ABSTRACT

of the dissertation for the PhD degree
in specialty 6D072000 - Chemical technology of inorganic substances

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«Enhancement of the ammonium nitrate technology with the purpose of improvement of its physicochemical and agrochemical characteristics»

Relevance of the dissertation. Ammonium nitrate is a universal fertilizer that is widely used in agriculture. However, in recent years, it has been used in limited quantities due to many problems caused by its fire and explosion hazard. In 2001 and 2003, there were explosions at industrial warehouses of ammonium nitrate in Toulouse and Saint-Romain-en-Jarez (France). Similar cases occurred in North Korea and Georgia (Azot JSC) in 2004 during the transportation of ammonium nitrate as a result of violations of the rules of technical operation in the granulation tower. In 2005, 2007 and 2020, there were explosions at warehouses of ammonium nitrate in Ukraine and in the Beirut seaport, Lebanon. Therefore, at present, both producers and consumers of this important fertilizer are faced with acute issues due to the need to improve ammonium nitrate consumer and agrochemical properties by eliminating its explosion and fire hazard. In this regard, the development of new technological solutions to improve the traditional production technology of ammonium nitrate by means of transferring it without radical modernization to the manufacturing stabilized complex fertilizers with improved consumer, agrochemical and physicochemical properties on the basis of a primary evaporated ammoniated nitric acid solution and mineral salt additives is an urgent task.

Relation to research projects and government programs. The dissertation work was carried out in accordance with the scientific direction of M. Auezov South Kazakhstan University held in the framework of a state financed theme B-16-02-03 «Research on the development of alternative and innovative technologies of raw material concentration and manufacture of products of the synthesis of inorganic compounds from natural ore-mineral resources and industrial wastes of various industries»implemented at department «Chemical technology of inorganic substances»and the contract No. 2106 with “KazAzot” JSC “Establishment of new opportunities to increase the ammonium nitrate agrochemical value, physicochemical and consumer properties”.

Research objects: ammonium nitrate; a ground phosphate rock of the Chilisay and Kokjon deposits; samples of target products with ratios of $N/P_2O_5/K_2O$ and N/P_2O_5equal to 16/7/7 and 13/10; 19/7; 21/6; 23/5.

Research purpose and tasks. Scientific substantiation and development of an improved ammonium nitrate production technology that makes it possible to produces tabilized fertilizers with improved consumer, agrochemical and physicochemical properties. Optimization of the developed technology, its pilot testing, feasibility study, development of practical recommendations to introduce the technology in manufacture

To achieve the purpose of the dissertation thesis, the following tasks were solved:

- study of kinetics and equilibrium of the ammonium nitrate thermal decomposition in solutions;
- study of the acid absorption of the ammonium nitrate thermal decomposition product - ammonia;
- making material balances of the thermal decomposition of ammonium nitrate in solutions and acid absorption of ammonia;
- selection of composite and modifying additives to the ammonium nitrate solution, study of their composition and properties;
- determination of the chemism and the thermodynamic substantiation of the processes underlying the production of ammonium nitrate with improved composition and properties using a primary evaporated ammoniated nitric acid solution and mineral salt additives;
- planning and carrying out the research for determination of regime parameters, optimizing the processes under study, and regulating the content of nutrients in target products;
- obtaining samples of the ammonium nitrate with improved composition and properties and their physicochemical analysis;
- development of an improved technology for obtaining ammonium nitrate with improved consumer and agrochemical properties based on a primary evaporated ammoniated solution of nitric acid and mineral salt additives;
- pilot tests of the developed technology in the conditions of "KazAzot" JSC, its feasibility study and development of practical recommendations for the introduction of the suggested technology in manufacture.

Scientific novelty of the work:

1. The regularities of the thermal decomposition of ammonium nitrate in solutions were studied. It was found that ammonium nitrate in solutions, in contrast to its solid state, can undergo the thermal decomposition even at temperatures below 110°C starting with the thermal decomposition degree of 0.1% and the process equilibrium constant of 62×10^{-7}mol/l in the room temperature range and reaching the maximum decomposition degree of 4.0% and the equilibrium constant of 4751×10^{-7}mol/lat a temperature of 110°C.

2. It was established that the thermal decomposition degree of ammonium nitrate in its solutions in the temperature interval of 110-130°C depends on the concentration: the lower the ammonium nitrate concentration in its solution, the higher the thermal decomposition degree, and the higher its concentration, the lower the thermal decomposition degree. In addition, it was found that if the ammonium nitrate concentration in its solution is less than 65%, its decomposition degree exceeds 6.0%, and at the concentrations of higher than 95%, the decomposition degree decreases almost to zero.

3. It was determined that the activation energy of the thermal decomposition of ammonium nitrate in its solutions is about 4.07 J/mol; it is quite convincing evidence

in favor of the new fact that this process is limited by the diffusion removal of products of ammonium nitrate thermal decomposition into the solution volume.

4. For the first time in experimental practice, targeted studies were conducted to obtain reliable balance data on the processes of thermal decomposition of ammonium nitrate in its boiling solutions and full utilization of the ammonium nitrate thermal decomposition product -ammonia -by means of its absorption with nitric acid. It was found that in a case of identical concentrations of the initial ammonium nitrate solution (11.76 mol/l) with increasing the nitric acid concentration in the sorption solution, the ammonium nitrate decomposition degree increases about eight times and is 0.06% and 0.40% for the sorption solution concentrations of 0.05 mol/l and 0.20 mol/l, respectively. It follows that for every single increase in the nitric acid concentration, there is a double increase in the ammonium nitrate decomposition degree. It was also found that the simultaneous decrease in the ammonium nitrate concentration in the initial solution (up to 7.45 mol/l) and increase in the nitric acid concentration in the absorption solution (up to 2.0 mol/l) leads to a sharp increase in the ammonium nitrate decomposition degree to 5.5%.

5. Using modern techniques of physical and chemical analysis, the composition and properties of mineral additives (the Kokjon and Chilisay ground phosphate rock) and samples of new fertilizers produced on the basis of a primary evaporated ammoniated nitric acid solution, the ground phosphate rock and potassium chloride were studied.

6. The chemism of the processes of obtaining the ammonium nitrate with improved composition and properties on the basis of primary evaporated ammoniated nitric acid solution, ground phosphate rock and potassium chloride was identified and substantiated from the thermodynamic point of view.

7. A mathematical model is proposed to calculate specific consumptions of ammonium nitrate, phosphate and potassium chloride for preparation of the initial suspension; using the Box-Hunter second-order rototable modeling technique the adequate regression equation was obtained for estimating ratios of nutrients in the target product; optimization of the process of obtaining new fertilizers based on the ammoniated nitric acid solution, ground phosphate rock and potassium chloride was carried out.

The main provisions to be defended:

- results of the kinetic and equilibrium studies of ammonium nitrate thermal decomposition in its boiling solutions and absorption of the ammonia liberated with nitric acid;

- material balances based on the results of kinetic and equilibrium studies of the processes of ammonium nitrate thermal decomposition in its boiling solutions and nitric acid absorption of the product of ammonium nitrate thermal decomposition – ammonia;

- results of complex study of the composition and properties of the Chilisay and Kokjon ground phosphate rock and samples of target products that are ammonium nitrate with improved composition and properties;

- chemistry and thermodynamics of processes occurring in the medium of a primary evaporated ammoniated nitric acid solution in the presence of ground phosphate rock and potassium chloride;

- method for calculating the specific consumptions of ammonium nitrate, phosphate and potassium chloride for the preparation of the initial suspension;

- results on optimization of the effect of specific consumption indicators of ammonium nitrate, phosphate and potassium chloride on the regulated ratio of nutrients - nitrogen, phosphorus pentoxide and potassium oxide in the target products;

- the improved production technology of ammonium nitrate with improved composition and properties based on a primary evaporated ammoniated nitric acid solution, ground phosphate rock and potassium chloride, its material balances;

- results of pilot tests of the improved technology for obtaining ammonium nitrate with improved composition and properties based on an ammoniated solution of nitric acid, ground phosphate rock and potassium chloride;

- results of the feasibility study of the developed technology and its introduction in the current ammonium nitrate manufacture.

The reliability degree of the results. The reliability of the results is ensured by using modern analysis techniques: analytical, kinetic, thermodynamic, chemical, complex metric, titro metric, permanganate metric, potentio metric, photocolori metric, gravimetric ones; research methods and devices: computational, mathematical, traditional methods and methodologies for conducting laboratory and pilot tests, a scanning electron microscope (JEOL, JSM6490LV), a spectrophotometer (SPECORD 75), anIR-Fourier spectrometer (ShimadzuIR Prestige-21), an X-ray phase analyzer (DRON-3), a differential thermal analyzer (THERMOSCAN-2), a humidity meter (Mettler Toledo), a granule strength meter(IPG-1M); data of analysis of modern scientific and technical literature.

The developed technology has passed pilot testing at the existing ammonium nitrate production-“KazAzot” JSC. The test results are is suedas the test certificates, protocol of intent to implement, and practical recommendations for implementation.

Approbation of the research results. The materials of the dissertation work were presented and discussed at various international and national conferences and symposiums: “Agrofoodzones of megacities and agricultural cooperation in Kazakhstan: problems, searches and solutions” (Shymkent, 2017); international scientific and practical conference “International science project” (Finland, Turku, 2018); V International conference dedicated to the 75thanniversary of M. Auezov SKSU and the 90th anniversary of academician S.T. Suleimenov “Industrial technologies and engineering” (Shymkent, 2018); conference “Auezov readings-17: new impulses of science and spirituality in the world” (Shymkent, 2019).The results of the dissertation research were introduced in the educational process of training bachelors, masters and PhD students of specialty 6D072000 - “Chemical technology of inorganic substances” and confirmed by certificates of introduction of the research results, certificates of participation in interactive seminars “Publication and

commercialization of research results in domestic and international databases", "Current issues of management and commercialization of research projects".

The personal contribution of the doctoral student: analysis of scientific literature and patents on the dissertation topic; formulation of the research purposes and tasks; choice of research and analysis methods; conducting theoretical and experimental study; generalization of the results obtained; development of new technological solutions, their pilot testing and development of practical recommendations to introduce them in the current ammonium nitrate manufacture; preparation and publication of scientific papers on the work; introduction of the results in the educational process.

Publication of the research results. The main provisions of the dissertation were published in 18 scientific papers including 3 ones in the international scientific journals cited in the database Scopus, 4 – in the journals recommended by Committee for control in education and science of MES of the Republic of Kazakhstan, 7 articles in materials of international conferences, 4 articles in other scientific journals. The papers were published in the following journals: International Journal of Engineering Research and Technology (India); Periodico Tche Quimica (Brazil); Bulletin of the Karaganda University (Kazakhstan); KazNRTU Bulletin; Chemical journal of Kazakhstan; Bulletin of the Kazakh-British Technical University as well as in materials of international and other specialized scientific and technological conferences: "Agrofoodzones of megacities and agricultural cooperation in Kazakhstan: problems, searches and solutions"(Shymkent, 2017); "International science project"(Finland, Turku, 2018); V International conference dedicated to the 75thanniversary of M. Auezov SKSU and the 90th anniversary of academician S.T. Suleimenov "Industrial technologies and engineering" (Shymkent, 2018); conference "Auezov readings-17: new impulses of science and spirituality in the world" (Shymkent, 2019).In addition, 4 applications for the invention were submitted in KazPatent.

Practical significance of the work.

1. The implemented research was a basis for the development of new technological solutions to improve the traditional ammonium nitrate production technology by means of converting it to manufacturing the ammonium nitrate with improved composition and properties using a primary evaporated ammoniated nitric acid solution and mineral additives such as the ground phosphate rock and potassium chloride. The main advantages of new product, in contrast to the ammonium nitrate produced by the traditional way, are its thermal stability and high agrochemical value.

2. The developed technology does not require a radical change of the traditional ammonium nitrate production technology; the difference consists in elimination of the second evaporation stage and the stage of additional neutralization of nitric acid in the ammoniated solution. Therefore, the suggested technology is a simplified version of the current technology for the production of ammonium nitrate.

3. The samples of ammonium nitrate with improved composition and properties were produced using the technological equipment of the current ammonium nitrate

production observing all the operating parameters of the traditional scheme. In addition, and this was also reliably established at the processing of the experimental data, for the same consumption indicators of raw materials the unit production capacity of the developed technology increases by 1.5 times and more in comparison with the traditional technology.

4. The new target product is produced at a significantly lower cost, gives the economic effect of about 3.61%-8.98% depending on its composition, and thus it can be sold with high added value. The results of pilot tests of the developed technology at the “KazAzot” JSC have convincingly confirmed its important significance and high efficiency.

5. The methods for obtaining ammonium nitrate with improved composition and properties and a regulated nutrients ratio were suggested. Applications for the invention were submitted to Kazpatent (No. 2019/0638.1, No. 2019/0640.1, No. 2020/0105.1, No. 2020/0108.1).

The dissertation structure and volume. The dissertation thesis contains 138 pages of typewritten text, 57 tables, 57 figures. The thesis consists of the introduction, 7 parts, the conclusion, the reference list including 202 titles and 24 annexes.