Method of obtaining lime-ammonia fertilizer

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Resume: The invention relates to the production of mineral fertilizers. Lime-ammonium fertilizer is obtained by mixing ammonium nitrate melt with crushed carbonate raw materials containing calcium carbonate or calcium and magnesium carbonate, granulating the mixture, drying and cooling the product, while before mixing with ammonium nitrate melt, crushed carbonate raw materials are treated with ammonium hydrosulfate with a concentration of $20 \div 45$ wt.% in the ratio of mass parts 1:(0.01÷0.3). The crushed carbonate raw material has particle sizes from 0.8 mm to 1.5 mm, and granulation is carried out in a drum granulator at 80-90°C.

Key words: Lime-ammonia fertilizer, melt, mixture granulation, ammonium nitrate, carbonate raw materials, concentration.

The invention relates to the production of mineral fertilizers, in particular to methods for obtaining granular lime-ammonium nitrate, as well as other complex granular fertilizers based on ammonium nitrate and magnesium carbonate and / or calcium, intended for use in agriculture, and can be used in the chemical industry.

A method for obtaining lime-ammonia fertilizer is known, consisting in mixing the floating of ammonium nitrate with crushed chalk and subsequent granulation of the mixture [1]. Granulation by the method of application requires a deep pool of floating, which increases energy consumption. The interaction of calcium carbonate and ammonium nitrate at elevated temperatures leads to a decrease in strength and increased caking of the fertilizer due to the formation of calcium nitrate, as well as to the loss of ammonia ammonia nitrogen with waste gases through emissions from granulation towers due to the decomposition of ammonium carbonate.

A method for obtaining a complex fertilizer containing nitrogen, calcium and sulfur is known, including mixing the float of ammonium nitrate with components containing calcium and sulfur, granulation of the product in a drum granulator [2]. The disadvantage of the method is that when mixing the float of ammonium nitrate with a component containing calcium carbonate (limestone, chalk, dolomite, etc.), heating the mixture and subsequent granulation of the mixture, reactions occur with the formation of calcium nitrate and the release of ammonia, which reduces the quality of the product and leads to nitrogen losses.

A method for obtaining lime-ammonia fertilizer is known, including mixing the float of ammonium nitrate and the crushed lime component, granulation, drying and cooling of the product [3]. The technological method of separating the float into the mixed (with the lime component) and sprayed (mixture) parts does not reduce the reactivity of the components for the formation of calcium nitrate, which increases with increasing dispersion of the lime component, mixing temperatures, granulation and drying and the duration of mixing and granulation, but only limits the time of contact of the float with the lime component at high temperatures. Therefore, the growth of the mixed part does not sufficiently reduce the formation of calcium nitrate and ammonia losses.

The closest in technical essence is the method of obtaining lime-ammonia fertilizer, which consists in mixing the float of ammonium nitrate with crushed carbonate raw materials containing calcium carbonate or calcium and magnesium carbonate, granulation of the mixture, drying and cooling the product [4]. However, the introduction of an inhibitory additive containing a sulfate ion into a float and then, together with a float,

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into a mixture of float and carbonate raw materials does not sufficiently reduce the formation of calcium nitrate and ammonia nitrogen losses. The consequence of this is a deterioration in the quality of the granular product.

The proposed invention solves the problem of creating a lime-ammonia fertilizer. The main technical result of the invention is to reduce the loss of ammonia nitrogen, reduce the content of calcium nitrate or magnesium nitrate and calcium nitrate in fertilizer and, as a result, improve the quality of the product. The first additional technical result is the possibility of utilization of the absorption fluid obtained during the purification of gases captured in the production of complex fertilizer. The second additional technical result is to increase the strength and reduce the caking capacity of fertilizer granules.

The achievement of the main technical result is ensured by the fact that in the method of obtaining lime-ammonia fertilizer, including mixing the floating of ammonium nitrate with crushed carbonate raw materials containing calcium carbonate or calcium and magnesium carbonate, granulation of the mixture, drying and cooling of the product, the crushed carbonate raw materials are treated with a solution of ammonium nitrate with a concentration of 20-45 wt.% before mixing with a float of ammonium nitrate with a concentration of 20-45 wt.% subject to the mass ratio crushed carbonate raw materials and ammonium hydrogen sulfate equal to 1: $(0.01 \div 0.3)$.

At the same time, a solution of ammonium hydrosulfate with a concentration of $20\div45$ wt.% in the absorption liquid obtained by capturing the exhaust gases of the production of a complex fertilizer is used for processing (this ensures the achievement of the first additional technical result). In addition, the crushed carbonate raw materials can have particle sizes of the fraction from 0.8 millimeters to 1.5 millimeters, and granulation of the mixture is carried out in a drum granulator at $80\div90$ °C (this ensures the achievement of the second additional technical result).

To implement the proposed method, a melt of ammonium nitrate (ammonium nitrate), ammonium hydrogen sulfate (another name - ammonium monosulfate), crushed carbonate raw materials containing calcium carbonate carbonate or calcium and magnesium carbonate (hereinafter referred to as crushed carbonate raw materials) are used, as which dolomite, limestone, chalk, carbonate sludge, technical calcium carbonate, other raw materials containing calcium carbonate (calcium carbonate) are used. Crushed carbonate raw materials are used in the form of a dispersed powder (lime flour, crushed calcium carbonate, etc.) of different fractions. Ammonium hydrogen sulfate is used in the form of a $20 \div 45\%$ solution by weight (hereinafter referred to as wt.%) in water or in an absorption liquid obtained by capturing gases producing a complex fertilizer.

When treated with a solution of ammonium hydrogen sulfate, the solution is applied (sprayed) to the carbonate raw material. In this case, the solution is applied to the surface of the solid particles of the raw material. On the surface of the particles, calcium carbonate, magnesium $(CaMg(CO3)_2)$ or calcium carbonate (CaCO3) react with ammonium hydrogen sulfate (NH4HSO4) by reaction:

$$CaMg(CO_3)_2 + 2NH_4HSO_4 = CaSO_4 + MgSO_4 + 2NH_4HCO_3$$
 (1)
 $CaCO_3 + NH_4HSO_4 = CaSO_4 + NH_4HCO_3$, (2)

due to which a thin layer of calcium sulfate or calcium and magnesium sulfate, acidic ammonium carbonate is formed on the surface of solid particles of carbonate raw materials. With the subsequent mixing of the crushed carbonate raw materials with the ammonium nitrate melt, this layer isolates the solid particles from the float. Under conditions of temperatures that ensure and maintain the fluidity of the mixture, the formed layer, consisting mainly of calcium sulfate or calcium and magnesium sulfate, performs a protective function, limiting the reactivity of the crushed carbonate raw materials to the formation of magnesium nitrate and / or calcium nitrate by reactions:

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$$NH_{4}NO_{3} = HNO_{3} + NH_{3} \qquad (3)$$

$$CaO + 2NH_{4}NO_{3} = Ca(NO_{3})_{2} + 2NH_{3} + H_{2}O \qquad (4)$$

$$CaCO_{3} + 2HNO_{3} = Ca(NO_{3})_{2} + CO_{2} + H_{2}O \qquad (5)$$

$$CaO + 2HNO_{3} = Ca(NO_{3})_{2} + H_{2}O \qquad (6)$$

$$CaMgO + 2NH_{4}NO_{3} = Ca(NO_{3})_{2} + Mg(NO_{3})_{2} + 2NH_{3} + H_{2}O \qquad (7)$$

$$CaMg(CO_{3})_{2} + 2HNO_{3} = Ca(NO_{3})_{2} + Mg(NO_{3})_{2} + 2CO_{2} + 2H_{2}O \qquad (8)$$

$$CaMgO + 2HNO_{3} = Ca(NO_{3})_{2} + Mg(NO_{3})_{2} + H_{2}O \qquad (9)$$

The content of $_{\rm MgCO3}$ and CaCO3 in raw materials and the reactivity of raw materials to form magnesium nitrate and / or calcium nitrate depend on the specific type, composition of carbonate raw materials, features of its industrial processing. Since this layer is formed before mixing carbonate raw materials with a float, in comparison with the traditional method of introducing an inhibitory additive into the float [4], the formation of magnesium nitrate and calcium for various types of carbonate raw materials is significantly reduced. by preventing the occurrence of these reactions.

Since the decomposition of ammonium carbonate by reaction:

$$NH_4HCO_3 = NH_3 + CO_2 + H_2O$$
 (10)

begins at the stage of formation of the protective layer and is completed when mixed with a float, then the ammonia released due to the reaction at the mixing stage has a high degree of time to react with nitric acid, which is afloat in the form of an impurity:

$$HNO_3 + NH_3 = NH_4NO_3$$
 (11)

Due to pretreatment prior to mixing with play and forming a protective layer, ammonia losses due to the prevention of reactions (4), (7) and initiation (11) are significantly lower than when using the ingestion of introducing an inhibitory additive containing a sulfate ion into a float [4].

Sources

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