(54) Method for preparation of chlorine-free NPK fertilizer

The invention refers to technology for the preparation of complex mineral fertilizers, in particular chlorine-free fertilizers, through the decomposition of natural phosphates by nitric acid. The essence of the method is that the ammoniation of a nitrate-phosphate solution is carried out first to a pH [value of] 2.5-3.0 and then to a pH [value of] 5.8-6.0; the prepared solutions are evaporated to a residual moisture content of 0.4-1.0%, and a homogeneous, low-viscosity fusion cake is obtained as the result; the NPK fertilizer is [then] granulated by prilling, where in this case potassium sulfate is used as a potassium component and is added directly before prilling. The method provides a preparation of NPK fertilizer that contains sulfur in a water-soluble form and has high agrochemical efficacy.
3 tables.

Specification

The present invention relates to technology for the preparation of mineral fertilizers and can be used in the production of prilled complex fertilizers.

A method is known for the preparation of complex NPK fertilizers, which involves the nitric acid decomposition of natural phosphates, separation of insoluble impurities by precipitation, freezing out and separation of calcium nitrate from the NP solution, adding either phosphoric acid or ammonia, mixing the solution with potassium sulfate, removing calcium sulfate, evaporating the solution and finally granulating or prilling. [Patent, India, № 168731, IPC C 05 D 11/00, 16.12.1986]

The disadvantages of the method are as follows:

- the cumbersome manufacturing scheme;
- the formation of production wastes (insoluble impurity residues, calcium sulfate);
- the two-stage removal of calcium from the decomposition solution (freezing and precipitating with the use of potassium sulfate, which increases the complexity and costs of the scheme);
- the removal of calcium in the form of calcium sulfate or technical gypsum, which is not widely used;
- the use of an additional reagent – phosphoric acid.

As for the technical essence and the result attained, the most similar method to that offered is the preparation of chlorine-free NPK fertilizers according to which the phosphate raw material is decomposed with nitric acid and a portion of calcium in the form of calcium nitrate is separated from the decomposition solution by crystallization and filtration. The filtrate obtained – a nitrate-phosphate solution – is ammoniated in two steps. In the first step, this is performed with the use of gaseous ammonia to pH = 1.5, and in the second step with aqueous and/or gaseous ammonia to pH = 5.0-5.5. The neutralized solution is evaporated to a slurry that contains 10-20% residual moisture; potassium sulfate is added to this, and it is simultaneously granulated and dried to give the finished product

[Patent RU № 2141462, IPC C 05 B 7/00]. The product prepared according to the prior art is granulated in a drum. The essence of this method lies in the dispersion of the slurry into a finely-ground unconditioned product (recycle) in the rotating drum that results in the formation of granules with an irregular form.

The disadvantages of the method are as follows:

- impractical implementation of the ammoniation of the nitrate-phosphate solution, namely, the ammoniation in the first step to pH = 1.5 leads to an intensive ammoniation in the second step, which gives a rise to the occurrence of local supersaturation and an increase in the solution viscosity. This is associated with the precipitation of impurities (calcium, aluminum and iron compounds, etc.) under unfavorable conditions, which causes the formation of finely-dispersed crystals that have a distorted (semi-amorphous) crystalline lattice. Under conditions of supersaturation, calcium precipitates as a rule in the form of finely-crystalline tribasic calcium phosphate;
- it is impractical to use aqueous ammonia in the second step, since additional water is introduced that must later be evaporated;
- a significant moisture content in the slurry after mixing with potassium sulfate and before granulation. This results in the occurrence of an ion-exchange process between potassium sulfate and calcium compounds with the formation of calcium sulfate. The interactions indicated cause the transformation of the water-soluble sulfur species (potassium sulfate) into a common form (calcium sulfate), which decreases the agrochemical efficacy of the fertilizer;
- drying of the product is required;
- the granules have an irregular form.

The objective of the present invention is the development of a method for the preparation of chlorine-free NPK fertilizers that contain sulfur in a water-soluble form and have high agrochemical efficacy, through the use of a simple and practical manufacturing scheme followed by granulation by prilling.

To realize said objective, a method is offered wherein the distribution of the neutralizing reagent for the ammoniation steps, namely gaseous ammonia, is more practical, and which comprises the evaporation of the obtained ammoniated solution to a low-viscosity homogeneous fusion cake, mixing it with potassium sulfate and the granulation of NPK fertilizer by the prilling method. The physicochemical properties of the fusion cake play a significant role for the granulation performed by prilling. The slurry obtained according to the method indicated in the prior art cannot be used for granulation by prilling in towers because of its significant moisture content and high viscosity. In the method offered, the low-viscosity homogeneous fusion cake obtained is dispersed into the tube of the granulating tower, while the globules are cooled by a countercurrent air flow, and spheroidal granules are formed.

According to the method claimed, chlorine-free NPK fertilizer that contains sulfur in a water-soluble form is prepared by the nitric acid decomposition of an apatite concentrate, accompanied by freezing out of calcium nitrate and its further processing into the product chalk, neutralization of the nitrate-phosphate solution with gaseous ammonia in two steps, the first step to pH = 2.5-3.0 and the second to pH = 5.8-6.0, evaporation to a residual moisture content of 0.4-1.0 mass%, mixing with potassium sulfate, and granulation by prilling.

The technical result attained is as follows:

- a more practical distribution of the neutralizing reagent, namely gaseous ammonia, in the ammoniation steps, which avoids local super-ammoniation and increases the solution viscosity;
- the use of gaseous ammonia instead aqueous ammonia in the second ammoniation step decreases [both] the loading of the evaporation system and the use of additional amounts of water at other stages of the technological process, for example, for rinsing the calcium nitrate or chalk;
- the nitrate-phosphate solution is evaporated to a residual moisture of 0.4-1.0 mass%, which provides a homogeneous salt fusion cake;
- good rheological properties (viscosity, homogeneity) of the fusion cake obtained allows the preparation of the fertilizer by the prilling method;
- the prepared product does not require drying;
- the preparation of the product in a spheroid form improves its marketable appearance;
- the product prepared contains sulfur in a water-soluble form, which is an additional nutrient and leads to an increase in the agrochemical value of the fertilizer;
- the preparation of chlorine-free NPK fertilizer with high agrochemical efficacy.

Example 1. Industrial testing of the offered method was carried out by operating the nitroammophoska process in accordance with the following scheme.

The nitric acid decomposition of an apatite concentrate was performed with 58% nitric acid at 55 – 60 ºC with the consumption of 1.3 t of 100% acid per 1 t of apatite concentrate.

Then the decomposition solution was cooled down to (-7) ~ (-10) ºC, and the calcium nitrate crystals formed were separated and processed into chalk. The nitrate-phosphate solution was neutralized with gaseous ammonia in two steps: the first step gave a pH = 2.5-3.0 and the second step gave a pH = 5.8-6.0, with simultaneous dilution with ammonium nitrate solution. The ammoniated solution was evaporated to a residual moisture of 0.5-0.7 mass%, this was then mixed with potassium sulfate in the ratio of NP:K_2SO_4 = 2.5:1, and granulated by prilling in a tower. For this case, the product obtained had the composition presented in Table 1.

The efficacy of NPK that contains potassium sulfate was tested under field conditions for humic podzol soils. The use of said fertilizer increased crop yields and the quality of various plantings by 15-

35% in comparison with the control, and by 4-6% in comparison with the use of NPK that contains potassium chloride (Table 2). During the agrochemical testing, a high return on the fertilizer cost was observed, due to good crop yields for a number of plantings (Table 3).

Claim

A method for the preparation of chlorine-free NPK fertilizer that comprises the nitric acid decomposition of a phosphate raw material, freezing and separating out of calcium nitrate, ammoniation of the nitrate-phosphate solution, evaporation, mixing with potassium sulfate and granulation, wherein the ammoniation of the nitrate-phosphate solution is performed with the use of gaseous ammonia in two steps, in the first step to a pH = 2.5 ~ 3.0 and in the second step to a pH = 5.8 ~ 6.0, the evaporation is carried out to a residual moisture of 0.4 ~ 1.0 mass% to yield a low-viscosity homogeneous fusion cake, and an NPK fertilizer that contains sulfur in a water-soluble form is granulated by prilling.

Chemical composition of the finished NPK product with potassium sulfate (mass%) Table 1

№	N general	P_2O_5 assimil.	N/ P_2O_5	P_2O_5 aq.	K_2O	S	Cl	Moisture
1	16.4	16.1	1.02	12.5	15.4	5.7	0.2	0.26
2	16.7	16.5	1.01	12.8	15.4		0.25	0.22
3	16	15.8	1.01	13.1	15.7		0.42	0.18
4	16	15.8	1.01	13.1	15.7		0.37	0.33
5	16	16.5	0.97	13.3	16.1	5.8	0.29	0.29

Chlorine-free ammophos effect on the crop yield Table 2

Experiment Variants	Crop yield, centner/hectare[1]						
	Many types of grass	Barley grain	Potato	Cabbage	Fiber flax		
					Straw	Seed	Fiber
Control (without fertilizer)	135.5	17.5	178.0	895.0	42.5	6.0	6.7
NPK containing	160	22.8	194.5	974.5	54.0	7.6	8.7

[1] “Centner” is a unit of weight used in the former Soviet Union that is equal to 220.46 pounds <*editor*>.

KCl							
NPK containing K_2SO_4	167.0	23.6	203.0	1035.0	58.5	8.0	10.0
Significant difference, centner/hectare	19.9	1.7	11.8	42.5	7.1	1.1	1.2

Reimbursement of fertilizer nutrients by crop yield (kg/kg) Table 3

Experiment variants	Many types of grass	Barley grain	Potato	Cabbage	Fiber flax		
					Straw	Seed	Fiber
NPK containing KCl	16.7	4.9	10.9	26.7	10.0	1.5	1.7
NPK containing K_2SO_4	26.7	5.2	10.0	47.8	14.2	2.0	2.7