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ПРИМЕНЕНИЕ БЕНТОНИТА В ПОЛУЧЕНИЕ СЕРОСОДЕРЖАШЕГО КАРБАМИДА НА ОСНОВЕ ПЛАВА КАРБАМИДА И СЕРЫ

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В данной работе рассмотрен процесс получения гранулированного серосодержащего карбамида из серы и жидкого расплава карбамида с использованием бентонита. Выявлено, что добавка бентонита к сере перед смешением ее с плавом карбамида предотвращает расслоение плавов серы и карбамида. Процесс проводили при температурах 135-145 °С и массовых соотношениях $(NH_2)_2CO$: бентонит : сера = 100 : (1-7) : (1-15). Определены оптимальные условия получения, состав и свойства гранулированного серосодержащего карбамида с уравновешенным содержанием азота и серы. В полученных удобрениях прочность гранул повышена от исходной 2,65 до 4,76 МПа, гироскопическая точка повышается с 58,4 % до 62,3 %, pH и пористость снижаются от 8,02 до 5,32 и от 5,60 до 4,55 соответственно, а скорость растворения гранул в воде снижается в 3,36 раз. Также выявлено, что при добавлении смеси серы с бентонитом в плав карбамида плотность и вязкость расплава повышаются с увеличением количества вводимой добавки. Увеличение количества серы и бентонита, добавленных на 100 г плава карбамида, от 1 до 15 и от 1 до 7 г, соответственно, при температуре 135 °С приводит к повышению плотности расплавов от 1,16 до 1,33 г/см^3 и вязкости от 2,56 до 3,06 сПз. Микроскопическим исследованием показано, что добавление смеси серы с бентонитом в плав карбамида приводит к уменьшению размеров микропор и микротрещин. На основе результатов исследования предложена принципиальная технологическая схема получения серосодержащего гранулированного карбамида и рекомендованы оптимальные технологические параметры процесса.

Ключевые слова: карбамид, сера, бентонит, плав, смешение, азот, поверхностное натяжение

APPLICATION OF BENTONITE IN OBTAINING SULFUR-CONTAINING UREA BASED ON A FLUSH OF UREA AND SULFUR

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This paper presents the results of a study of the processes for obtaining granular sulfur-containing carbamide from sulfur and a liquid carbamide melt using bentonite to influence the

surface tension between two phases of sulfur and urea to obtain a mixed homogeneous phase. It was revealed that the addition of bentonite to sulfur before adding the latter to the melt of urea, which has a temperature of 135-145 °C at mass ratios $(NH_2)_2CO$: bentonite : sulfur = 100 : (1-7) : (1-15) prevents the stratification of melts sulfur and urea. The optimal conditions for obtaining, the composition and properties of granular sulfur-containing urea with a balanced content of nitrogen and sulfur are determined by adding a mixture of sulfur with bentonite to the urea melt before granulation. In fertilizers obtained with the addition of a mixture of sulfur with bentonite to the melt of carbamide at the studied ratios, the strength of the granules increases from the initial 2.65 to 4.76 MPa, the gyroscopic point increases from 58.4% to 62.3%, pH and porosity decrease from 8 02 to 5.32 and from 5.60 to 4.55, respectively, and the dissolution rate of the granules decreases 3.36 times. It was also found that when adding a mixture of sulfur with bentonite to the melt of carbamide, the density and viscosity of the melt increase with an increase in the amount of added mixture of sulfur with bentonite. An increase in the amount of addition of a mixture of sulfur and bentonite from 1 to 15 and from 1 to 7 g per 100 г melt of urea at a temperature of 135 °C leads to an increase in the density and viscosity of the melts from 1.16 to 1.33 g/cm^3 and from 2.56 to 3.06 cPz. Microscopic examination showed that adding a mixture of sulfur with bentonite to the carbamide melt leads to a decrease in the size of micropores and microcracks up to 0.93 microns wide. On the basis of the results obtained, optimal technological parameters and a process flow diagram for the production of sulfur-containing granulated carbamide are proposed.

Key words: urea, sulfur, bentonite, melt, mixing, nitrogen, surface tension

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INTRODUCTION

Sulfur, along with nitrogen, phosphorus and potassium, is one of the most important elements of the mineral nutrition of plants. In recent years, in most countries with developed agriculture, a negative balance has been formed between the input and removal of sulfur from the soil. In the context of reducing atmospheric pollution with sulfur dioxide and insufficient use of organic fertilizers, sulfur-containing mineral fertilizers become the most promising form of eliminating sulfur deficiency in agrozems. Fertilizers based on free sulfur have recently attracted particular interest, since they have a number of advantages compared to other forms of sulfur-containing fertilizers – the absence of ballast components, low cost, a prolonged period of action, and compatibility with other types of fertilizers [1].

It is known that due to the use of fertilizers, an average of 40-50% of the increase in crop yields is provided. Currently, carbamide is successfully used all over the world as a nitrogen fertilizer. Urea is the most versatile type of fertilizer suitable for almost all types of crops. It is used as a base fertilizer for top dressing, with immediate incorporation into the soil to prevent loss in the form of gaseous ammonia. The world production of carbamide exceeds more than 200 million tons, in Uzbekistan it is produced more than 1 million tons per year [2].

Effective agriculture requires N : S in a ratio of 10 : 1 to 5 : 1, since with a lack of sulfur, protein synthesis in plants is delayed, nitrogen accumulates in non-protein form or in the form of nitrates. The functions of sulfur in plant life are characterized by great agrochemical and physiological significance for the formation of high yields and commercial quality of plant products, increasing plant resistance to adverse weather conditions. Sulfur provides prevention of late blight and root rot. Insufficient supply of sulfur to plants not only reduces the yield and quality of products, but also reduces the efficiency of using nitrogen from fertilizers by plants [3-6]. At present, numerous agrochemical studies have shown that the lack of sulfur adversely affects the productivity of agricultural crops, therefore, special attention is paid to the production and use of sulfur-containing fertilizers [7-9].

It should be noted that the increase in agrochemical efficiency and improvement of the properties of mineral fertilizers, the development of new technologies for the production of various types of fertilizers are important for increasing the productivity of crops [10, 11].

Therefore, the production and use of granulated carbamide with a sulfur content based on carbamide and sulfur melts is relevant for increasing the agrochemical efficiency of urea, as well as for improving its quality, however, under normal conditions, it is impossible to obtain a homogeneous mass or a homeogenic mixed phase based on carbamide and sulfur melts, since melt of urea and sulfur differs greatly in surface tension and density (at 140 °C, the density of sulfur melt is 1.787 kg/m^3, urea 1.214 kg/m^3), therefore, when sulfur melt is added to the carbamide melt, they immediately separate into two parts.

At present, obtaining high-quality mixtures of heterogeneous dispersed materials continues to be an urgent technological and scientific task; for these purposes, various methods are used by physical action and the addition of various additives [12, 13]. However, having methods and additives for obtaining a homogenous mixed phase based on carbamide and sulfur melts with subsequent production of granular fertilizer is not advisable.

As additives to influence the surface tension, as well as to improve the physicochemical and agrochemical properties of carbamide, the most preferred additive is alkaline earth bentonites, which have large pore space values compared to alkaline ones, they are characterized by a less pronounced swelling ability. However, they have a larger number of active centers on the surface of the particles, through which the effect on surface tension is carried out. In addition, bentonites and preparations from them are used in agriculture as additives to sandy and other infertile soils to improve their agrochemical properties [14]. The use of bentonite increases the resistance of plants to various diseases, increases the yield of vegetable crops, potatoes, sugar beet, wheat, and cotton [15]. The experience of using alkaline earth bentonites with mineral fertilizers to increase the fertility of soddy-podzolic soil is known. Thanks to bentonite, the potato yield increased one and a half times [16]. When using bentonites, the mean values over the years of the study retained a high conjugation during all the years of interaction between clay and soil, which allows us to speak of a material that exhibits stabilization signs in relation to its acid-base and nutritional regimes [17].

The addition of bentonite before granulation into the urea melt mixed with sulfur does not lead to a decrease in the strength of the granules, the formation of a porous structure as a result of preventing the release of water vapor and free ammonia from the carbamide melt, and also to a decrease in agrochemical properties, as usually occurs during the production of carbamide, but to a significant an increase in the strength of the granules, the formation of a more perfect internal structure, an increase in agrochemical properties.

Based on the foregoing, in this work, the processes of obtaining sulfur containing granular carbamide based on the melt of urea and ground sulfur mixed with bentonite were studied, the properties of the carbamide melt containing the melt of sulfur and bentonite, sulfur containing granular carbamide, and the optimal conditions for obtaining sulfur containing granular carbamide were determined.

TECHNIQUE OF EXPERIMENTATION

To obtain sulfur containing granular carbamide, the main component was the factory product of Joint-stock company “Maxam - Chirchiq“ - urea $(NH_2)_2CO$ grade A with a content of 46.3% N , ground sulfur having the composition %: S – 99.91; free H_2SO_4 – 0.001; ash – 0.005; organic substances – 0.004; moisture – 0.001 and bentonite crushed to a particle size of not more than 0.1 mm and having a composition%: SiO_2 – 46.06; Al_2O_3 – 8.78; Fe_2O_3 – 3.0; MgO – 4.33; CaO – 12.2; Na_2O – 0.75; K_2O – 1.05; P_2O_5 – 0.77; SO_3 – 1.39; CO_2 – 9.35; TiO_2 – 0.39.

The experiments were carried out as follows: urea was melted in a metal cup on an electric stove, a mixture of sulfur and bentonite was introduced into the melt at 135-140 °C at a mass ratio of $(NH_2)_2CO$: bentonite : sulfur = 100 : (1-7) : (1- 15) the temperature was maintained constant by heating, the melt was kept after dosing a mixture of sulfur with bentonite for 1-2 min with constant stirring until a homogeneous state, after which it was poured into a granulator, which is a metal cup with a perforated bottom, the diameter of the holes in which was 1.0 mm. The pump in the upper part of the glass created pressure and the melt was sprayed from a height of 35 m. In this case, granules of sulfur-containing carbamide were obtained. Then the chemical composition and properties of fertilizer granules were determined. The strength of fertilizer granules with a granule size of 2-3 mm was determined on an IPG-1M electronic device [18].

The nitrogen content in the products was determined using a catalyst for the conversion of nitrogen in carbamide to ammonia by heating in a sulfuric acid solution, followed by distillation and absorption of ammonia in an excess of a standard sulfuric acid solution and back titration with a sodium hydroxide solution in the presence of an indicator [19], and the content of biuret was determined by [19]. The sulfur content was determined by sintering a sample with an Eshka mixture, transferring sulfate ions into solution, and their gravimetric determination in the form barium sulfate [20], the hygroscopic points of the feedstock and finished fertilizers were determined by the desiccator method at 25 °C [21], and the storage capacity of fertilizers was determined by the method [22]. Briquetting conditions: sample compression pressure with a load of 2.8 kg, temperature - 40 °C; the length of stay of the cylindrical cassette in the mold is 8 h. The briquettes were tested for destruction using the MIP-10-1 instrument. The pH value of 10% aqueous solutions of initial substances and finished fertilizers was measured in an I-130M laboratory ionometer with an electrode system of ESL 63-07, EVL-1M3.1, and TKA-7 electrodes with an accuracy of 0.05 pH units. Determination of the content of CaO and MgO was carried out by volumetric complexometric method by titration with a 0.05 N solution of Trilon B in the presence of indicators fluorexone and dark blue chromium. Analysis of K_2O by the flame method. [23]. The porosity value of fertilizer granules was determined by the volumetric method [24]. To do this, a certain volume of cryoscopic benzene (V_1) was poured into a 25 ml burette equipped with a tap. Then, about a sample was poured into it 10 g, and after 1-2 min, the volume changed in the buret (V_2) was recorded. Then the tap was opened, the benzene between the carbamide granules was lowered into the second burette and its volume was measured (V_3). The porosity in % was calculated by the formula:

$$P = \frac{V_1 - V_2}{V_2 - V_3} \cdot 100$$

Also, in order to determine the rheological properties of the melts, their density and viscosity were studied at the above ratios in the temperature range of 130-145 °C. The density was established by the pycnometric method with a measurement accuracy of 0.05 rel. %, kinematic viscosity - using a glass capillary viscometer VPJ-1 with an error of 0.2 rel. % in the temperature range of 130-145 °C. For this, the mixture of the resulting product was ground. The resulting powder was introduced into a pycnometer and a viscometer, which were then placed in a thermostat filled with glycerol. The temperature in the thermostat rose to a predetermined value. In this case, the powder melted. The melt was kept for 1-2 min, then measurements were made. The rate of dissolution of sample granules in water was determined as follows. The fertilizer granule was lowered into a glass with 100 ml of distilled water, in which its complete dissolution was visually observed and recorded. Room temperature, tests five times. All results obtained are shown in tables 1-3.

RESULTS AND ITS DISCUSSION

From Table 1 it can be seen that in order to influence the surface tension between the two phases of sulfur and urea and to obtain a homogeneous mass, i.e. By evenly distributing sulfur in the carbamide granule, with an increase in the amount of sulfur per 100 g of carbamide melt, it is necessary to increase the amount of bentonite. So the addition of bentonite 1 g of bentonite per 100 g of melt carbamide makes it possible to add up to three grams of sulfur, 2 g of bentonite up to 6 g of sulfur, etc. The data in Table 2 show that with an increase in the addition of sulfur and bentonite, the strength of the product granules increases. When changing the mass ratio of the mixture of sulfur and bentonite to the melt of carbamide, the strength of the granules changes as follows: At a ratio of $(NH_2)_2CO$: bentonite : sulfur = 100 : 0 : 0 - 2.53 MPa; 100 : 1 : 2 - 2.71 MPa; 100 : 2 : 4.6 - 3.12 MPa; 100 : 7 : 15 - 4.76 MPa.

Table 1

Composition of sulfur-containing granular urea

***Таблица 1.* Состав серосодержащего гранулированного карбамида**

Mass ratio $(NH_2)_2CO$: bentonite : sulfur	N, %	S, %	CaO, %	MgO, %	K_2O, %	Biuret, %	Moisture, %
100 : 0 : 0	46.2					1.40	0.16
100 : 1 : 1	45.29	0.98	0.12	0.04	0.01	1.37	0.16
100 : 1 : 1.5	45.07	1.46	0.12	0.04	0.01	1.36	0.16
100 : 1 : 2	44.84	1.94	0.12	0.04	0.01	1.36	0.16
100 : 1 : 3	44.42	2.88	0.11	0.04	0.01	1.35	0.15
100 : 2 : 2	44.42	1.92	0.24	0.08	0.02	1.34	0.16
100 : 2 : 3	44.01	2.86	0.23	0.08	0.02	1.33	0.15
100 : 2 : 3.5	43.79	3.32	0.23	0.08	0.02	1.33	0.15
100 : 2 : 4	43.58	3.77	0.23	0.08	0.02	1.32	0.15
100 : 2 : 4.5	43.38	4.23	0.23	0.08	0.02	1.31	0.15
100 : 2 : 4.6	43.33	4.33	0.23	0.08	0.02	1.31	0.15

Продолжение таблицы

Mass ratio $(NH_2)_2CO$: bentonite : sulfur	N, %	S, %	CaO, %	MgO, %	K_2O, %	Biuret, %	Moisture, %
100 : 2 : 5	43.18	4.67	0.23	0.08	0.02	1.30	0.15
100 : 2 : 6	42.78	5.56	0.23	0.08	0.02	1.29	0.14
100 : 3 : 3	43.58	2.83	0.35	0.12	0.03	1.32	0.15
100 : 3 : 4	43.18	3.74	0.34	0.12	0.03	1.30	0.15
100 : 3 : 4.5	42.98	4.19	0.34	0.12	0.03	1.30	0.15
100 : 3 : 5	42.78	4.63	0.34	0.12	0.03	1.29	0.15
100 : 3 : 6	42.38	5.56	0.34	0.12	0.03	1.28	0.15
100 : 3 : 7	42.01	6.36	0.33	0.12	0.03	1.27	0.14
100 : 4: 7.5	41.43	6.73	0.44	0.16	0.04	1.25	0.15
100 : 4: 8	41.25	7.14	0.44	0.15	0.04	1.25	0.15
100 : 5 : 5	42.01	4.55	0.56	0.20	0.05	1.27	0.15
100 : 5 : 5.5	41.81	4.98	0.55	0.20	0.05	1.27	0.15
100 : 5 : 6	41.62	5.41	0.55	0.20	0.05	1.26	0.15
100 : 5 : 7	41.25	6.25	0.55	0.19	0.05	1.25	0.14
100 : 5 : 8	40.88	7.08	0.54	0.19	0.05	1.24	0.14
100 : 5 : 8.5	40.70	7.49	0.54	0.19	0.05	1.23	0.14
100 : 5 : 9	40.53	7.89	0.53	0.19	0.05	1.23	0.14
100 : 5 : 9.2	40.45	8.07	0.53	0.19	0.05	1.22	0.14
100 : 5 : 9.5	40.35	8.29	0.53	0.19	0.05	1.22	0.13
100 : 5 : 10	40.17	8.69	0.53	0.19	0.05	1.21	0.13
100 : 6 : 10.5	39.66	9.01	0.63	0.22	0.05	1.20	0.14
100 : 6 : 11	39.49	9.40	0.63	0.22	0.05	1.20	0.14
100 : 6 : 11.5	39.32	9.79	0.62	0.22	0.05	1.19	0.14
100 : 6 : 12	39.15	10.17	0.62	0.22	0.05	1.18	0.14
100 : 7 : 7	40.53	6.14	0.75	0.27	0.06	1.23	0.14
100 : 7 : 8	40.17	6.96	0.74	0.26	0.06	1.22	0.14
100 : 7 : 9	39.83	7.76	0.74	0.26	0.06	1.21	0.14
100 : 7 : 10	39.49	8.55	0.73	0.26	0.06	1.20	0.13
100 : 7 : 10.5	39.32	8.94	0.73	0.26	0.06	1.19	0.13
100 : 7 : 11	39.15	9.32	0.72	0.26	0.06	1.18	0.13
100 : 7 : 11.5	38.99	9.70	0.72	0.26	0.06	1.18	0.13
100 : 7 : 12	38.82	10.08	0.72	0.25	0.06	1.17	0.13
100 : 7 : 12.5	38.66	10.46	0.71	0.25	0.06	1.17	0.12
100 : 7: 13	38.51	10.83	0.71	0.25	0.06	1.16	0.12
100 : 7 : 13.5	38.34	11.20	0.71	0.25	0.06	1.16	0.12
100 : 7 : 14	38.18	11.57	0.71	0.25	0.06	1.15	0.12
100 : 7 : 14.5	38.02	11.93	0.70	0.25	0.06	1.15	0.11
100 : 7 : 15	37.87	12.29	0.70	0.25	0.06	1.14	0.11

Table 2

Properties of sulfur-containing granular urea

***Таблица 2.* Свойства серосодержащего гранулированного карбамида**

Mass ratio $(NH_2)_2CO$: bentonite : sulfur	Dissolution rate rhenium granules in water, seconds/granules	Other-granule capacity, MPa	pH (10% solution)	Temperatura cristalization °C	Hygrosminecal point %	Poris toast %
100 : 0 : 0	93.8	2.53	8.02	128	58.4	5.75
100 : 1 : 1	102.2	2.65	7.11	125.8	59.5	5.60
100 : 1 : 2	112.2	2.71	6.95	123.4	60.5	5.56
100 : 2 : 4	123.2	3.06	6.62	123.8	61.9	5.50
100 : 2 : 4.6	129.4	3.12	6.46	122.8	62.3	5.48
100 : 3 : 7	163.6	3.39	5.81	120.2	63.9	5.42
100 : 4 : 7.5	179.6	3.54	5.80	121.2	64.7	5.37

Продолжение таблицы

100 : 4 : 8	182.2	3.60	5.78	119.4	65.6	5.31
100 : 5 : 9	224.8	3.85	5.77	120	66.4	5.21
100 : 5 : 9.2	229.6	3.87	5.72	119.6	67.2	5.18
100 : 5 : 10	243.2	3.97	5.68	120.2	67.7	5.05
100 : 6 : 12	279.2	4.29	5.54	117.4	68.3	4.87
100 : 7: 13	281.8	4.53	5.47	116.4	68.9	4.61
100 : 7 : 15	315.4	4.76	5.32	114.8	69.2	4.55

Table 3

Density and viscosity of the melt of fertilizers obtained by introducing into the urea melt a mixture of sulfur and bentonite

Таблица 3. **Плотность и вязкость плава удобрений, полученных введением в расплав карбамида смеси серы с бентонитом**

Mass ratio $(NH_2)_2CO$: BT : S	Density (g/cm^3), at temperature, °C				Viscosity (cPz), at temperature, °C			
	130	135	140	145	130	135	140	145
$(NH_2)_2CO$	1.16	1.16	1.15	-	2.72	2.56	2.40	-
100 : 1 : 1	1.26	1.25	1.25	1.24	2.99	2.84	2.70	2.61
100 : 1 : 2	1.25	1.24	1.23	1.22	2.87	2.70	2.56	2.48
100 : 2 : 4	1.34	1.33	1.31	1.30	2.94	2.80	2.69	2.64
100 : 2 : 4.6	1.33	1.32	1.31	1.30	2.91	2.78	2.62	2.51
100 : 3 : 7	1.28	1.28	1.25	1.24	2.43	2.37	2.28	2.19
100 : 4 : 7.5	1.31	1.30	1.29	1.28	2.69	2.48	2.39	2.23
100 : 4 : 8	1.29	1.28	1.27	1.26	2.62	2.41	2.32	2.16
100 : 5 : 9	1.33	1.32	1.31	1.30	3.14	3.02	2.87	2.81
100 : 5 : 9.2	1.32	1.31	1.30	1.30	3.06	2.96	2.80	2.75
100 : 5 : 10	1.32	1.31	1.30	1.29	2.95	2.87	2.73	2.67
100 : 6 : 12	1.35	1.34	1.34	1.33	3.05	2.99	2.87	2.79
100 : 7: 13	1.36	1.35	1.34	1.33	3.33	3.28	3.22	3.15
100 : 7 : 15	1.34	1.33	1.32	1.31	3.11	3.06	2.98	2.88

The given data show that an increase in the amount of addition of a mixture of sulfur with bentonite from 1 to 7 and 1 to 15 per 100 g of carbamide melt leads to an increase in the strength of the granules from 2.65 to 4.76 MPa. The values of the hygroscopic points of fertilizers obtained at various mass ratios $(NH_2)_2CO$: bentonite : sulfur according to the hygroscopicity scale of N.E. Pestov are hygroscopic substances, but they are significantly non-hygroscopic than the original carbamide (58.4%). In fertilizers obtained at a mass ratio of $(NH_2)_2CO$: bentonite : Sulfur = 100 : 2 : 4.6 i.e. under optimal conditions in terms of agrochemical efficiency, the gyroscopic point rises to 62.3%. It can also be seen from the table that due to the addition of a mixture of sulfur with bentonite, the pH of the SGC at the studied ratios decreases from 8.02 to 5.32. In addition, it should be noted that the obtained fertilizer granules in the studied ratios when testing for caking under the conditions of the above method, caking of fertilizers was not detected, i.e. briquette and agglomerates were not formed.

One of the indicators of urea affecting the quality is the porosity of its granules. The porosity of pure $(NH_2)_2CO$ granules amounted to 5.75%. Table 2 shows that the addition of $(NH_2)_2CO$ mixture of sulfur with bentonite to the melt leads to a decrease in porosity and the internal specific surface of the product granules. So, when changing the mass ratio $(NH_2)_2CO$: bentonite : sulfur from 100 : 1 : 1 to 100 : 7 : 15, the porosity of carbamide granules decreases from 5.60 to 4.55%.

The lower the rate of dissolution of granules of soluble mineral fertilizers in water, the slower the release of nutrients from the fertilizer, which shows its prolonged effect on the plant. So, if the complete dissolution of the granules of industrial urea is on average 93.8 s, then the introduction of mixtures of sulfur with bentonite into its composition in an amount of from 1 to 7 and from 1 to 15 g reduces the dissolution rate of the product granules from 102.2 to 315.4 s. or 3.36 times. Table 2 shows that the mixture of sulfur with bentonite effectively neutralizes the alkalinity of carbamide from the initial pH = 8.02 to 5.32 in the product.

When processing sulfur and bentonite-containing urea melts into granular fertilizers, their rheological properties play an important role. In this regard, the density and viscosity of melts were studied at the above weight ratios $(NH_2)_2CO$: bentonite : sulfur in the temperature range 130-145 °C. The results are shown in Table 3. Experimental data show that the value of density and viscosity mainly depends on temperature and mass fraction of additives introduced into the melt of urea. Both density and viscosity decrease with increasing temperature, and vice versa increase with increasing amount of sulfur-bentonite mixture in the carbamide melt. An increase in the amount of a mixture of sulfur and bentonite from 1 to 7 and from 1 to 15 g per 100 g melt of carbamide at a temperature of 135 °C leads to an increase in the density and viscosity of the melts from 1.16 to 1.33 g/cm^3 and from 2.56 to 3.06 cPz. A similar pattern is observed at other temperatures. At the studied ratios $(NH_2)_2CO$: bentonite : sulfur and temperature ranges of 130-145 °C, all samples of urea – sulfur – bentonite melts have sufficient fluidity, which creates favorable conditions for their granulation in the existing grantower without any special technological difficulties.

At the next stage of research, an electron microscopic study of carbamide granules and urea samples obtained with the addition of a mixture of sulfur with bentonite was carried out at mass ratios $(NH_2)_2CO$: bentonite : sulfur = 100 : 2 : 4.6. Microscopic studies were carried out using a scanning electron microscope REM-200. For viewing, the samples were pre-sputtered with silver in a VUA-4K vacuum station. Fig. 1 and 4 show an electron microscopic photograph of the surface of the granules and the cut of the initial urea granules (Fig. 1 and 2) and urea granules with sulfur and bentonite (Fig. 3 and 4). It can be seen from them that the granules of the original carbamide and sulfur containing granular carbamide obtained on the basis of the melt of urea and the mixture of sulfur with bentonite are almost identical on the surface, do not have pores and cracks. On the cut of the granules of the original urea in the center, there are obvious pores and microcracks, in contrast to the sulfur containing granular carbamide. The length of the microcracks in the original urea is 1.62 m, and the sulfur containing granular carbamide is 0.93 m. In addition, sulfur containing granular carbamide are more monolithic than granules of the original urea. The results of the study and electron microscopy show that sulfur and bentonite, added to the urea melt, neutralize free ammonia, as a result of which the porosity in the sulfur containing granular carbamide is reduced than that of conventional urea.

Sulfur and bentonite are available in many countries of the world, which ensures the expediency of its use in the production of urea. It should be noted that the average consumption of sulfur when applied together with mineral fertilizers is 20-40 kg per 1 ha of sown area, and the application rate of urea, depending on the type of plant, is from 100 to 200 kg per 1 ha in terms of nitrogen [25].

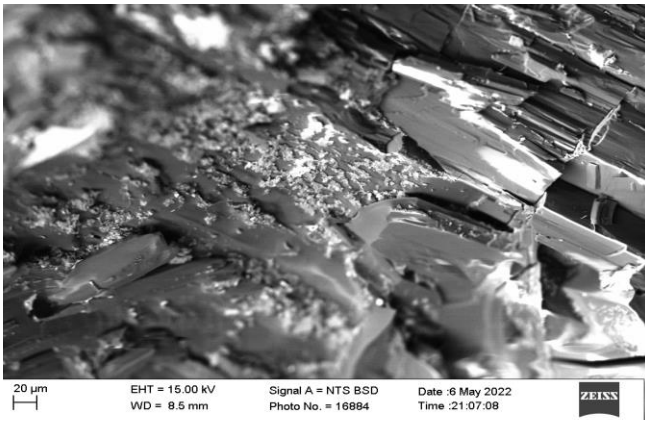

Fig. 1. Electron microscopic photograph of the surface of a carbamide granule
Рис. 1. Электронно-микроскопическая фотография поверхности гранулы карбамида

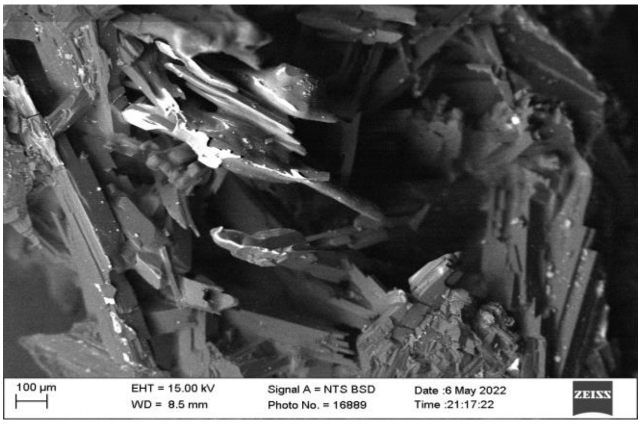

Fig. 2. Electron microscopic photograph of the internal section of a carbamide granule
Рис. 2. Электронно-микроскопическая фотография внутреннего разреза гранулы карбамида

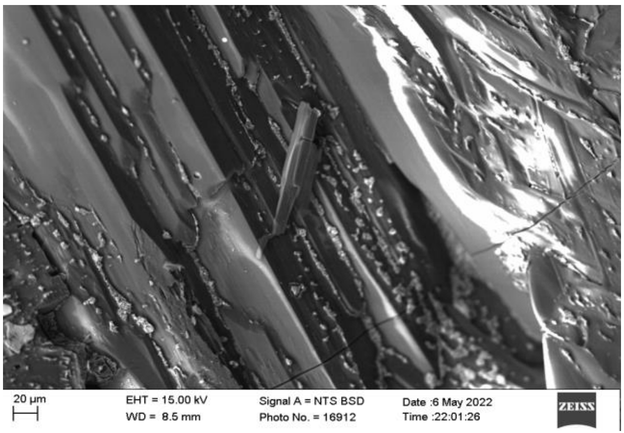

Fig. 3. Electron microscopic photograph of the surface of a granule of sulfur-containing urea
Рис. 3. Электронно-микроскопическая фотография поверхности гранулы серусодержащего карбамида

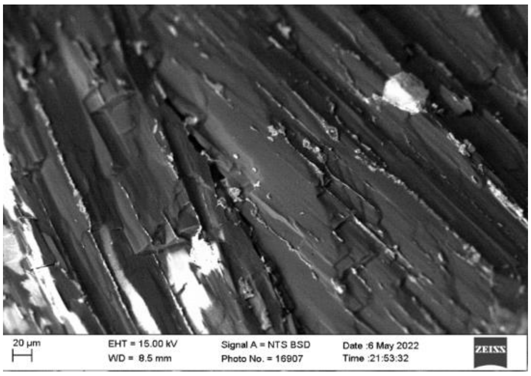

Fig. 4. Electron microscopic photograph of the internal section of a granule of sulfur-containing carbamide

Рис. 4. Электронно-микроскопическая фотография внутреннего разреза гранулы серусодержащего карбамида

Considering the above, we consider the optimal mass ratio lies within $(NH_2)_2CO$: bentonite: sulfur = 100: (2-5): (4.6-9.2) In this case, carbamide contains 43.33-40.53% N and 4.33-8.09% sulfur, and the strength of its granules is 3.12-3.87 MPa.

On the basis of the results obtained, the optimal parameters for the production of sulfur containing granular carbamide were established, and the basic technological scheme and the material flows of production are drawn up. The technological process for obtaining sulfur containing granular carbamide based on carbamide melt and a mixture of sulfur with bentonite consists of the following main stages:

1. Drying and grinding of bentonite;

3. Mixing of bentonite with ground sulfur;

3. Mixing 99.7% carbamide melt with a mixture of sulfur and bentonite;

4. Granulation of urea - sulfur - bentonite melt and cooling of the product;

5. Packaging and storage of the finished product.

Optimal parameters for obtaining sulfur containing granular carbamide :

particle size of crushed bentonite, mm less than 0.1;

inlet temperature mixture of sulfur with bentonite, 95-100 °C;

concentration of urea melt, 99.7%.;

weight ratio $(NH_2)_2CO$: bentonite : sulfur 100 : (2-5) : (4.6 -9.2);

temperature of the mixing process, 137-140 °C;

duration of the process, 4-5 min;

granulation temperature, 137-140 °C;

temperature of the granule after cooling, 40-50 °C;

The principal technological scheme for the production of sulfur containing granular carbamide based on carbamide melt with the addition of a mixture of sulfur with bentonite is shown in Fig. 5.

The production of carbamide melt is carried out according to the technology for the production of pure granular carbamide. According to this scheme, the carbamide melt (99.7% $CO(NH_2)_2$) after the evaporator (6) enters the mixer (9), while simultaneously from the hopper (7) a mixture of sulfur and bentonite enters. At 137-140 °C the mixture is stirred for 4-5 min. After that, the process is carried out according to the traditional scheme: granulation, cooling and packaging. After that, the process is carried out according to the traditional scheme: granulation, cooling and packaging. According to which the sulfur containing granular carbamide melt is sent to the granulation tower, where it is sprayed through the granulator. At the bottom of the granulation tower there are metal cones through which air enters. Air is sucked into the tower by fans through holes in the lower part of the tower, cools drops of sulfur-containing urea melt falling towards it. Hardened granules from the bottom of the tower fall on the belt conveyor, then passing through the fluidized bed pellet cooling apparatus, it is transported through the belt conveyor and the elevator to the finished product warehouse. At the same time, the temperature of the chilled product in winter should not exceed 27 °C, and in summer it should be in the range of 45-50 °C. Thus, a technology for producing sulfur-containing granular urea using existing technological equipment for urea production has been proposed. The material balance of obtaining 1 ton of sulfur containing granular carbamide was calculated (Fig. 6).

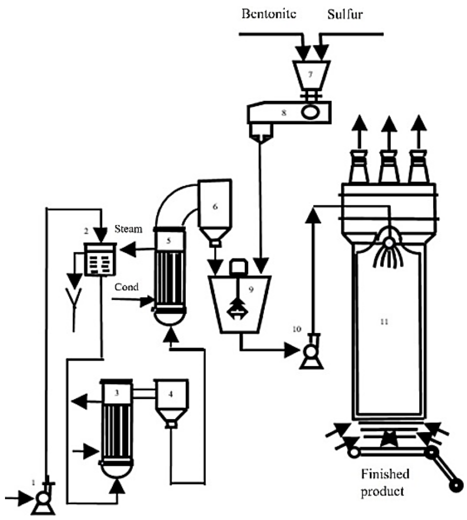

Fig. 5. Schematic diagram of the production process of sulfur containing granular carbamide. 1, 10 - pumps; 2 - water seal; 3- evaporator; 4 - separator; 5 - evaporator; 6 - vacuum dryer; 7 - bunker; 8 - dispenser; 9 - mixer; 11 - granulation tower

Рис. 5. Принципиальная технологическая схема процесса получения серусодержащего гранулированного карбамида. 1, 10 - насосы; 2 - гидразатвор; 3- выпарной аппарат; 4 - сеператор; 5 - выпарной аппарат; 6 - вакумм сушилка; 7 - бункер; 8 - дозатор; 9 - смеситель; 11 - грануляционная башня

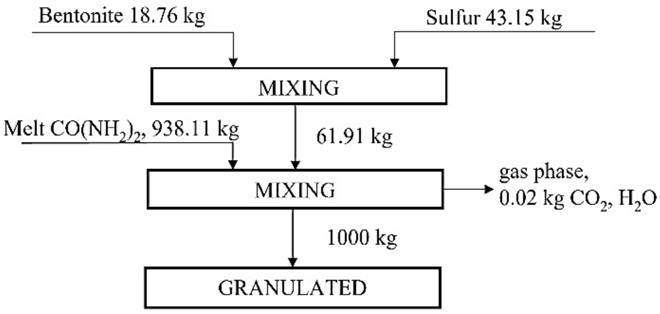

Fig. 6. Material balance of obtaining sulfur containing granular carbamide

Рис. 6. Материальный баланс получения серусодержащего гранулированного карбамида

CONCLUSION

The performed studies allow us to conclude that the mixing of sulfur with bentonite not only affects the surface tension between the two phases of sulfur and carbamide to obtain a homogeneous mass, but also has a positive effect on the properties of carbamide by influencing the formation of a more stable and compact crystal structure of carbamide granules. Sulfur containing granular carbamide granules have a weaker solubility compared to pure carbamide, i.e. they will gradually give away nutrients, by reducing the rate of dissolution of fertilizer granules, nitrogen losses in the soil are reduced, sulfur and bentonite in the composition of urea increase its agrochemical efficiency, which help to significantly improve the agrochemical and agrophysical properties of the soil and increase its fertility.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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