Technology and physico-chemical properties of humic urea obtained on the basis of urea melt and oxidized coal.

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Annotation: The article presents the results of studying the decrease in the content of free ammonia in carbamide granules by adding oxidized coal to the melt of urea before granulation, the commodity properties of fertilizers are determined: hygroscopicity, moisture capacity, caking, granule strength. An electron microscopic study of humic carbamides has been carried out. It is shown that when oxidized coal is added to the carbamide melt before granulation, it neutralizes free ammonia, due to this, pores do not form inside the carbamide granules, unlike standard urea. A basic technological scheme has been proposed, an optimal technological regime has been given, and the material balance for the production of humic carbamide has been calculated. The distinctive characteristics of humic carbamide compared to urea obtained without the addition of oxidized coal are shown. The possibility of stopping the release of ammonia from the finished product into the atmosphere due to the binding of free ammonia by oxidized coal contained in the carbamide melt in the process of obtaining humic urea is substantiated.

Keywords: *urea, ammonia, humic acid, oxidized carbon, biuret.*

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Introduction. Currently, all over the world, more and more attention is paid to the use and production of humic fertilizers along with mineral fertilizers, their raw material base, analysis methods, methods of application, and production technologies are expanding. Integrated systems for the use of mineral fertilizers in combination with humic substances are being developed in order to create the most optimal conditions for the development of plants and obtain high and high-quality yields, taking into account the state of the soil, plant species and other conditions [1,2].

It is known that, at present, carbamide is used all over the world as a nitrogen fertilizer. Carbamide is a universal type of fertilizer suitable for the treatment of 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 650 thousand tons per year [3].

It should be noted that due to the high solubility in water and the low content of humic substances in soils, carbamide and other nitrogen fertilizers have an efficiency of about 30-40%, the rest is washed into subsoil horizons and leads to pollution of subsoil waters, reservoirs, lakes, rivers and seas. In addition, low efficiency leads to an increase in the rates of these fertilizers. When using humic-containing mineral fertilizers, humic substances that are part of fertilizers in the soil contribute to the adsorption of nutrients and moisture, while reducing the possibility of leaching of nutrients [4,2].

In, the results of studying the effect of humic acids on the physicochemical properties of the soil, microbial diversity and enzymatic activity during continuous cultivation of peanuts are presented. Compared to control experiments, humic acids increased the yield and quality of peanuts in continuous cultivation. To elucidate the mechanism of the influence of humic acids, various soil indicators were evaluated and compared. It has been shown that humic acids increase the content of available forms of nutrients. In addition, the activity of urease, sucrase and phosphatase in the soil increased significantly after treatment with humic acids. Thus, humic acids have improved the yield and quality of peanuts in continuous cultivation due to improved physico-chemical properties, enzymatic activity and microbial diversity of the soil, which is useful for eliminating the obstacles associated with continuous cultivation of peanuts[5].

Humic substances are a readily available and inexpensive material that is used to increase crop yields and improve the efficiency of mineral fertilizers. The effect of urea with and without addition of humic components derived from weathered coal on corn yield and nitrogen nutrient efficiency was studied. Humic components are obtained by extraction at pH 3-4, 6-7, 9-10. At harvest, the dry biomass of plants grown with urea enriched with humic substances was increased by 11.50-21.33% compared to plants grown with urea. Also, the yield of corn when treated with urea enriched with humic substances was 5.58-18.67% higher than when treated with urea. This high yield was due to an increase in the number of grains per plant rather than the weight of individual grains. The absorption of N fertilizers when treated with urea enriched with humic substances was also higher than when treated with urea, by 11.49-29.46%, while unaccounted for N losses decreased by 12.37-30.05%. In the soil layer of 0-30 cm, when treated with urea enriched with humic substances, more nitrogen was retained than when treated with urea. The results of all three options did not differ significantly. However, the studied humic fertilizers obtained as a result of extraction, with pH values from 6 to 7, led to the best improvement of all evaluation targets [6].

Positive results were obtained from the use of urea in combination with humic substances in the foliar feeding of sugar cane. Three different foliar applications were used in this study: 1. urea; 2. urea with humic substances; 3. Urea with humic acid. It has been shown that when sugar cane is foliarly fed with urea in combination with humic substances and humic acid, nitrogen is quickly absorbed and stored in the form of protein and starch. Also caused changes in photosynthesis, the internal efficiency of the use of water and other substances. These results showed the promise of using humic substances with urea to improve sugar cane compared to using urea alone[7].

By studying of the effect of urea and urea-humic acid on the amount and form of absorbed nitrogen and on the growth of rice development are presented. The results showed that the urea-humic fertilizer increased the content of ammonium and nitrate forms of nitrogen in the soil, increased plant height, number and total dry weight of rice. The mass of harvested grain was 22% more compared to the control[8].

There is a method for obtaining a humated mineral fertilizer is given, according to which carbamide granules are treated with powdered potassium humate with a moisture content of 12% while they are mixed together in a rotating drum. The mixing of carbamide with potassium humate is carried out at their ratio (25-30):1. Then it is sprayed with vigorous stirring with a 10% solution of potassium humate and urea-formaldehyde resin, enveloping the primary humate shell with a second layer. Humatized carbamide is dried and then fed for packaging[9].

A patented method for obtaining mineral fertilizer in a humate shell has been patented. Fertilizers are obtained by mixing and granulating the mineral component (urea, ammonium sulfate, precipitate, ammonium and diammonium phosphate, nitrophoska, simple and double superphosphate) (20-50 wt %), alkali metal humate (Na, K, NH_3) (0.1 -10 wt %) and soil nutrient mixture with vermicompost. First, humic substances in liquid form in the amount of 0.1-3 wt % are added to the shell of the mineral fertilizer or to the pulp. Then, at a temperature of 80-100°C, it is dried. Then the resulting fertilizer is mixed with a soil-nutrient mixture with a moisture content of 60-65% and subjected to granulation[10].

There is also a method for obtaining organomineral fertilizer by mixing brown coal with urea. Mixing is carried out at a ratio of components of 1 : 1, and the resulting mixture is subjected to treatment with high-frequency electromagnetic radiation with a frequency of 2450 ± 50 MHz for 7-10 minutes[11].

There is a method for the production of a slowly soluble nitrogen fertilizer, 13.5 kg of finely ground brown coal is mixed with 4.1 kg of powdered urea. Thereafter, 337 g of concentrated HNO_3 are added to the mixture, followed by 84 g of NaOH dissolved in a small amount of water. Then, 14 kg of an aqueous solution of NH_4OH with sp. the weight. 0.880 g/cm^3. The gel is dried and used as fertilizer[12].

To assess the physical and mechanical properties and agro-chemical efficiency of urea with the addition of sodium humate are presented. Samples of an experimental batch of carbamide obtained at the Novomoskovsky Production Association "Azot" by introducing 0.1% sodium humate into the melt before its granulation were subjected to tests. It is shown that with the introduction of sodium humate, caking decreases, and hygroscopicity increases compared to the control sample. To assess the agrochemical effectiveness of carbamide with sodium humate, this fertilizer was tested in open ground. The research results indicate that under dry conditions, the addition of sodium humate to carbamide provided an increase in wheat yield. The use of sodium humate not only increased the yield of wheat, but also affected the quality of the grain. With the pre-sowing application of the drug in the amount of 13 kg/ha in a mixture with carbamide, the mass of gluten in the grain increased by 0.5%, with post-sowing - by 1.9% [13].

From the above, it can be seen that the production of mineral fertilizers with the addition of humic substances and humates increases their agrochemical efficiency and environmental safety.

Based on the foregoing, the processes of obtaining humic carbamide based on the melt of carbamide and oxidized brown coal of the Angren deposit with hydrogen peroxide in an alkaline medium were studied. To obtain humic carbamide, brown coal was used as the initial organic component, having the following composition (weight %): moisture 15.66; ash 14.90; organic 69.44; humic acids 3.82% and fulvic acids 0.91% on organic mass. To increase the content of humic acids, this coal was subjected to oxidation with a solution of hydrogen peroxide in an alkaline medium created using a 40% potassium hydroxide solution. The oxidation process was carried out with a 10% hydrogen peroxide solution in an alkaline medium at a temperature of 70°C for two hours. The weight ratio of the organic part of brown coal to the anhydrous part of hydrogen peroxide and potassium hydroxide solution was 1 : 0.2 : 0.005. First, the coal was processed in a mechanical mortar with a solution of potassium hydroxide for 30 minutes. Then, the resulting mass was added to the tubular reactor, where a solution of hydrogen peroxide was pre-filled with stirring, and processed for 2 hours. As a result of oxidation, the resulting oxidized coal after drying and grinding had the following composition: moisture - 0.78%, ash - 9.18%, organic matter - 90.04% and, in terms of the organic mass of oxidized coal, humic acids - 52.96 %, fulvic acids - 3.25% and residual carbon - 43.79%. And the main component was the factory product (JSC "Maxam-Chirchiq") - carbamide ($CO(NH_2)_2$) grade A with a content of 46.3% N and oxidized coal of the above composition.

As a result of the research, the possibility of obtaining humic urea with sufficient granule strength has been shown. Granules of humic carbamide have a weaker solubility compared to pure carbamide, that is, they will gradually release nutrients, resulting in reduced nitrogen losses in the soil, humic substances in the composition of urea improve the moisture supply of plants, enhance biological activity and increase the number of microorganisms in the soil, which help to significantly improve the agrochemical and agrophysical properties of the soil and increase its fertility [14-16].

It is known that in industry the synthesis of carbamide is carried out at a temperature of 458-468 K and a pressure of 19-20 MPa from liquid ammonia and gaseous carbon dioxide. In the process of obtaining urea, a solution is formed consisting of water, carbamide, carbamate, ammonium carbonates and ammonia. The solution is subjected to distillation for thermal decomposition of carbamate and carbonates and removal of ammonia and carbon dioxide not converted into carbamide, and the extracted aqueous carbamide is processed into a solid product by granulation. During evaporation and granulation of carbamide at high temperature, one molecule of ammonia is released from two urea molecules, resulting in the formation of biuret. The increased content of biuret in the fertilizer reduces the germination of seeds, inhibits the growth and development of plants. Therefore, in the finished product, the content of biuret is allowed no more than 0.6% (highest) in grade A and 1.4% in grade B. The formation of biuret is observed to varying degrees at all stages of the process. The greatest influence on the increase in the yield of carbamide and the decrease in the formation of biuret is exerted by an excess of ammonia in the initial mixture against the stoichiometric amount determined by the molar ratio $NH_3 : CO_2 = 2$. Excess ammonia reduces the harmful effect of the water released in the process, and it binds water and thereby shifts the equilibrium of the reaction of the conversion of ammonium carbamate to carbamide towards the latter. Since the synthesis of carbamide is carried out in an excess of ammonia, the resulting product also contains free ammonia, therefore, when urea is released, the resulting product is not immediately packed in bags, to remove free ammonia, urea is stored in a warehouse for a certain time before packaging. At the end of the curing stage, the resulting solid product contains a certain amount of free ammonia, which was contained in liquid urea, is transferred to the curing and also to the cooling air, and therefore enters the atmosphere, polluting it.

Experimental technique.

To determine the binding of free ammonia found in the melt of urea with oxidized coal, special experiments were carried out. To do this, 100 g of urea was placed in a conical flask and dissolved in 300 cm^3 of water, 25% ammonia was added until 0.1% free ammonia was reached in terms of 100 g of carbamide, then oxidized coal was added at a mass ratio of $CO(NH_2)_2$: oxidized coal = 100 : (2.5-10) was stirred and filtered, and the content of free ammonia in the filtrate was determined according to the state standard 2081-2010. The results showed (Table - 1) that in the studied ratios in solutions where oxidized coal was added, the content of free ammonia was practically absent.

Table 1

The content of free ammonia in urea solutions and in humic carbamides

Components	Mass ratio $(NH_2)_2CO$: oxidized carbon				
	100 : 0	100 : 2,5	100 : 5	100 : 7,5	100 : 10
Mass fraction of free ammonia, %	0,09	0,01	0,002	0,0005	-

Based on the studies, the optimal technological regime was determined, the material balance was calculated, and a technological scheme for the production of humic urea was proposed [14–18].

The technological process for obtaining humic carbamide based on oxidized brown coal with hydrogen peroxide in an alkaline medium, created on the basis of a solution of potassium hydroxide and carbamide melt, consists of the following main stages:

1. Oxidation of brown coal with hydrogen peroxide in an alkaline environment;
2. Drying and grinding of oxidized coal;
3. Mixing 99.7% carbamide melt with oxidized coal;
4. Granulation of carbamide-humic melt and cooling of the product;
5. Packaging and storage of the finished product.

Testing of the technology for obtaining humic carbamide based on oxidized coal and urea melt was carried out on a laboratory model unit, consisting of a 0.5-liter cylindrical reactor made of 12X18H10T stainless steel, equipped with a paddle mixer driven by a motor. The required amount of granulated carbamide was loaded into the reactor and subjected to its melting. Oxidized coal was dosed into the urea melt gradually. The experiments were carried out at mass ratios of urea melt: oxidized coal from 100:2.5 to 100:7.5. The temperature in the thermostat in all cases was - 137-140 °C. The duration of mixing of the initial components was 2–4 min. The granulation of the blended products was carried out by simulating granulation in a granulation tower to obtain rounded granules, the appearance of which is close to the shape of traditional carbamide granules, but in black. To establish the necessary technological parameters for the process of obtaining humic carbamide, the experiments were carried out three times. The average compositions of the samples obtained are shown in Table 2.

Table 2

Composition of humic carbamides obtained on the basis of carbamide melt and oxidized coal with hydrogen peroxide in an alkaline medium

Mass ratio (NH2)2CO : oxidized carbon	Total N, %	Organic matter, %	Humic acids, %	pH (10% solution)	Moisture, %	Granule strength, MPa
100 : 2,5	44,98	2,43	1,14	8,06	0,14	2,11
100 : 7,5	42,77	6,98	3,19	7,64	0,16	2,72

Based on the approbation of the technology for obtaining humic urea at the pilot plant, the main technological parameters of the process were determined (Table 3), a basic technological scheme of production was proposed (Figure 1) and material flows were compiled (Figure 2)

Table 3

The optimal technological regime for the process of obtaining humic urea

№	Main process parameters	Parameter values
1	crushing coal to particle size	less than 1 mm
2	hydrogen peroxide concentration	10%
3	potassium hydroxide concentration	40%
4	weight ratio of the organic part of coal to H_2O_2	1 : 2
5	weight ratio of the organic part of coal to potassium hydroxide	1 : 0,005
6	concentration of carbamide melt, %	99,7
7	weight ratio carbamide : oxidized carbon	100 : 2,5 : 7,5
8	temperature of the mixing process, °C	137-140
9	process duration, min	4-5
10	granulation temperature, °C	137-140
11	pellet temperature after cooling, °C	40-50

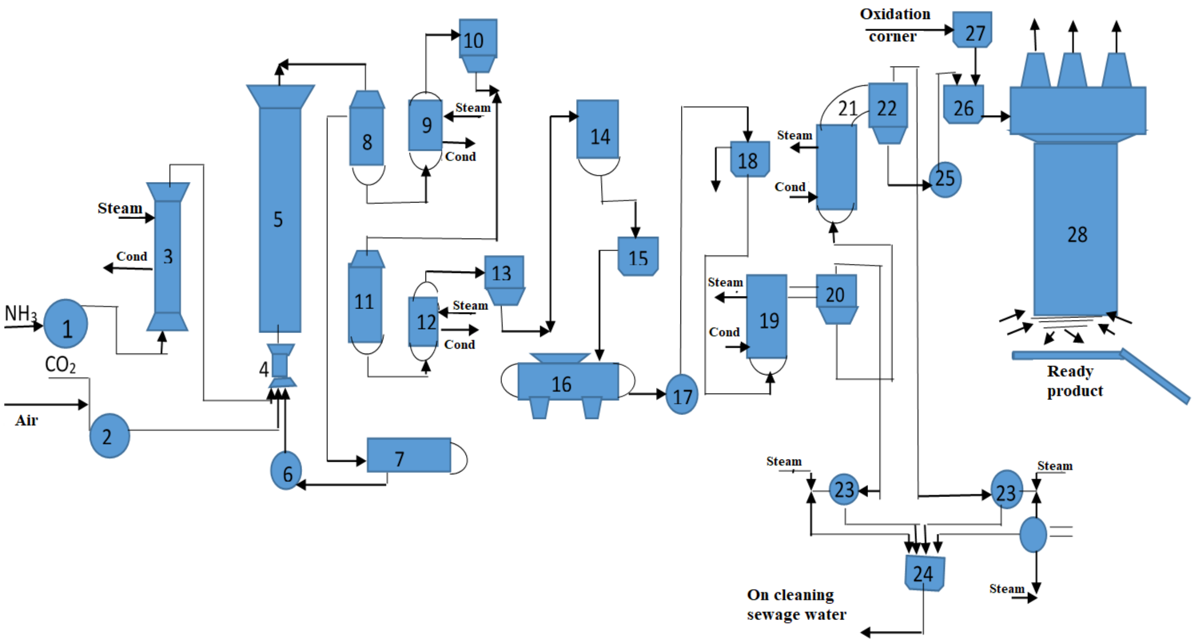

Fig - 1. **Figure 1.** Principal and technological scheme for obtaining humic urea

1- plunger pump for ammonia; 2 - CO_2 compressor; 3 - heater; 4- mixer; 5- synthesis column; 6, 17, 18, 25 - pumps; 7- gas mixer; 8 - distillation column (1-stage); 9, 21 - heater (1-stage); 10 – 1-stage separator; 11- distillation column (2-stage); 12 - heater (2-stage); 13

– 2-stage separator; 14- mixer; 15, 23 - hydraulic seal; 16 - solution collector; 19-evaporator (1-stage); 20 – 1-stage separator; 21- evaporator (2-stage); 22-vacuum dryer; 26 - mixer; 27 - container for oxidized coal; 28 - granulation tower.

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 (21) enters the tank (22). Next, the carbamide melt, having a pH value of 7.5-8.0, is pumped into the pressure tank (26), and oxidized coal is simultaneously supplied here from the bunker (27). At 137-140 °C, the mixture is stirred for 3 minutes, then it enters the homogenizer by gravity in order to obtain a homogeneous mass. After that, the process is carried out according to the traditional scheme: granulation, cooling and packaging. According to which the melt of humic urea enters 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 humic urea melt falling to meet it. Hardened granules from the bottom of the tower fall on the belt conveyor, then passing through the pellet cooling apparatus in a fluidized bed, 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 within 45-50°C.

The proposed scheme allows the production of both humic and humated urea with the addition of potassium humate or other types of humates. Thus, a technology for the production of humic urea with the addition of oxidized coal using the existing technological equipment for the production of carbamide has been proposed. The material balance of obtaining 1 ton of humic urea was calculated (Figure - 2). The data are given on the basis of the results of laboratory studies and experimental work carried out on a model facility.

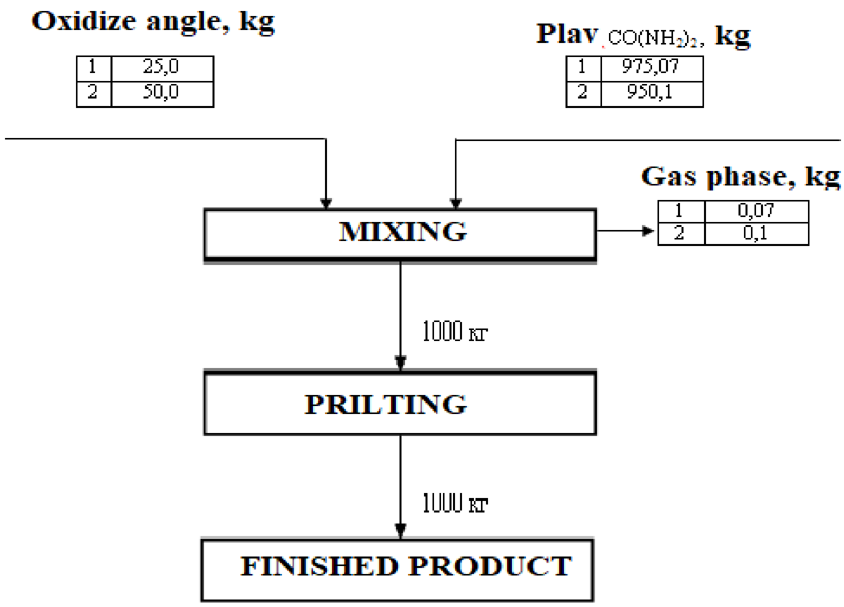

Figure. 2 Material balance of obtaining humic carbamide

As already noted, the physicochemical properties of fertilizers are one of the most important characteristics that are important during storage, transportation and application to the soil, which also determine the agrochemical efficiency. In connection with the above, the physicochemical properties of humic carbamide have been studied. Granules of initial urea and humic urea were selected for study, obtained at a ratio of melted carbamide : oxidized coal = 100 : 5.

Figures 3-8 show an electron microscopic photograph of the surface of the granule and the internal section of the granule of the original carbamide and

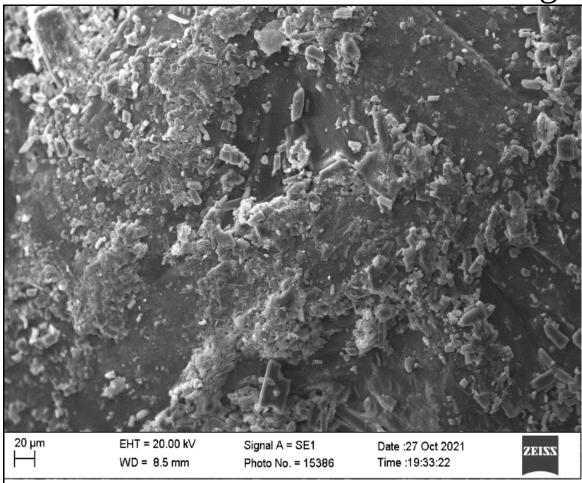

Figure 3. An electron microscope photograph of the surface of a carbamide granule

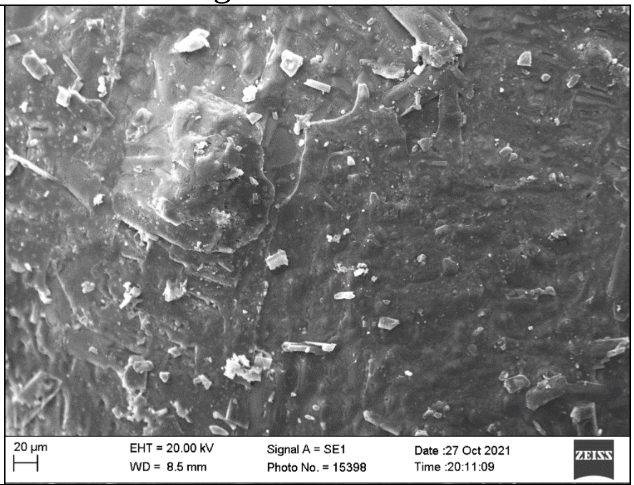

Figure 4. Electron microscopic photograph of the surface of a humic urea fertilizer granule

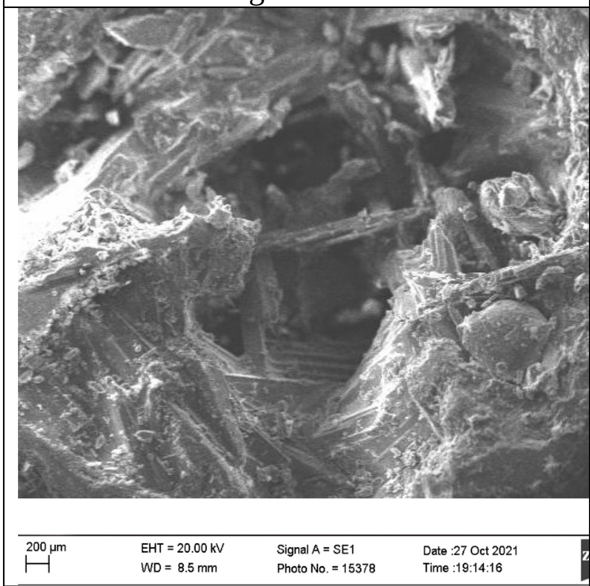

Figure 5. Electron microscopic photograph of the internal section of a carbamide granule

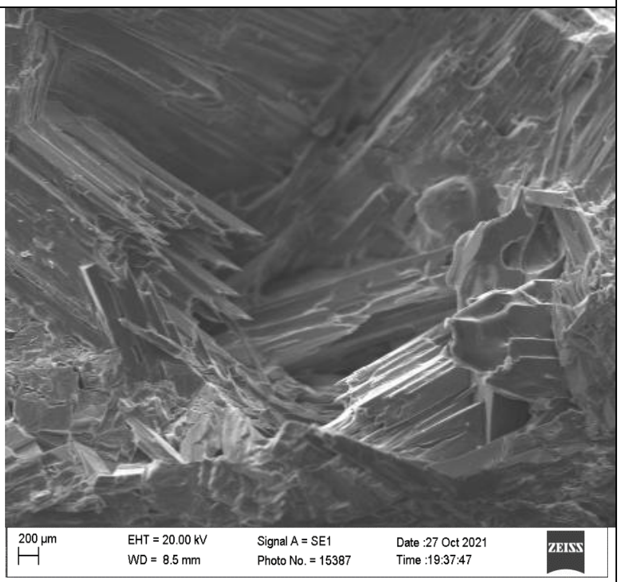

Figure 6. Electron microscopic photograph of the internal section of a humic carbamide granule

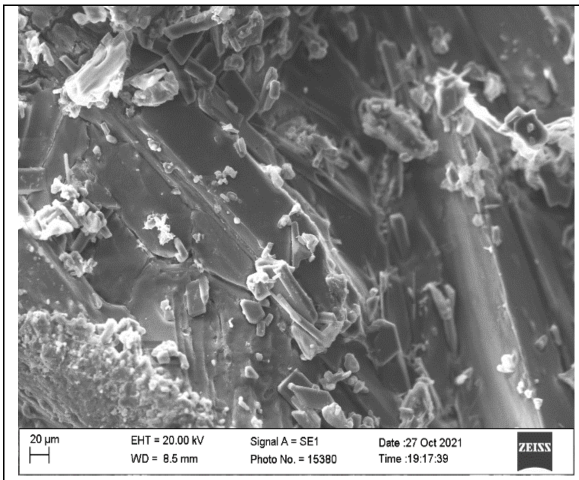	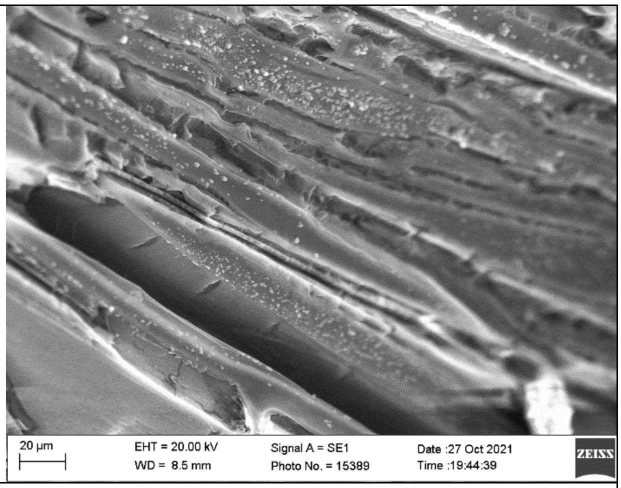
Figure 7. Electron microscopic photograph of the internal section of a carbamide granule	Figure 8. Electron microscopic photograph of the internal section of a humic carbamide granule

humic urea. It can be seen from them that the surface of the granules of the original and humic carbamide are almost the same and do not have pores, as well as cracks, however, inside the section, the granules of the original urea, unlike humic carbamide, have different pores, especially in the center of the carbamide granule (Fig. 6). In addition, the granules of humic carbamide are more monolithic than the granules of the original urea. The results of an electron microscopic study show that when oxidized coal is added to the urea melt, free ammonia is neutralized before granulation, due to this, pores are not formed inside the carbamide granule, unlike standard urea.

The main physical and chemical properties of humic carbamides are also determined. To determine the hygroscopic point of humic fertilizers, the desiccator method according to N.E. Pestov was used at a temperature of 25□ C, 2-3 mm granules. The initial moisture content of the original carbamide and two samples of humic carbamides were 0.17, 0.21, 0.24, respectively. The measurements carried out showed that the tested fertilizers had the following hygroscopic points: sample 1 - 74.21%; sample 2 - 79.14%; 3 - 81.22% relative humidity. In accordance with the scale of N.E. Pestov, according to the degree of hygroscopicity, humic urea belongs to weakly hygroscopic substances. Also, for two samples of humic fertilizers, the kinetics of water vapor sorption at 25°C was determined. It has been established that the equilibrium between the pressures of water vapor over humic fertilizers occurs: at a relative air humidity of 65% - after 2-4 days, 90% - after 5-7 days and 95% - after 14-15 days. At 100% relative air humidity, equilibrium was established slowly after 21–22 days.

The sorption capacity of humic carbamides was also determined at relative air humidity of 65, 70, 80, 90 and 95%. The results show that at a relative air humidity of 65%, sample 2 absorbs moisture in the amount of 2.3%, and at 80% humidity, the moisture content in it reaches 4.2%. At the same time, the granules retain their appearance, but their friability is lost with increasing moisture. With an increase in humidity, the fertilizer granules begin to moisten due to the transition of soluble urea and humate into the liquid phase. At 65%

humidity, both fertilizers remain completely crumbly. To determine the caking ability of humic carbamide at a relative air humidity of 65%, a fertilizer with a certain granulometric composition was poured into gauze bags and pressed for one day. After that, they were dried at 100-105 C to a constant weight, then dropped from a height of 1.5 m and sifted through a sieve with a diameter of 3 mm. The caking of humic carbamide was determined depending on the initial moisture content and load. At the initial humidity and moistening up to 2.1%, the fertilizers practically did not cake. The strength of humic carbamides with granule sizes of 2-3 mm was determined by the well-known method N.E. Pestov. The average strength of the granules for the second and third samples was 2.31 and 2.72 MPa, respectively. Thus, the commercial properties of fertilizers were determined: hygroscopicity, moisture capacity, caking and strength of granules obtained on the basis of oxidized coal and urea melt. It is shown that when oxidized coal is added to the carbamide melt before granulation at the above ratios, the strength of the granules increases, the dissolution rate decreases, which leads to a slowdown in hydrolysis and nitrification in the soil, and the nutritional value increases due to the introduction of additional nutrients.

Conclusions.

The process of obtaining humic carbamide by oxidation of Angren brown coal with hydrogen peroxide in a weakly alkaline medium created with potassium hydroxide and subsequent addition of oxidized coal to the melt of carbamide before granulation has been studied. The oxidation process was carried out with a 10% hydrogen peroxide solution in an alkaline medium at a temperature of 70 °C for two hours. The weight ratio of the organic part of brown coal to the anhydrous part of hydrogen peroxide and potassium hydroxide solution was 1 : 0.2 : 0.005.

Experiments have shown the possibility of obtaining humic carbamide with sufficient granule strength. Granules of humic urea have a weaker solubility compared to pure urea, that is, they will gradually release nutrients, resulting in reduced nitrogen losses in the soil.

The commercial properties of fertilizers were determined: hygroscopicity, moisture capacity, caking, strength of granules. An electron microscopic study of humic carbamides has been carried out. It is shown that when oxidized coal is added to the carbamide melt before granulation, it neutralizes free ammonia, due to this, pores do not form inside the carbamide granules, unlike standard urea. A basic technological scheme has been proposed, an optimal technological regime has been given, and the material balance for the production of humic carbamide has been calculated.

When using humic carbamide in agriculture, the content of humus in the soil will certainly increase, the structure, physical and mechanical properties of the soil will significantly improve. Due to the content of all nutrients necessary for plants, it is possible to obtain higher and better yields, the nutritional properties of plants and their viability to diseases are increased. In addition, the introduction of oxidized coal into the melt of urea reduces ammonia emissions during storage of the finished product in a warehouse before packaging.

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