text{CO(NH}_2\text{)}_2 + \text{Mg(OH)}_2 \rightarrow \text{Mg(OCN)}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O},
\]

(1)

\[
\text{Mg(OCN)}_2 + 3\text{H}_2\text{O} \rightarrow \text{MgCO}_3 + 2\text{NH}_3 + \text{CO}_2,
\]

(2)

In addition, the reaction is possible

\[
\text{Mg(OCN)}_2 + 2\text{H}_2\text{O} \rightarrow \text{MgCO}_3 + \text{CO(NH}_2\text{)}_2.
\]

(3)

These processes must inevitably lead to losses of the nutrient component - nitrogen.

Therefore, one of the tasks of this work was to study the physicochemical processes occurring while fusing carbamide with fine crystalline additives, especially those processes that can lead to a loss of nitrogen.

As well the most important commodity characteristics of any fertilizer are absorbability and strength of granules. Absorbability is associated with the ability to burn polycrystalline products and their clumping during storage. The content of hygroscopic moisture in the substance affects its fluidity, thermal decomposition ability, the loss of moisture, etc. The degree of absorbability of the substance depends on the technology of its further processing and storage.

Therefore, another task of the work was to optimize the technology of alloying carbamide with fine crystalline additives in order to improve the properties (qualitative composition, absorbability, strength) of the fertilizers obtained.

**Experimental part:** Synthesis of \( \text{NK} \) and \( \text{NMg} \) complex fertilizers included the following stages: production of mixed fertilizer of various composition, its melting at 140°C temperature in the isothermal reactor, solidification of the fertilizer mixture melt on the cooled surface, grinding of the obtained tile and separation of the granules of complex fertilizer by isolating the commodity fraction. In order to determine the composition of complex fertilizers qualitatively, an IR spectroscopic analysis method was used. IR spectra were recorded on a spectrometer SPECORD 75-IR. Samples were prepared in the form of tablets with KBr. The parameters of thermal stability of \( \text{NK}, \text{NMg} \) fertilizers samples were determined using Q 1500 (Hungary) derivatograph in the range of 20-600°C with heating rate of 2.5 and 5-degree x min\(^{-1}\).

The samples of \( \text{NK}, \text{NMg} \) fertilizers were determined using Q 1500 (Hungary) derivatograph in the range of 20-600°C with heating rate of 2.5 and 5-degree x min\(^{-1}\). Calcined \( \text{Al}_2\text{O}_3\) was used as a standard. X-ray phase analysis was carried out on DRON-3 M diffractometer with a monochromator on a primary beam, radiation \( \text{CuK}_\alpha\). The rotation rate of the sample was set at 2 or 4 degree /min\(^{-1}\). The samples of the materials for analysis were prepared in the form of powders. The processing of the diffractograms was carried out according to the commonly used procedure [7-9].

N. E. Pestov’s method concluding estimation of the critical moisture content was used to study the absorbability of the samples of the fertilizers obtained [10-11]. Evaluation of the strength of solidified melt samples of complex fertilizers was carried out using apparatus 2054 P-5. Samples in the form of cylindrical tablets with a diameter of 12 mm and a length of 16-36 mm were studied for the critical breaking force by compression. The value of the critical strength was calculated as the ratio of the destruction force of the sample to the area of its destruction (cross-sectional area of a cylindrical sample). In figure 1 a: b on derivatograms of fertilizers \( \text{CO(NH}_2\text{)}_2\cdot\text{K}_2\text{SO}_4\) and \( \text{CO(NH}_2\text{)}_2\cdot\text{MgO}\) the first effect (endothermic), corresponding to the melting of carbamide is observed about 10-15 °C below the melting point of pure carbamide (132°C).
The onset of reactions with loss of mass (decomposition of urea) corresponds to temperature over 150-145°C for a mixture of carbamide and magnesium oxide and over 150-155 °C for carbamide, a mixture of carbamide and potassium sulfate. Decrease in the temperature of the beginning of carbamide decomposition up to 145°C is probably due to the catalyzing action of the dusty particles of the process of carbamide decomposition, since they represent ready fuse for the primary formation of the solid phase nuclei of the carbamide decomposition products. Nevertheless, on the base of DTA data, it can be stated that the studied systems are stable up to temperatures of 10-20°C over the melting point. It makes possible the fusion of fertilizer mixtures without loss of nitrogen.

Analysis of IR spectra, X-ray phase and thermos-gravimetric analyzes of these mixtures showed no specific reactions occurring while introducing K₂SO₄ into carbamide melting at 140°C.

However, IR spectra of NMg-fertilizers obtained at the same temperature including a low-intensity absorption band of 2170 cm⁻¹, indicates the presence of cyanate ions [9-11] in the granulate. It shows that in carbamide melting an interaction with finely dispersed MgO is proceeded by the reaction [1] with the formation of magnesium cyanate. The low intensity of the absorption band of cyanate ions depends on the content of MgO in the mixture.

By means of differential thermal analysis of mixtures CO(NH₂)₂-MgO (Fig.1,b), the effect corresponding to the reaction [1] was not detected, probably because its possible location is overlapped by the strong endothermic effect of carbamide melting. X-ray phase analysis confirms that the basis of NMg-fertilizer is the phases of carbamide and magnesium oxide, while the magnesium cyanate phase was detected.

Consequently, the content of magnesium cyanate in the granulate is insignificant and is of impurity nature, due to which considerable nitrogen losses occur. The specific mechanism for the formation of magnesium cyanate remains questionable. However, it can be assumed that a small amount of magnesium cyanate is associated with low solubility of MgO in carbamide melting and a short time of contacting MgO with carbamide melting.

X-ray phase analysis showed that a significant portion of pure carbamide melt solidifies in an amorphous state. With the introduction into the melt of fine-dispersed solid-phase particles K₂SO₄ or MgO, amorphization of the carbamide structure sharply decreases. This is due to the increase of crystallization rate, since the process can proceed on already prepared embryos of the solid phase with minimal undercooling of melt.

Thus, physical-mechanical methods of the analysis showed that during fusion of K₂SO₄ or MgO with carbamide in melt of the fertilizer mixture, unwanted chemical reactions leading to significant losses of valuable nutrient components do not occur. Laboratory studies of the synthesis of nitrogen-potassium (nitrogen-magnesium) fertilizers showed that in NK fertilizer the ratio of the elements N:K₂O should be not less than (1.2-1.3):1, and in NMg fertilizer the ratio of N:MgO—less than (1.0-1.1):1.5. With a smaller carbamide content, the fluidity of the melt decreases and the operations as melt discharge from the smelter and formation of a melting layer of a given thickness on the cooled surface of the crystallizer are impeded. Exceeding the 3:1 ratio of N:K₂O leads to the formation of non-uniform granules due to delamination of the melt with its slow solidification. Absorbability of fertilizers was investigated on the samples of + 2–5 mm commodity fraction. The generalized results of parallel experiments are shown in Fig.2.
Absorbability of complex NK and NMg – fertilizers is higher than in granulated carbamide, as there are two different crystalline phases in their granules. The data of Fig.2 shows that with increasing ratio N:\K\(_2\)SO\(_4\) and N:\MgO in fertilizer, the critical moisture value passing through the minimum one begins to increase, i.e. with increasing carbamide content, fertilizer becomes less hygroscopic. This can be explained by the fact that with the increase of carbamide amount in the fertilizer, the probability of cracks in the volume and on the surface of the granules decreases, the granules have a more monolithic structure, which leads to a decrease of the adsorbing surface of the material.

Taking into account the fact that critical air humidity values for pellets of the obtained fertilizers are low, in the production technology it is necessary to provide the stage of packing the product. Moreover, the indicators of melt strength of complex fertilizers were studied on the base of carbamide. Generally, the effect of dispersed particles and MgO on the strength of granules is obviously related to the change in the kinetics of structure formation, the creation of dendritic crystals penetrating the volume of granules, with the change in the strength of single phase contacts and their concentration. Adding insoluble, highly disperse modifying additives to carbamide melt creates a large phase contact surface, which accelerates the process of nucleation of carbamide particles adsorbed on the nuclei of the solid phase. The increase in the strength of such a micro-heterogeneous structure is due to the large number of bonds and contacts of the two crystalline phases formed.

In such materials, the matrix perceives the entire load, and the dispersed particles of the reinforcing filler prevent the development of plastic deformation resisting the movement of both single dislocations and dislocation formations (sub-boundaries, grain boundaries) [12-14].

Strength of NK-fertilizer tablets is slightly higher than the tablets strength of pure carbamide ones (Fig.3).

The maximum strength is achieved with melt content of 55 mass % \(\text{K}_2\text{SO}_4\), with a further increase of the concentration \(\text{K}_2\text{SO}_4\) in the melt, the strength of the tablets somewhat reduces, obviously due to the decrease in the number of single phase-to-phase contacts and poor wetting of solid-phase particles due to molten carbamide and solid potassium sulfate. It can be assumed that phase-to-phase contacts are weakened by low content of carbamide and in comparison with the crystallization obtained by fusing carbamide and potassium sulfate, the strength of the carbamide crystals decreased by a high carbamide content.

The strength of NMg-fertilizer tablets increases with concentration growth in MgO fertilizer for the entire fluidity suspension interval (Fig. 3). This is due to the better wettability of the particles (caustic magnesite powder) because of their smaller size in
comparison with the $\text{K}_2\text{SO}_4$ particles. As a result, in the carbamide melt, MgO particles form a great number of crystallization centers with a larger phase interface, which is accompanied by a higher reinforcing effect.

**Conclusion**

1. Physicochemical methods of analysis showed that while fusing potassium sulfate with carbamide at temperature of 140°C, unwanted chemical reactions do not proceed in fertilizer mixture melt and there are no significant losses of valuable nutrient components.
2. Fine magnesium oxide, dissolved in carbamide melt, forms magnesium cyanate. However, the rate of this process is little, so the amount of the formed magnesium cyanate is of impurity nature.
3. Because of sufficient hygroscopic nature of the obtained fertilizers it is required to pack the product. Optimal compositions ensuring maximum strength of NK -fertilizers samples have been developed.
4. A significant portion of pure carbamide melt is crystallized in an amorphous state. The introduction of fine-dispersed solid-phase particles of potassium sulfate or magnesium oxide into the carbamide melt reduces the amorphization of its structure, promotes the crystallization and reinforcement of the solidified melt structure.

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