(54) Method for the preparation of ammonia-nitrate fertilizer

The present invention relates to technology for the preparation of homogeneous mineral ammonium nitrate-based fertilizers that can be used in the manufacture and production of ammonium nitrate fertilizers that contain 10-15 mass% of calcium nitrate and not more than 90% of ammonium nitrate. The essence of the method is that a 49-56% aqueous calcium nitrate solution with a pH of 6.5-7.5 that contains no more than 0.05% of water-insoluble impurities is added to an 85-93% solution of ammonium nitrate, obtained either by the ammonia neutralization of nitric acid or by the conversion of calcium nitrate. This additive in the amount of 10-15% of $Ca(NO_3)_2$ is added before the evaporation stage to give an NH_4NO_3:$Ca(NO_3)_2$ ratio equal to (5.7-9):1 in the fertilizer, and granulation is then performed by prilling. The fertilizer thus prepared has improved physicochemical and agrochemical indicators and has a reduced tendency toward thermal decomposition.

1 table

Specification

The present invention relates to chemical technology for the preparation of homogeneous water-soluble mineral fertilizers, in particular, ammonium nitrate-based ammonia-nitrate fertilizers, and can be used in chemical industry for the preparation of granulated ammonium nitrate with improved physicochemical, physicomechanical and agrochemical properties.

The properties specific to ammonium nitrate, such as the polymorphic transformations upon heating and cooling during product storage, make it difficult to maintain the mechanical strength values of the granules, which results in their decomposition during bulk transportation and introduction into soil. They also lead to caking and lumping of the ammonium nitrate. In addition, ammonium nitrate is a physiologically acidic nitrogen fertilizer, which reduces its value for long-term applications. It is known that ammonium nitrate can explode when detonated or due to intensive thermal decomposition, and therefore it is treated as a substance with fire and explosion hazards. In this connection, its market is restricted, and importation is prohibited since ammonium nitrate is considered a potentially dangerous product for storage and transportation in a number of European countries.

To improve ammonium nitrate quality characteristics, various additives have been used.

Methods are known for the improvement of the physicomechanical properties of ammonium nitrate, and the objective is accomplished by the introduction to the fusion cake of various inorganic additives before granulation, such as a finely-dispersed silicate filler – silica gel in the amount of 0.5-5.0 mass% (SU № 1004325, C 05 C 1/02, 13.11.1981); copper borate in the amount of 1.0-3.0 mass% (SU № 1375625, C 05 C 1/02, 18.04.1984); perlite, calcium carbonate, zinc oxide, etc. (**Bulgarian** patent № 37123, C 01 C 1/18, 09.12.1983).

The above-listed methods do not provide better results as compared to the existing ones for the following reasons:

- Complicated nature of the technological process since it is necessary to deal with free-flowing and dust-forming materials;
- The necessity of additional equipment for the fine milling of additives (to 0.1-100 μm) and for the intensive stirring with the fusion cake to obtain a homogeneous system;
- The necessity of adding to the number of process steps, namely the preliminary drying of the additives;
- Periodical clogging of the granulators with additive particles, which decreases the efficiency of the unit;
- The use of scarce and expensive additives.

Methods are known for improvement of the physicomechanical properties of ammonium nitrate according to which the objective is attained by the use of a sulfate additive in the amount of 0.4 % of $(NH_4)_2SO_4$ in the finished product. This is added in the form of sulfuric acid or ammonium sulfate at the neutralization stage; a phosphate-sulfate additive, which is obtained from a mixture of phosphoric and sulfuric acid or a mixture of their salts, and which is added either at the neutralization stage or to the ammonium nitrate solution before its evaporation, in the amount of 0.3-0.5% of P_2O_5 and 0.05-0.2% of $(NH_4)_2SO_4$ in the finished product (Ammonium nitrate technology. Edited by Doctor of Techn. Sci., Prof. V.M. Olevsky. M.: Khimiya, 1978, p. 158-164).

Disadvantages of the above methods are as follows:

- the use of expensive thermal phosphoric acid or ammonia phosphates;
- insufficiently high mechanical strength of the granules despite their increased bulk.

A method is known for increasing the mechanical strength of ammonium nitrate granules by adding calcium nitrate and sulfuric acid, according to which, the calcium nitrate solution is added after the neutralization stage in the form of a nitrogenous dolomitic extract that contains calcium and magnesium ions, and sulfuric acid is added at the granulation stage (UA patent, № 44008, C 05 C 1/02 A, 16.01.2001).

The disadvantages of the above method are as follows:

- the fertilizer is inhomogeneous due to the formation of calcium sulfate, $CaSO_4$, and therefore, it is not completely water soluble;
- the gypsum formation leads to clogging of the granulators, which causes a decrease in the efficiency of the unit;
- in the process of preparing the dolomitic extract, nitrogen oxides are released into the ambient environment;

- when sulfuric acid is added to the fusion cake before granulation, the product pH value is lowered, which increases the tendency of the product toward thermal decomposition and deterioration of its quality characteristics.

In terms of the technical essence and the result attained, the most similar method is that for the improvement of the physicomechanical properties of ammonium nitrate, according to which the objective is attained with the introduction of a magnesia additive in the form of a magnesium nitrate solution that contains $Mg(NO_3)_2$ equivalent to 120 – 135 g/L of MgO in a technological process for ammonium nitrate production before the evaporation stage (Ammonium nitrate technology. Edited by Doc. of Techn. Sci, Prof. V. M. Olevsky. M.: Khimiya, 1978, p. 155-157).

The amount of the additive introduced in the finished product is equivalent to 0.35-0.5% of MgO. Ammonium nitrate granules with a magnesia additive improved the physicochemical properties.

The disadvantages of the above technical solution are as follows:

- as in the earlier described methods, the stability of ammonium nitrate toward thermal decomposition is not increased, which prevents any reduction of its potential fire and explosion hazard;
- the use of a scarce raw material, magnesite, does not permit raising the amount of the additive to increase the agrochemical value of the fertilizer and to improve its physicomechanical properties;
- insufficient mechanical strength of the granules, which does not exceed 1.5 kg/granule.

The preparation of magnesium nitrate by the decomposition of magnesite with nitric acid is associated with environmental problems, in particular, nitrogen oxides released into the ambient environment.

The objective of said invention is the preparation of homogeneous water-soluble ammonia-nitrate fertilizer based on ammonium nitrate with advanced physicomechanical properties, better thermal stability, reduced fire and explosion hazards of the product and increased agrochemical value.

The given problem is solved by changing the parameters of the technological process as compared to the prototype:

- the additive is introduced in the amount of 10-15% for the finished product;
- the qualitative and quantitative composition of said additive is changed, namely, a solution of calcium nitrate is added to an 85-93% ammonium nitrate solution (obtained by conversion or from pure media) before the evaporation stage; its pH is 6.5-7.5 and it contains 49-56% of $Ca(NO_3)_2$ and no more than 0.05% of water-insoluble impurities.

Calcium nitrate is a universal physiologically alkaline fertilizer, which is suitable for all types of soil, and primarily for soils with an insufficient calcium content. Calcium nitrate is very important for the

fertilization of sowings of flax, hemp, barley, potatoes, etc. (Technology of Mineral Salts. M. Ye. Pozin. L.: Khimiya, 1974, v. 2, p. 1210). Due to this reason, the inclusion of calcium nitrate in the composition of ammonia-nitrate fertilizers is advantageous.

The technical result of the invention claimed is as follows:

- preparation of homogeneous water-soluble fertilizer with a granule mechanical strength not less than 3.0 kg/granule;
- a fertilizer that contains not more than 90% of ammonium nitrate, which allows it to be considered an ammonia-nitrate fertilizer with a reduced fire and explosion hazard;
- the fertilizer prepared has better thermal decomposition stability;
- the fertilizer has higher agrochemical value because the additive contains an additional useful element – calcium – in an amount (2.4-3.6 mass%) that is sufficient for the indicated purposes.

The claimed method is realized in the following way.

Calcium nitrate is separated by polythermal crystallization from a nitric acid extract that is obtained as the result of the decomposition of apatite by nitric acid, and this is then purified from impurities; its pH is 6.5 – 7.5, and it contains 49-56 mass% of $Ca(NO_3)_2$ and not more than 0.05% of water-insoluble impurities; further, it is mixed with an 85-93 mass% solution of ammonium nitrate in a ratio of NH_4NO_3:$Ca(NO_3)_2$ equal to (5.7-9.0):1. For this case, ammonium nitrate is prepared either by the conversion of calcium nitrate or in an ITN apparatus by the neutralization of nitric acid with gaseous ammonia.

The mixture is evaporated in the film evaporator, and then the fusion cake is granulated in the granulators by prilling. After cooling in a fluidized bed in the apparatus, the fertilizer granules are treated with a conditioning additive.

Calcium nitrate is added to the ammonium nitrate in an amount that provides 10 mass% in the finished product to yield a new type of fertilizer – ammonia-nitrate fertilizer with better thermal stability and improved physicomechanical, physicochemical and agrochemical properties when compared to the ammonium nitrate obtained according to the prior art. The preparation of a fertilizer with a calcium nitrate content of more than 15% using the equipment for ammonium nitrate production is problematic, since then there is a decrease in the temperature of the fusion cake crystallization.

The product obtained has the following characteristics:

- ammonium nitrate content 85-90%;
- calcium content 2.4-3.6 %;
- moisture (measured by the Fisher method) 0.3-0.4%;
- the content of water-insoluble impurities does not exceed 0.02%;
- mechanical strength of the granules is 3.0-4.4 kg/granule;
- content of the 2-4 mm fraction is 95-99%;
- conditioning additive amount is 0.05-0.15 mass%;

- temperature at the beginning of the product decomposition rises by 5-8 ºC compared to the ammonium nitrate obtained according to the prior art.

Our investigations show that the fertilizer obtained is more hydroscopic compared to the ammonium nitrate obtained according to the prior art (see Table). In this case, even with wetting of granules with an H_2O content of 4 mass%, there is no formation of monoliths, which would be associated with the dehydrating property of calcium nitrate.

The realization of said technological process according to the claimed method provides a new product – ammonia-nitrate fertilizer with the above characteristics with modest expenditures for materials using a simplified technology.

Claim

A method for the preparation of homogeneous water-soluble fertilizers based on ammonium nitrate, comprising the preparation of a solution, introduction of an additive to said solution, evaporation, granulation and granule conditioning, wherein to an 85-93% ammonium nitrate solution, prepared either by neutralization of nitric acid with gaseous ammonia or by conversion of calcium nitrate, an additive in the form of a 49-56% aqueous solution of calcium nitrate that has a pH of 6.5-7.5, and contains not more than 0.05% of water-insoluble impurities for a $Ca(NO_3)_2$ amount of 10-15%, is added before the evaporation stage to give a NH_4NO_3:$Ca(NO_3)_2$ ratio equal to (5.7-9):1 in the fertilizer, and the granulation is performed by prilling.