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Carbonate-Ammonium Nitrate: Production and Property

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ABSTRACT: In the survey article information on removal of some drawbacks of ammonium nitrate in particular it's caking and explosiveness by introduction to fusion of ammonium nitrate of lime materials has given. The optimal conditions of process for obtaining carbonate-ammonium nitrate (CAN) were formulated. In the world produced such saltpetre with maintenance of nitrogen of 20-33%. Besides, it with maintenance of nitrogen not above 28% does not burn and during strong detonation ignores is an explosive substance. In the production of CAN a limestone or chalk can be replaced by a dolomite. Application of ammonium nitrate based on dolomite is not only harmful, but it leads to increase of harvest as compared to CAN obtained by an ordinary way.

KEYWORDS: ammonium nitrate, limestone, chalk, dolomite, carbonate-ammonium nitrate, obtain, properties.

I.INTRODUCTION

The essence of the production process of lime-ammonium nitrate (LAN) is to mix finely ground $CaCO_3$ (limestone, dolomite or chalk) with NH_4NO_3 melt and granulate the mixture in mechanical granulators or granulation towers. Ammonium nitrate in the molten state decomposes noticeably according to the equation

$NH_4NO_3 = NH_3 + HNO_3 – 41,7$ kkal

and acidity gradually increases. Therefore, when calcium carbonate is mixed with an ammonium nitrate melt, the reaction proceeds

$2NH_4NO_3 + CaCO_3 = Ca(NO_3)_2 + (NH_3)_2CO_3$

At a relatively high mixing temperature of the components, ammonium carbonate decomposes into NH3, CO2, and water. Therefore, the reaction of calcium carbonate with an ammonium nitrate melt is as follows:

$2NH_4NO_3 + CaCO_3 = Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O$

Due to this reaction, part of the bound nitrogen is lost in the form of gaseous ammonia and a certain amount of calcium nitrate appears in the mixture, the presence of which has a significant effect on the physical properties of the resulting LAN, increasing its hygroscopicity. Losses of NH_3 during mixing of NH_4NO_3 melt with $CaCO_3$ depend on the duration of the process of mixing the components, the temperature of the mixture, the content of carbonate introduced into the melt, the degree of grinding and the quality of carbonate raw materials. When ground limestone is mixed with 96-98% AS melt at a temperature of 150-153ºC, the loss of total nitrogen under these conditions increases from 1,2 to 1,8% with an increase in the mixing time from 15 to 25 minutes. With an increase in the temperature of the melt, the loss of ammonia nitrogen sharply increases [1, 2]. So, at 125º and the ratio $NH_4NO_3 : CaCO_3 = 60 : 40$ they are 0,2%, and at 145ºC – 0,8%. An increase in the content of calcium carbonate at the same temperature (135ºC), degree of grinding (0,12 mm) and duration of fusion (10 min) significantly increases the loss of ammonia. At a ratio of $NH_4NO_3 : CaCO_3 = 80 : 20$; 60 : 40; 50 : 50 they are respectively 0,21; 0,32; 0,46% of the total nitrogen content in the mixture. The amount of loss depends on the duration of the fusion process and is for 10 min – 0,32%, 30 min – 0,82% and 60 min – 1,47% of the total nitrogen content in the alloy. The loss of ammonia nitrogen also increases with an increase in the degree of crushing of limestone [2]. In the same work, the optimal conditions for the process of obtaining LAN are formulated: the fusion temperature is 125-135ºC, the concentration of the melt NH_4NO_3 is 94%, the ratio of the initial substances $NH_4NO_3 : CaCO_3 = 60 : 40$, the duration of fusion is 10 min, the degree of crushing of limestone is 0,12 mm, moisture content of finely ground limestone – 0,1-0,3%. In this case, limestone should contain at least 94% $CaCO_3$ and impurities SiO_2 – 1,5%, MgO 0,5%,

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$(Al_2O_3 + Fe_2O_3)$ – 1,5% [3]. Under these optimal conditions for fusion of NH_4NO_3 with limestone, the content of calcium nitrate in the finished product is a minimum value of approximately 1,0%.

The LAN production technology consists of the following main stages:

1 - obtaining melt NH_4NO_3 according to the usual technological scheme adopted in the production of granulated AN;

2 - crushing and grinding of limestone to obtain limestone flour with a fineness of grinding less than 100 microns;

3 - drying limestone powder to a moisture content of 0,1%;

4 - mixing of ammonium nitrate melt with limestone flour;

5 - granulation of the resulting mixture in a granulation tower, or in a screw granulator;

6 - product sieving;

7 - crushing of the coarse fraction of the product and returning together with the fine fraction for mixing with the ammonium nitrate melt;

8 – commercial fraction cooling;

9 - processing of the finished product with powdering additives and sending the product to the warehouse for storage in bulk.

On fig. 1 shows a flow chart for the production of LAN using a screw granulator [2]. The initial 94-98% NH_4NO_3 melt with a temperature of 125-140ºC is mixed in a screw granulator (1) with crushed limestone. The optimal outlet temperature is 108-109ºC. The resulting granules are sent to a heated with warm air dryer drum (2), from which they go to the screen (3) to separate the coarse fraction and then to the screen (4) to separate the fine fraction. The coarse fraction is ground in a roller mill (10) and, together with fines and dust, is returned to the granulator. The production fraction is cooled in two chambers of a fluidized bed refrigerator (5) to 30°C, and then processed in a drum (6) with conditioning additives and transported to a warehouse. The exhaust air from the dryer is cleaned in a cyclone (7) and a scrubber (8) with a droplet separator (9) connected in series and is discharged into the atmosphere. To carry out a normal granulation regime, it is necessary to maintain a constant moisture content and temperature in the granulator in order to work in the optimal zone. Too wet or too dry granulation results in larger or smaller granules, respectively. To obtain 1 ton of 25% nitrogen LAN, it is necessary to feed about 750 kg of a 95-96% NH_4NO_3 solution, 250 kg of limestone (with a moisture content of about 0,5%) and 3 tons of dry recycle (with a moisture content of 0,1-0 ,5%). To evaporate moisture, warm air is supplied to the granulator.

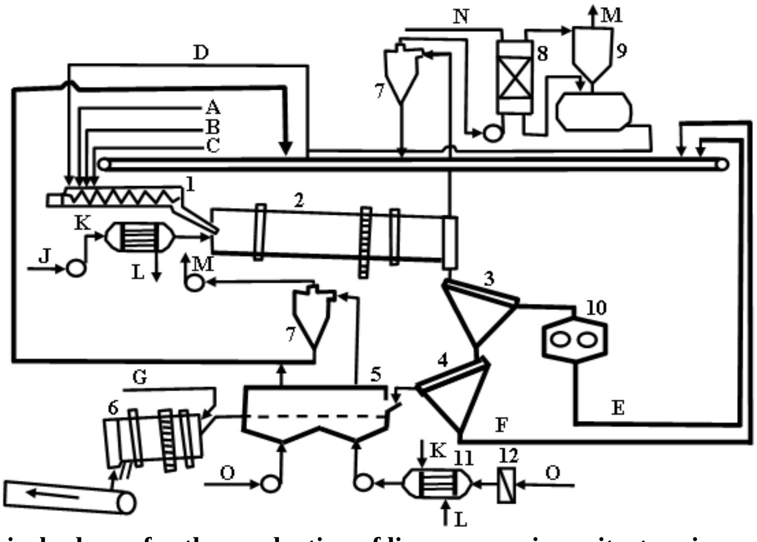

Fig. 1. Technological scheme for the production of lime-ammonium nitrate using screw granulators:

1 - granulator; 2 - drying drum; 3 - a screen for separating a large fraction; 4 - screen for separation of fine fraction, 5 - fluidized bed cooler; 6 - drum for conditioning, 7 - cyclone for dedusting the exhaust air from the dryer drum, 8 - scrubber for cleaning the exhaust air from the dryer drum; 9 - separator for cleaning wet air; 10 - roller mill for coarse fraction; 11 – air heater; 12 - air filter directed to create a fluidized bed; A - 95% melt of ammonium nitrate; B - crushed limestone; C - return; D - ammonium nitrate solution from the wet cleaning system; E - ground large particles; F - fine fraction; G - conditioning additives; H is the finished product; I - product to the warehouse; J is dry air from the atmosphere; K - steam; L - condensate; M - exit to the atmosphere; N is the main condensate; O - air supply from the atmosphere to create a fluidized bed.

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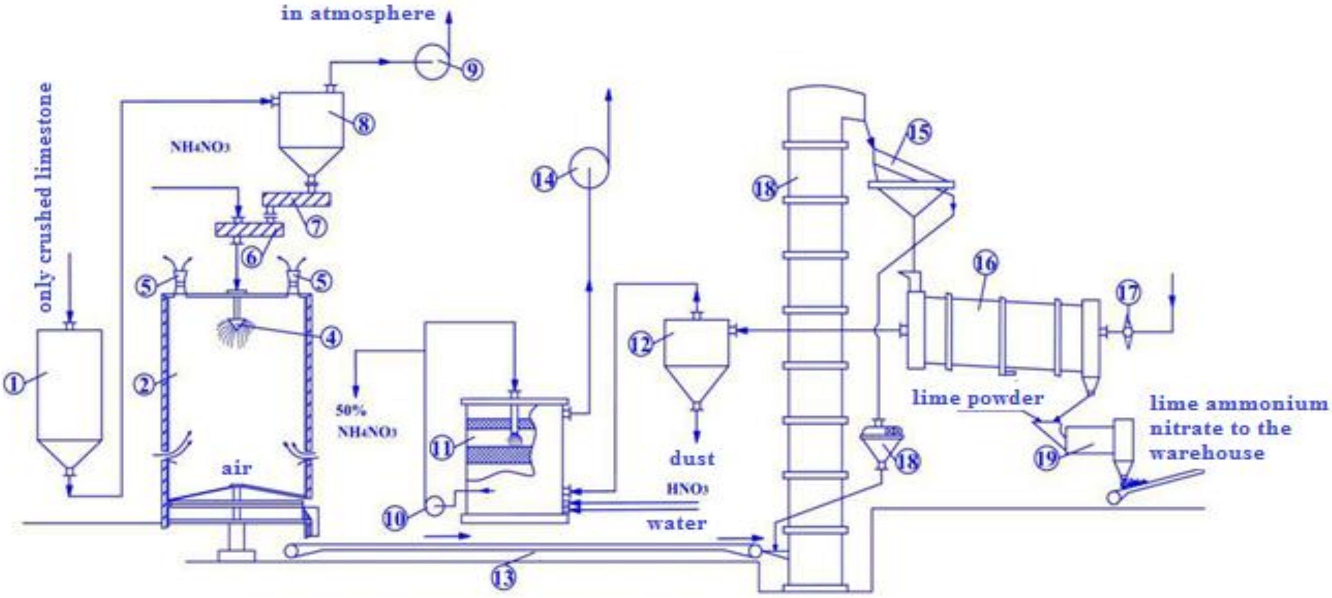

Fig. 2. Scheme of lime-ammonium nitrate production with granulation process in a granulation tower:

1 – limestone flour storage; 2 – granulation tower; 3 – scraper dumper; 4 – granulator; 5, 9, 17 – fans; 6 – mixing auger; 7 – conveyor auger; 8 – limestone flour hopper; 10 – centrifugal pump; 11 – scrubber; 12 – cyclone; 13 – conveyor; 14 – elevator; 15 – vibrating screen; 16 – drum for cooling; 18 – crusher; 19 – drum for dusting.

Drying drum (2), from which they are fed to the screen (3) for separating the large fraction and then to the screen (4) for separating the small fraction. The coarse fraction is ground in a roller mill (10) and, together with the fines and dust, is returned to the granulator. The production fraction is cooled in two chambers of a refrigerator with a boiling layer (5) to 30 ° C, and then processed in a drum (6) with conditioning additives and transported to the warehouse. The air leaving the drying drum is cleaned in a cyclone (7) and a scrubber (8) with a drip separator (9) connected in series and discharged into the atmosphere. To carry out the normal granulation regime, it is necessary to maintain a constant moisture content and temperature in the granulator in order to work in the optimal zone. Too wet or too dry granulation leads to the formation of larger or smaller granules, respectively. To obtain 1 ton of 25% nitrogen LAN, it is necessary to feed about 750 kg of 95-96% NH_4NO_3 solution, 250 kg of limestone (with a humidity of about 0.5%) and 3 tons of dry recycle (with a humidity of 0,1-0,5%) to the granulator. To evaporate moisture, warm air is supplied to the granulator.

Figure 2 shows the scheme of LAN production with the granulation process in a granulation tower [2]. Crushed limestone from the storage (1) is pneumatically transported to the hopper (8), from which it is dosed by a screw (7) into a mixing screw (6), which simultaneously receives 94-95% NH_4NO_3 melt. The mixer body (6) is made of chrome-nickel cast iron, and the shaft with blades is made of acid-resistant steel. The mixer (6) has dimensions: 4,5x0,8x1 m and provides a capacity of up to 600 tons/day for the finished product. From the mixing screw (6), the mixture with a temperature of 125-135°C is directed to a centrifugal sprinkler (granulator) (4) located in the upper part of the gran tower (2), which is a cylindrical reinforced concrete structure with a diameter of 20 m and a height of 20 m. The inner surface of the tower is lined with thin aluminum sheet, which in turn is coated with oppanol. Atmospheric air is sucked into the tower by fans (5) through holes in the lower part of the tower, cools the floating drops falling to meet it. Hardened granules with a temperature of 70-80ºWith a humidity of about 3.5%, the scraper (3) is fed to the conveyor (13). With a tower capacity of 20 t/h for the finished product, the air consumption (25ºS) is about 100 thousand m3/h. Pellets from the granary (2) are sent by a conveyor (13) and an elevator (14) for classification into vibrating sieves (15). The commodity fraction (2-5 mm) enters for cooling (up to 25-30°C) into the drum (16), into which the cooled air (up to 3-

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1°C) is fed. The air after the drum (16) enters the cyclone (12), in which about 70% of the lime-ammonium nitrate dust carried away from the drum is captured, fine dust particles are captured in a scrubber (11) irrigated with an AC solution. Part of this circulating solution, with a concentration of 50% NH_4NO_3, is diverted to mixing with the main stream of the saltpeter solution directed to evaporation to obtain 94-95% NH_4NO_3 melt. To prevent calcium carbonate from entering the evaporators, HNO_3 is added to the scubber liquid. The cooled granules from the drum (16) enter the drum (19) for powdering with lime flour. The large fraction that has not passed through the vibrating screen (15) is crushed in the crusher (18) and returns to the classification again, the small fraction is used as a retour, as well as dust after cyclones. The main difficulty in granulating LAN in the tower is the frequent clogging of the granulator holes with solid particles. Filtration before carrying out the granulation process is not possible in many cases, since suspensions are an integral part of the fertilizer. Successful pilot tests of LAN granulation in a tower with a diameter of 16 m and a height of 37,5 m were described in [39]. In the French patent [40], the NH_4NO_3 float (65 h.) obtained by evaporation of the solution at 170-210º With and containing less than 0,5% water, after mixing with finely ground (93% particles less than 149 microns, 72% less than 74 microns, 62% less than 44 microns) $CaCO_3$ (35 h.) with a humidity of less than 0,05% and a temperature of more than 70°C, it is recommended to granulate in a tower. The granules contain less than 0,5% $Ca(NO_3)_2$ and are practically non-hygroscopic.

Works [4-8] are devoted to the improvement of the LAN granulation process in towers. As a result of these works, the causes of failures of the centrifugal granulator (clogging of holes with solid particles) were established, constructive ways of eliminating them were patented, an algorithm for calculating the centrifugal granulator was proposed and a new centrifugal granulator was created in which holes are no longer clogged with solid particles of the ammonium nitrate-limestone melt [8]. In addition to the classical methods of production of LAN described above, there are a number of patents aimed at improving the methods of its production.

In [9], a method for obtaining lime-ammonia fertilizer was patented, including mixing NH4NO3 melt with crushed limestone or dolomite, granulating the mixture, drying and cooling the product, characterized in that the crushed carbonate raw materials are treated with a solution of ammonium hydrosulfate with a concentration of 20-45 wt before mixing with NH_4NO_3 melt. % while observing the mass ratio of crushed carbonate raw materials and ammonium hydrosulfate equal to 1 : (0,01-0,3). The particle size of the crushed carbonate raw materials is 0,8-1,5 mm, its temperature is 70-80°C, the temperature of the ammonium hydrosulfate solution is 40-50ºC. Further, the processed carbonate raw materials are mixed with NH_4NO_3 melt with a concentration of 85-98 wt. % taken in an amount that provides the required brand of fertilizer, for example, in the ratio of carbonate raw materials to NH_4NO_3 1 : (3,2-4). At the same time, the temperature in the mixer is maintained at 130-165°C. The mixture is granulated in a drum granulator, the temperature in which is 80-90ºC. Then the product is dried in a drying drum at 100-110 With and cooled. In this case, LAN is obtained with a total nitrogen content of 27.9%, calcium carbonate in terms of CaO 14.5% and calcium nitrate 0,6%. Granule strength is 42 n/m^2, friability is 100%, fractions 1-5 mm are 99%, ammonia losses are 0,12%.

The invention [10] relates to the production of LAN. Dolomite or magnesium carbonate (magnesite), or calcium carbonate are used as carbonate raw materials. The method involves obtaining an 87-93% solution of NH_4NO_3, its evaporation, mixing with carbonate raw materials in the presence of sulfate and/or magnesium nitrate, followed by granulation and cooling of the target product, while an 87-93% solution of ammonium nitrate is mixed with a solution of sulfate and/or magnesium nitrate in the first stage at a pH of 1,5-3,0, and at the second stage, neutralization is carried out to a pH of at least 5,0. The pH adjustment at the first stage of mixing is carried out by dosing nitric or sulfuric acids or by regulating the content of nitric or sulfuric acids in a solution of magnesium salts in the range of 1,5-7,0%, and neutralization is carried out with gaseous ammonia. A solution of magnesium salts is dosed based on the calculation of ensuring the content of water-soluble forms of calcium and magnesium in the target product in terms of $Mg_{water.}$ + CaO_{water} content 0,3-0,9% with a ratio of $Mg_{water.}$ + CaO_{water}. at least 2.0, preferably 3,0-4,0. The method provides an increase in the strength of fertilizer granules by 5-50% and, in combination with a low content of calcium nitrate in the product, allows you to obtain fertilizer with high consumer properties. Closed Joint Stock Company "Kuibyshev Azot" has developed and patented [11] a technological scheme for the production of LAN based on the interaction of finely ground limestone with NH_4NO_3 melt, which makes it possible to eliminate the loss of a valuable component of powdered limestone, eliminate pollution of the air basin with dust emissions, and also use pulverized limestone particles as a dusting agent. In the same joint-stock company, the above-mentioned technological scheme was improved in order to reduce atmospheric pollution, increase safety and reduce nitrogen losses by eliminating the formation of ammonia gas release when mixing NH_4NO_3 melt with finely ground limestone. The mixing node underwent reconstruction. The use of a new mixing unit provides gas–free contacting of the "ammonium nitrate float - finely ground limestone" system [12]. The most common and effective nitrogen fertilizer in the world is AC. But it has three very serious drawbacks. Firstly, it is explosive, secondly, it is traceable during storage, and thirdly, its physiologically acidic nature, which does not allow it to be used on acidic soils. In order to eliminate these disadvantages, the technology of obtaining LAN was developed by

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introducing lime materials (limestone, chalk or dolomite) into the melt of ammonium nitrate. Optimal conditions for the process of obtaining LAN are formulated in the literature. Inhibitors of the formation of calcium nitrate during the fusion of limestone with ammonium nitrate are also sulfuric acid, ammonium, magnesium, calcium, iron sulfates, sodium, potassium and ammonium silicofluorides, diammonium and dicalcium phosphates introduced into limestone in small quantities. Limestone or chalk can be replaced with dolomite in the production of LAN. Its use not only does not harm, but leads to an increase in yield compared to the LAN obtained in the usual way. The creation of LAN production using dolomite, with a lower content of carbonate mineral and a high content of nitrogen is also promising for Uzbekistan with its neutral and alkaline soils. The raw material base of dolomites in Uzbekistan is extensive. Their deposits are: Jarkak, Mamajurgaty, Kermine, Karakia. And their outputs are observed in the fields of Gaz, Kokpatas, Jasaul, Burchmulla, Nurekaty and Almalyk No. 9. Large reserves of limestones and dolomites are available in the fields of Dzhetymtau and Muruntau. The issues of interaction of dolomites of Uzbekistan with the melt of ammonium nitrate, the composition and properties of the products obtained, their agrochemical efficiency on the gray soils of Uzbekistan during the cultivation of various crops require study. Proceeding from the above, conducting systematic research on the development and implementation of export-oriented modified AN technology with the addition of local dolomite is a very urgent task, to which this dissertation work is devoted.

REFERENCES

[1] Chernyshov A.K., Levin B.V., Tugolukov A.V., Ogarkov A.A., Ilyin V.A. Ammonium nitrate: properties, production, application. – Moscow: CJSC INFOCHIM, 2009. - 544 p.

[2] Kilman Ya.I. Investigation of the process of obtaining lime-ammonium nitrate. Message 1. // Tr. State Scientific research. and the project. institute of nitrogen Industry. – 1956. - issue 5. - pp. 292-305.

[3] Bulatov M.A., Bondareva T.I., Kibrik E.D., Kutepov A.M., Pikulin Yu.G. Improving the process of obtaining lime-ammonium nitrate // Chemical industry. - 1996. - No. 8. – pp. 489-496.

[4] Taran A.L., Dolgalev E.V., Taran Yu.A. Obtaining lime-ammonium nitrate in granulation towers of ammonium nitrate production // Chemical engineering. - 2006. - No. 1. – pp. 28-31.

[5] Dolgalev E.V. Technology and hardware design of lime-ammonium nitrate production in granulation towers: Abstract. diss. ... Candidate of Technical Sciences. – M.: 2006. - 23 p.

[6] Taran A.L., Dolgalev E.V., Taran A.V. Hardware and technological design and economic efficiency of lime-ammonium nitrate production on existing AS-60 and AS-72 aggregates // Advances in chemistry and chemical technology. - 2007. - vol. 21, No. 9. – pp. 20-22.

[7] Taran A.L., Dolgalev E.V., Taran Yu.A. Centrifugal granulator of suspensions for the production of lime-ammonium nitrate in towers // Chemical industry today. - 2008. - No. 3. – pp. 45-48.

[8] Patent of the Russian Federation.№ 2277011 . Granulator / Rustambekov M.K., Taran A.L., Troshkin O.A., Dolgalev E.V., Sundiev S.A., Poplavsky V.Yu., Bubentsov V.Yu

[9] Patent of the Russian Federation. No. 2265001 Cl. From 05 G 1/08, From 05 D 3/02 / Avramenko A.N., Kononov S.M., Shirobokov O.A., Gromotkov V.N., Perepechko V.F., Kostyuchenko S.S., Kontareva E.N., Tsarevsky V.A., Mitsak I.A., Zorov V.G., Ovchinnikov V.M.Method of obtaining lime-ammonia fertilizer // B.I. 2005, No. 33.

[10] RF Patent No. 2290391. Cl. From 05 G 1/08, From 05 To 1/02 / Kuznetsov A.G., Polyakova O.A., Soloviev B.A., Sitnikov A.P., Sklyarenko T.N.Method of obtaining nitrogen fertilizer // – B.I. 2006, No. 36.

[11] Patent of the Russian Federation. No. 2252206 Cl. From 05 G 1/08 / Ogarkov A.A., Vasiliev V.V., Kuznetsov S.N. Technological line for the production of lime-ammonium nitrate // B.I. 2005, No. 14.

[12] Patent of the Russian Federation No. 2309135. Cl. From 05 G 1/08 / Ogarkov A.A., Kuznetsov S.N., Mukalin K.V. Technological line for the production of lime-ammonium nitrate // dated 27.10.2007.