(54) Complex Ammonium Nitrate-Based Fertilizers and Methods for their Production

(57) Abstract

Field: mineral fertilizers.

The present invention relates to the production of mineral fertilizers and to technology for producing water-soluble complex fertilizers based on ammonium nitrate; it can be used in manufacturing, in the production of ammonium nitrate. Complex ammonium nitrate-based fertilizers comprising potassium nitrate are ternary and completely water-soluble N-K-Ca-containing fertilizers that include 5 – 15% of calcium nitrate, no more than 30% for the total of potassium and calcium nitrate, with ammonium, potassium and calcium nitrates in a mass ratio of (70-90):(5-20):(5-15), respectively, and no more than 0.01% of water-insoluble impurities. The mass ratio of nutrient elements and calcium macroelement is regulated within the range of N:K_2O:Ca = (29-33):(2-7.5):(1-3.5), respectively. Ternary mixtures of ammonium, potassium and calcium nitrates that contain a specified quantitative ratio of salts are granulated by prilling or by other known methods that use the equipment for producing ammonium nitrate; fertilizers are conditioned with the fatty amine-based additives, which are applied on the surface of the granules. Potassium and calcium nitrate are added to the fertilizer composition in the form of potassium carbonate solutions and calcium nitrate solutions that have been preliminarily purified from impurities. The invention allows the preparation of a completely water-soluble complex ternary NKCa-containing fertilizer that has improved agrochemical properties and reduced fire and explosion hazards.

4 claims and 4 dependent claims

Примечание [MFS1]: It looks like 1 claim and 7 dependent claims <*editor*>.

SPECIFICATION

The present invention relates to the chemical industry, and in particular to the production of mineral fertilizers and concerns compositions and methods for the preparation of complex ammonium nitrate-based fertilizers.

Ammonium nitrate is a fertilizer widely used in agriculture that contains nitrogen in an easily assimilable form.

The fertilizer is known to be physiologically acidic; therefore, the long-term application of ammonium nitrate leads to soil acidification and to a reduction in crop yield. (M. E. Pozin. “Mineral fertilizer technology”. L.: Khimiya. 1989, p.231).

The presence of only a single nutrient in the ammonium nitrate composition – nitrogen – reduces agrochemical value of the fertilizer.

Pure ammonium nitrate is strongly hygroscopic and tends to undergo caking while stored. (“Reference book for nitrogen researchers”. 2nd Edition. M.: Khimiya, 1987, p. 154). Insufficient mechanical strength of the ammonium nitrate granules (not more than 1.2 kg/granule) and the occurrence

of transformations are the reasons for the breakdown of the granules and further caking of the product during storage.

Ammonium nitrate possesses fire and explosive hazards, with the result that it is prohibited in a number of European countries because of the risks during storage and transportation; this has the effect of restricting the market opportunities for ammonium nitrate.

To eliminate the shortcomings inherent in ammonium nitrate, complex and mixed fertilizers based upon it are made through the use of various additives, the quantity and composition of which vary over a wide range.

The addition of nutrients and other useful elements to ammonium nitrate, in particular potassium, calcium and some microelements, imparts improved agrochemical efficacy to the fertilizer and an improvement in its physicochemical properties and performance characteristics. Moreover, the addition of some inorganic substances that are less dangerous than ammonium nitrate helps to reduce its fire and explosion hazard properties, and to expand its market opportunities.

One of the most frequently used ammonium nitrate-based fertilizers is lime ammonium nitrate (LAN), which is widely used in agriculture and has completely supplanted the application of ammonium nitrate in a number of European countries.

Methods are known for preparing lime ammonium nitrate and improving its properties ("Technology of ammonium nitrate". Edited by V. M. Olevsky. M.: Khimiya, 1978, pp. 240-247, RU 2077484 patent, 04.20.1997, US 3647412 patent, 07.03.1972, **EP** 00238972 patent, 16.09.1987, et al.). Lime ammonium nitrate is a granulated product, in which the mass fraction of ammonium nitrate is reduced to 53-80% due to the addition of calcium carbonate in the form of lime or chalk into the fusion cake or concentrated ammonium nitrate solution.

Calcium carbonate eliminates a number of the disadvantages of ammonium nitrate; in particular, soil acidification over the long-term application of this fertilizer. It improves the physicochemical properties and performance characteristics such as mechanical strength, and hydroscopic properties; it also reduces the tendency to caking, and reduces the ammonium nitrate fire and explosion hazards.

The disadvantages of lime ammonium nitrate are as follows:

- similar to ammonium nitrate, lime ammonium nitrate contains only one nutrient – nitrogen – from among the three elements (nitrogen, phosphorus and potassium) that are the most important for plant nutrition; this reduces its agrochemical value;
- due to the addition of an inert inorganic substance – calcium carbonate – the nitrogen content in lime ammonium nitrate (16 – 26%) is lower than that of ammonium nitrate (35%); therefore its nutrition value is inferior to that of ammonium nitrate;
- an additional macronutrient that is necessary for plants – calcium – is present in lime ammonium nitrate in water-insoluble form;

- lime ammonium nitrate contains 20-47% of water-insoluble calcium carbonate; therefore, it cannot be used for drip irrigation;
- the methods for the preparation of lime ammonium nitrate are technically rather complicated, as it is necessary both to grind lime or chalk to obtain a homogeneous mixture for a fusion cake or a concentrated ammonium nitrate solution that contains lime or chalk, and to use inhibiting agents.

A known nitrogen fertilizer based on ammonium nitrate contains ammonium nitrate and 6-24% of zeolite as an additive; the content of ammonium nitrate is thus reduced to 76-94%. (RU patent № 2111937, 09.05.98).

The fertilizer prepared has high agrochemical performance because of the properties of the zeolite added to the ammonium nitrate.

This fertilizer has the same shortcomings that are observed for lime ammonium nitrate.

Other kinds of fertilizers based on ammonium nitrate are known, which are prepared by the use of the method described in **Bulgarian** patent № 37123, 15.04.85.

The disadvantages of the fertilizers prepared through the use of the above method are as follows:

- the mass fraction of the additives in ammonium nitrate does not exceed 5%, which prevents the reduction of the fire and explosive properties of these ammonium nitrate-based fertilizers, and prevents the improvement of their physicochemical properties and performance characteristics;
- the amount of nutrients that are added to ammonium nitrate together with additives, in particular, potassium and phosphorus, is not sufficient for plant nutrition;
- the mechanical strength of fertilizer granules is low, not more than 1.6 kg/granule.

A complex nitrogenous potassium fertilizer that includes ammonium and potassium nitrate is the most similar to the fertilizer compositions offered as far as the technical essence and the result attained are concerned (RU patent № 21821446 10.05.02). In the method that is used, which is similar to the method of the prior art, potassium is added to ammonium nitrate in the form of a 30-70% aqueous potassium nitrate solution at 2-20 mass% based on the amount of ammonium nitrate at the stage of the ammonia neutralization with nitric acid.

The nitrogen mass fraction in the complex nitrogenous potassium fertilizer is 34.2-30.4% and the potassium mass fraction is 0.9-9.3% calculated as potassium oxide.

The disadvantages of the complex nitrogenous potassium fertilizer with the above composition, which contains ammonium and potassium nitrate (prior art), are as follows:

- the use of potassium nitrate, which is an expensive potassium raw material, leads to an increase in the cost of the fertilizer production;
- poor mechanical strength of granules, no more than 1.2 kg/granule;
- lower thermal stability compared to that of ammonium nitrate;

- decomposition of the granules upon minimal wetting, which increases their tendency to caking, worsens the product performance characteristics, and makes transportation, storage and application of the nitrogenous potassium fertilizer difficult.

The disadvantages of the complex nitrogenous potassium fertilizer (prior art) are presented on the basis of results obtained while studying its properties.

The objective of the present invention is the development of compositions for completely water-soluble complex ternary NKCa-containing fertilizers based on ammonium nitrate, which have improved physicochemical properties and performance characteristics, greater agrochemical value and reduced fire and explosive properties, and to develop methods for the preparation of fertilizers that have the above compositions.

The invention achieves the above objective by adding potassium nitrate and calcium-containing water-soluble calcium nitrate to ammonium nitrate.

Potassium nitrate is a valuable nitrogenous potassium fertilizer without inert material; however the application of potassium nitrate in agriculture as a fertilizer is limited due to its high cost; therefore, potassium carbonate (potash) is used for adding the second nutrient – potassium - to the composition of the complex ammonium-based fertilizers offered.

The choice of calcium nitrate is due to the fact that calcium nitrate is a physiologically alkaline fertilizer and contains a nutrient, nitrogen, and a plant macronutrient in the water-soluble form, calcium.

Calcium nitrate has a positive effect on the fire and explosion properties of granulated fertilizers and on their performance characteristics as well.

The addition of calcium nitrate to a mixture composition that comprises ammonium and potassium nitrate increases the temperature for the thermal decomposition of the fertilizer from 257-252 ºC to 264-262 ºC, and the rate of thermal decomposition of the fertilizer, which is measured as the rate of mass loss at 230-240 ºC, decreases by 15-35%, which indicates a reduction of fire and explosion hazard of the fertilizers.

The addition of calcium nitrate in the composition of the fertilizers offered increases the mechanical strength of the granules to 2.5 – 5 kg/granule, which is 2-5 times higher than that of the granules of the complex nitrogenous potassium fertilizer that contains ammonium and potassium nitrate (prior art).

In addition, in contrast to the complex nitrogenous potassium fertilizer (according to the prior art), wetting of the offered fertilizers to a moisture content of 3-4 wt.% does not lead to the decomposition of the granules. The fertilizers remain friable and retain their performance characteristics due to water fixation in crystalline calcium nitrate hydrates.

According to the present invention, complex ammonium nitrate-based fertilizers are prepared, which are ternary completely water-soluble NKCa-containing fertilizers, in which there is 5-15% of

calcium nitrate, the total amount of potassium and calcium nitrate does not exceed 30%, the mass ratio of ammonium nitrate, potassium nitrate and calcium nitrate is (70-90):(5-20):(5-15), the mass fraction of water-insoluble impurities does not exceed 0.01% and the mass ratio of nutrients and calcium macroelement is regulated within the range of N:K_2OCa – (29-33):(2-9, 3):(1-3, 5).

The mass fraction of the fatty amine-based conditioner amounts to 0.03–0.15%

The lower limit of the mass fraction of potassium and calcium nitrate is, on the one hand, depends on the amount of nutrients and, on the other hand, because of the strengthening effect produced by calcium nitrate, depends on obtaining a fertilizer with an ammonium nitrate content of no more than 90%, which refers to the class of ammonium nitrate-based fertilizers with reduced fire and explosion hazard.

The upper limit of the mass fractions of potassium and calcium nitrate is restricted by the solubility of ternary salt system and the viscosity of the fusion cake. Potassium and calcium nitrate increase the fusion cake viscosity, and as for the solubility of the salt system, they act differently; namely, potassium nitrate increases the melting temperature and calcium nitrate decreases it.

The temperature of crystallization and the viscosity of salt systems that contain 70-90% of ammonium nitrate and a total mass fraction of 10-30% potassium and calcium nitrate, provides various compositions of granulated fertilizer according to the technology of the ammonium nitrate production. The granulation of fusion cakes with a higher mass fraction of potassium and calcium nitrate and other quantitative ratio of components is impossible through the use of the ammonium nitrate production equipment.

According to the present invention, granulated fertilizers are prepared by the granulation of concentrated solutions or fusion cakes that contain a ternary mixture of ammonium, potassium and calcium nitrate with the above indicated quantitative ratio of these salts. The granulation is carried out with the use of prilling or other known methods.

We offer three methods for the preparation of new compositions of complex completely water-soluble NKCa-containing fertilizers based on ammonium nitrate.

According to the first method, a ternary mixture of ammonium, potassium and calcium nitrate is prepared by the NPK fertilizer production process by mixing potassium and ammonium nitrate solutions in which the total mass fraction of the salts is 60 ± 5% and the mass ratio of the salts is (5-25):(95-75), with the calcium nitrate solution purified from impurities to attain the specified ratio of salts in the finished product.

The solution of potassium and ammonium nitrate that is used for the preparation of the ternary mixture is prepared by the mixed conversion of calcium nitrate with potassium and ammonium carbonate. The composition and the salt ratio in the mixed solution of potassium and ammonium nitrate are regulated by changing the ratio of potassium and ammonium carbonate used in the conversion, in order to meet the requirements for the composition of the finished product.

According to the scheme for the preparation of ammonium nitrate in the NPK fertilizer production, solutions that contain the ternary mixtures of the salts are evaporated to obtain a total salt mass fraction of 90±3%; then they are further evaporated to obtain the fusion cake by using the equipment for ammonium nitrate production; next, a granulated fertilizer is prepared by prilling or other known methods. The conditioning of the granulated fertilizers is performed by a surface treatment of the finished product granules with a fatty amine-based conditioning additive in the amount of 0.03-0.15%.

According to the second method, the solution that contains the ternary mixture of ammonium nitrate, potassium and calcium nitrate is prepared by mixing a solution that contains potassium and ammonium nitrate in a ratio of (5-25):(95-75), which was prepared by the conversion of calcium nitrate with potassium and ammonium carbonate in the NPK fertilizer production, and preliminary evaporation to a total mass fraction of 90±3% for the salts, with the solution of calcium nitrate purified from impurities to obtain the desired ratio of the salts in the finished product. The solutions obtained, in which the total amount of the salts is not less than 85%, are further evaporated to yield a fusion cake and then processed into granulated fertilizers in the same way as described in the first method.

According to the third method, the claimed complex fertilizers are prepared through the use of the technology for ammonium nitrate production, namely, by ammonia neutralization with nitric acid and/or by the conversion of calcium nitrate with ammonium carbonate in the NPK fertilizer production. Either a neutralization apparatus or a pre-neutralizer are charged with potassium and calcium nitrate directly before the stage of evaporation of the mixed solutions followed by obtaining the fusion cake; then, the product obtained is granulated by prilling or other known methods.

Potassium nitrate in the amount of 5-20% based on the finished product is added to ammonium nitrate in the form of an aqueous potassium nitrate solution, which was obtained by decomposing potassium carbonate with non-concentrated nitric acid. Calcium nitrate in an amount of 5-15% based on the finished product is added to ammonium nitrate in the form of a purified calcium nitrate aqueous solution obtained in the NPK fertilizer production. The addition rate of the potassium and calcium nitrate solutions is regulated, depending on their concentrations, to meet the requirements of the compositions of the complex water-soluble NKCa-containing fertilizers prepared.

The methods offered enable the production of uniform complex completely water-soluble fertilizers with a mass fraction of water-insoluble impurities of no more than 0.01%. The use of reagents in the form of solutions provides their exact dosage and the process of the preparation of complex fertilizers with specified quantitative ratio of plant nutrients is automated.

The technical results obtained are as follows:

- various compositions of uniform complex completely water-soluble fertilizers based on ammonium nitrate have been developed, which have two main nutrients – nitrogen and potassium – and an additional macronutrient for plant – calcium – in a water-soluble form;

- a total of 10-30% of potassium and calcium nitrate are added to ammonium nitrate, which enables a reduction in the fire and explosion hazard of the fertilizers produced;
- the fertilizers have higher stability to thermal decomposition compared to that of ammonium nitrate and a complex N:K-fertilizer;
- wetting of the fertilizers to a moisture mass fraction of 3-4% does not lead to decomposition of granules, and the products retain their performance characteristics;
- the fertilizer granules have a mechanical strength of 2.5-5 kg/granule, which guarantees their integrity during transportation, storage and application;
- there is no necessity to use potassium nitrate to prepare the fertilizers since a less expensive potassium raw material is used, namely, potassium carbonate;
- the quantitative ratio of the components makes it possible to prepare NKCa-containing fertilizers in granulated form by prilling through the use of the equipment for ammonium nitrate production or by other known methods.

Testing of the methods offered was carried out with the use of the process media for the nitro-ammophos (NPK) production, in particular, calcium nitrate melt, ammonium carbonate solution, preliminarily purified calcium nitrate solution, ammonium nitrate solution obtained by the conversion of calcium nitrate with ammonium carbonate and evaporated to ammonium nitrate with a mass fraction of 89-93%, and chemical reagents: potassium carbonate sesquihydrate and non-concentrated nitric acid with a nitric acid mass fraction of not less than 58%. Examples 1-3 illustrate the preparation of the complex completely water-soluble NKCa-containing fertilizers with a specified ratio of ammonium, potassium and calcium nitrate according to the present invention.

Example 1.

A conversion reactor was continuously charged with calcium nitrate melt at [the rate of] 61.7 cm^3/min, ammonium carbonate at 97.3 cm^3/min and potassium carbonate at 9 cm^3/min.

The calcium mass fraction in the calcium nitrate melt was 14.9%, the nitric acid mass fraction was 3.8%, the phosphate mass fraction was 0.17% calculated as P_2O_5, and other impurities were not regulated.

The mass fraction of ammonium carbonate content in the ammonium carbonate solution was 31.2%, and the mass fraction of potassium carbonate in the potassium carbonate solution was 50.8%.

The technological parameters of the conversion process were as follows: the slurry temperature in the reactor was 60 ºC, and the conversion time was 30 min.

The slurry obtained was filtered, and the converted calcium carbonate residue was separated, rinsed with water and transferred to drying.

The filtrate formed after the slurry separation was a mixed solution of potassium and ammonium nitrate with a total salt mass fraction of 59%, and a mass ratio of potassium to ammonium nitrate of 12:88, respectively.

The obtained potassium and ammonium nitrate solution was mixed with the calcium nitrate solution from the NPK production, which was preliminarily purified from impurities, in a volume ratio 12:1; then the mixture was evaporated to obtaining a fusion cake that contained a water mass fraction of 0.4%; this was then granulated by prilling and conditioned with an amine-based additive. The granulated fertilizer had the following chemical composition, in mass%:

Ammonium nitrate 80.4

Potassium nitrate 10.8

Calcium nitrate 8.4

Water-insoluble residue 0.01

Water 0.4

Conditioning additive 0.05%

The content of nutrients and calcium macroelement in the fertilizer was, in mass%

N 31

K_2O 5

Ca 2.

The granule mechanical strength was 4.3 kg/granule.

Example 2.

A conversion reactor was continuously charged with a calcium nitrate melt at [a rate of] 63.5 cm^3/min, an ammonium carbonate solution at 90.7 cm^3/min and potassium carbonate at 12.2 cm^3/min.

The calcium mass fraction in the calcium nitrate melt was 15.1%, the nitric acid mass fraction was 3.6%, the phosphate mass fraction was 0.32%, calculated as P_2O_5; other impurities were not regulated.

The ammonium carbonate mass fraction in the ammonium carbonate solution was 30.3% and the potassium carbonate mass fraction in the potassium carbonate solution was 47%.

The technological parameters of the conversion process were as follows: the slurry temperature in the reactor was 60 °C, and the conversion time was 30 min.

The slurry obtained was filtered; the residue of the converted calcium carbonate was separated, rinsed with water and transferred to drying.

The filtrate formed after the separation of the slurry was a mixed solution of potassium and ammonium nitrate with a total salt mass fraction of 55%, and the mass ratio between potassium and ammonium nitrate was 17:83, respectively.

The prepared mixed solution of potassium and ammonium nitrate was evaporated to a concentrated solution with a total salt mass fraction of 90%. The concentrated solution was mixed with the preliminarily purified calcium nitrate solution from the NPK fertilizer production in the volume ratio of 4.8:1.

A prepared solution containing the ternary salt mixture with a total salt mass fraction of 86.9% was evaporated to obtain a fusion cake that contained a water mass fraction of 0.4%, and then the product obtained was granulated by prilling and conditioned with an amine-based additive.

The granulated fertilizer had the following chemical composition, mass%:

Ammonium nitrate 77.5

Potassium nitrate 16.0

Calcium nitrate 6.1

Water-insoluble residue 0.006

Water 0.4

Conditioning additive 0.1%

The content of nutrients and calcium macroelement in the fertilizer was, by mass%

N 30.4

K_2O 7.5

Ca 1.4.

The granule mechanical strength was 2.7 kg/granule.

Example 3.

An apparatus (reactor) with a stirring device was charged with 330 cm^3 of concentrated ammonium nitrate solution with an ammonium nitrate mass fraction of 91%; then 67 cm^3 of a calcium nitrate solution and 31 cm^3 of a potassium nitrate solution were added to the ammonium nitrate solution.

The ammonium nitrate solution was obtained via a calcium nitrate conversion with ammonium carbonate using the technology for the NPK fertilizer production.

Calcium nitrate was added to the ammonium nitrate in an amount of 10% based on the finished product in a form that was purified from impurities in the aqueous solution of calcium nitrate from the NPK fertilizer production.

Potassium nitrate was added to the ammonium nitrate in an amount of 5% in the form of an aqueous potassium nitrate solution, which was obtained by the decomposition of potassium carbonate sesquihydrate by non-concentrated nitric acid with a nitric acid mass fraction of 58%.

The flow rate of the potassium and calcium nitrate solutions was determined from the concentration of the solutions and was based on the requirements for the composition of the fertilizer prepared.

The prepared mixed ternary solution of ammonium, potassium and calcium nitrate was further evaporated to obtain a fusion cake with a water mass fraction of 0.4%; this was then granulated by prilling and conditioned with an amine-based additive.

The granulated fertilizer prepared had the following chemical composition, by mass%:

Ammonium nitrate 84.5

Potassium nitrate 5.1

Calcium nitrate 10.0

Water-insoluble residue 0.01

Water 0.4

Conditioning additive 0.009%.

The content of nutrients and calcium macroelement in the fertilizer was (by mass%):

N 33

K_2O 2.4

Ca 2.4

Mechanical strength was 4.5 kg/granule

Claims

1. A complex fertilizer based on ammonium nitrate comprising potassium nitrate that is a completely water-soluble ternary NKCa-containing fertilizer and comprises 5-15% of calcium nitrate, a total of not more than 30 wt.% of potassium and calcium nitrate, with ammonium, potassium and calcium nitrate in a mass ratio of (70-90):(5-20):(5-15) and water-insoluble impurities of no more than 0.01 wt.%, wherein the mass ratio of nutrients and calcium macroelement is regulated to be within the range N:K_2O:Ca – (29-33):(2-9.3):(1-3.5).
2. The complex fertilizer according to Claim 1, wherein the mass fraction of a conditioning amine-based additive is 0.03-0.15%.
3. The method for the preparation of complex fertilizers based on ammonium nitrate according to Claim 1, wherein the solution containing potassium nitrate and ammonium nitrate in a mass ratio of (5-25):(95-75) and a total salt mass fraction of 60±5% is prepared by the process of a mixed conversion of calcium nitrate with potassium and ammonium carbonate in the process of NPK fertilizers production, mixing with a solution of calcium nitrate that is purified from impurities to the specified ratio of salts, where the obtained ternary mixture of ammonium, potassium and calcium nitrate is evaporated to a total salt mass fraction of 90±3 wt.% in said solution, then further evaporated to obtain fusion cake, followed by granulation, and where the surface of the granules is treated with a conditioning additive.
4. The method according to claim 3, wherein the granulation is performed by prilling.

5. The method for the preparation of a complex ammonium nitrate-based fertilizer according to Claim 1, wherein a solution containing potassium and ammonium nitrate in a mass ratio of (5-25):(95-75) is prepared by the process of the mixed conversion of calcium nitrate with potassium and ammonium carbonate in the NPK fertilizers production, and this is preliminarily evaporated to a total salt mass fraction of 90±3%; then mixed with a calcium nitrate solution purified from impurities to the specified ratio of salts, the obtained solution that contains a ternary mixture of ammonium, potassium and calcium nitrate with a total salt mass fraction of no more than 85% is further evaporated to give a fusion cake which is then granulated, and the surface of the granules is treated with a conditioning additive.
6. The method according to Claim 5, wherein the granulation is performed by prilling.
7. The method for the preparation of complex ammonium nitrate-based fertilizers according to Claim 1, wherein ammonium nitrate prepared by ammonia neutralization with nitric acid and/or by the conversion of calcium nitrate with ammonium carbonate in the NPK fertilizers production is mixed with a purified solution of calcium nitrate and a solution of potassium nitrate prepared by the decomposition of potassium carbonate with non-concentrated nitric acid, to give a potassium nitrate mass fraction of 5-20% and 5-15% of calcium nitrate, then either an apparatus for neutralization and/or a pre-neutralizer are charged with the solutions of potassium and calcium nitrate before the stage of evaporation of the mixed solution, then the obtained ternary mixture of ammonium, potassium and calcium nitrate is further evaporated to give a fusion cake, that is then granulated, and the surface of granules is treated with a conditioning additive.
8. The method according to Claim 7, wherein the granulation is performed by prilling.