

PATENT SPECIFICATION

(11) 1 226 723

NO DRAWINGS

1 226 3

(21) Application No. 25161/69 (22) Filed 16 May 1969

(45) Complete Specification published 31 March 1971

(51) International Classification: C 01 c 1/18

(52) Index at acceptance

C1A C3C8

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(54) STABILISED AMMONIUM NITRATE COMPOSITIONS AND THEIR PRODUCTION

(71) We, MISSISSIPPI CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Mississippi, and having a place of business at Highway 49 East, Yazoo City, State of Mississippi, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The change in crystal type which normally occurs when ammonium nitrate passes through 184° F. (II—III), 90° F. (III—IV), and rapidly through the 113—124° F. (II—IV) range results in a breakdown of larger particles (+20 mesh and larger) into smaller particles. In commercial production of prilled, granulated and pelletized ammonium nitrate, such smaller particles, i.e., dust or fines, must be separated from the product and reprocessed in the plant. In prilled ammonium nitrate production, the dust is separated and then redissolved as a weak liquor solution. Evaporators then remove this water, which increases the cost of the process. The recovered ammonium nitrate is then re-prilled after evaporation, thereby increasing the load on the prilling tower, and the drying and cooling drums, which reduces the capacity of the plant. Thus, any reduction in the amount of dust produced in the plant provides a corresponding increase in the capacity of a given plant and decreases the cost of operation.

In the prilling process, ammonium nitrate solution at 280° F. or above is sprayed in a prilling tower countercurrent to cooling air which solidifies the droplets into prills which are ultimately cooled to ambient temperature. Thus, the prills pass through the 257°, 184° and 90° F. transition temperatures. Ordinarily, the prills contain residual moisture and are dried with hot air. Thus, in commercial production, the prills are often passed rapidly through the 113—124° F.

Type II—IV transition range more than once. Passage of the prills through these transition points produces cracked prills and formation of finely divided powder in the prilling tower and drying and cooling drums and weakens the structure of the unbroken prills so that they readily break on subsequent handling. A similar problem exists in the production of particulate fertilizer compositions comprising ammonium nitrate.

Even though elaborate equipment is used to remove the undesired fines or dust from the commercial product, some is nevertheless carried over. In some plants, the prills or granules are bagged at above 90° F. so that the crystals pass through the 90° F. transition point within the bag, causing some cracked prill and dust formation. However, the most complete physical breakdown of the ammonium nitrate compositions comprising it occurs on storage when prills gradually soften on long storage or crack as a result of passage through the 90° F. crystal transition temperature. This physical breakdown causes extensive formation of dust and granules or prills with cracks and/or a weak grainy structure. Therefore, even if all such dust were absent from the product when originally packaged, it will subsequently be formed on handling and during storage. Ten percent or less cracked prills produce a marked deterioration in the physical properties of the product.

The most serious consequence of the physical instability of particulate ammonium nitrate when used as a fertilizer is its tendency to turn into a solid, hard cake during storage. Even when this does not occur, the fines and dust produced make the product more difficult to handle and use and thus reduces the quality thereof.

In particulate crystalline ammonium nitrate according to the present invention the crystals comprise, in addition to ammonium nitrate, boric acid or an ammonium salt

thereof, diammonium phosphate and diammonium sulphate and the weight percentage of the boric acid or ammonium salt thereof, calculated as boric acid, is 0.015 to 0.15, the weight percentage of diammonium phosphate is 0.03 to 0.2, the weight percentage of diammonium sulphate is 0.0015 to 0.015, the weight ratio of diammonium phosphate to diammonium sulphate is from 10 to 35, the weight ratio of diammonium sulphate to boric acid or ammonium salt thereof, calculated as boric acid, is 0.05 to 0.2 and the weight ratio of diammonium phosphate to boric acid or ammonium salt thereof, calculated as boric acid, is from 1 to 3.5, at least one of (i) the weight ratio of diammonium phosphate to diammonium sulphate and (ii) twice the weight ratio of boric acid or ammonium salt thereof, calculated as boric acid, to diammonium phosphate being other than 20. The preferred weight ratio of diammonium phosphate to diammonium sulphate is from 12 to 20.

Particulate ammonium nitrate according to the invention has improved physical stability i.e. greater hardness and resistance to caking and lower moisture sensitivity and/or breakdown in particle size. In particular the ammonium nitrate has improved resistance to physical breakdown caused by repeated passage through the III—IV crystal type transition temperature; in preferred ammonium nitrate according to the invention physical breakdown due to the III—IV crystal transitions is substantially eliminated. Another advantage of the ammonium nitrate is that physical breakdown caused by passage through the II—III and II—IV crystal type transition temperatures is reduced.

The improved stability of the ammonium nitrate is achieved with only very small quantities e.g. less than 0.1% by weight of boric acid or ammonium salt thereof calculated as boric acid being present. This is particularly advantageous when ammonium nitrate is to be used as a fertilizer since the ammonium nitrate according to the invention only results in the addition of very small quantities of trace elements i.e. boron to the soil.

A method according to the invention for making particulate crystalline ammonium nitrate comprises crystallising ammonium nitrate from a liquid mixture comprising, in addition to ammonium nitrate, boric acid or ammonium salt thereof, diammonium phosphate and diammonium sulphate in the amounts and relative proportions specified hereinbefore.

The method is advantageous since it enables the amount of dust and fines formed in the production of particulate ammonium nitrate to be reduced. In particular physical breakdown caused by rapid heating or cooling through the II—IV crystal type transition

temperature range is reduced. The fact that physical breakdown due to passage through the II—III crystal type transition temperature is reduced also reduces the amount of dust and fines formed.

When stabilising materials are added to ammonium nitrate large amounts of any materials injurious to plant growth cannot be used when the ammonium nitrate is to be used as a fertilizer. A large amount of boron compound, for example, is undesirable if the soil already contains excessive amounts of boron. Also, in the fertilizer industry, a slight reduction in cost may influence the selection of one process or product over another. This is especially true with the present invention wherein a judicious choice of additives results in a stable product at a low per unit cost.

As used herein, "particulate" ammonium nitrate means in the form of separate, discrete macroparticles, e.g., prills, granules and pellets, as opposed to cast or powdered ammonium nitrate or solutions thereof. "Fines" and "dust" refer to the very small particles of ammonium nitrate, e.g., of -20 mesh, -30 mesh and smaller, normally associated with the production of granular, pelleted and prilled ammonium nitrate.

The starting liquid ammonium nitrate used in the process of this invention includes molten ammonium nitrate containing very little moisture, e.g., 0.2 to 6 percent, of the type conventionally used to produce prills and pelletized ammonium nitrate, and aqueous solutions of ammonium nitrate, e.g., those conventionally used to produce ammonium nitrate in prilled or granulated form. This aspect of the invention is directed primarily to the purer forms of ammonium nitrate, e.g., 94 percent and preferably 97 percent or higher, whose physical instability is particularly great.

Boric acid is usually used although an ammonium salt of boric acid is sometimes preferred when the starting liquid mixture is produced by the ammoniation of nitric acid. Because of the free ammonia often present in ammonium nitrate during its manufacture, some or all of the boric acid, when it is used, may be converted to an ammonium salt thereof.

The diammonium sulphate and diammonium phosphate function cooperatively and synergistically with the boric acid or ammonium salt thereof to improve the stability of the ammonium nitrate, particularly with respect to III—IV transition. Large amounts of diammonium phosphate by itself are usually required to improve materially the stability of the ammonium nitrate. However, when used in conjunction with the boric acid or ammonium salt thereof and diammonium sulphate, very small amounts effectively improve the stability of the am-

monium nitrate. Moreover, half as much or less of the boric acid or ammonium salt thereof is required to improve II—IV and III—IV transition stability than is the case if the diammonium phosphate and sulphate are absent. 0.03 to 0.2 percent by weight of diammonium phosphate more preferably about 0.04 to 0.2 percent by weight, is employed. Very small amounts, i.e. 0.0015 to 0.015 percent by weight, of diammonium sulphate are employed. A weight ratio of boric acid or ammonium salt thereof calculated as boric acid to diammonium sulphate from about 10 to about 20 appears to impart optimum stability.

In such mixtures, although up to 0.365 percent by weight of the three ingredients can be used to produce a stabilized ammonium nitrate composition, preferably from about 0.08 to 0.35 percent is used. Although the highest degree of stabilization thus far achieved was with 0.135 percent by weight H_3BO_3 , 0.01 percent by weight $(NH_4)_2SO_4$ and 0.2 percent by weight $(NH_4)_2HPO_4$ (no cracked prills in over 1400 III—IV transitions), excellent stabilization is also achieved with lesser amounts, e.g., as low as 0.04, 0.002 and 0.04 percent by weight, respectively, of these additives.

One or more of the boron, phosphate and sulphate compounds employed in this invention can be added to the starting liquid form of the ammonium nitrate or formed in situ by first adding boric, phosphoric and sulphuric acid thereto followed by addition of ammonia. The latter technique can be used when manufacturing ammonium nitrate from nitric acid. When additives are used per se rather than being formed in situ in the ammonium nitrate melt or aqueous solution or in the mixture used to produce the ammonium nitrate, they can be added as a finely divided solid or in a pre-formed aqueous or molten ammonium nitrate solution. Whatever technique is used, for best results thorough mixing should be employed to ensure a homogeneous mixture is obtained.

Three factors affect the degree of stabilization achieved with the stabilizing compositions of this invention. The first factor is the pH of the ammonium nitrate. If the pH is too high, i.e., so that free ammonia is present in or released from the ammonium nitrate mixture, or if the pH is too low, so that free acid is present in the mixture, improvement in stability is substantially reduced. The optimum pH for any selected stabilizing composition can readily be determined by the stability tests described herein-after. It varies with the selected stabilizing composition, but usually is between 5.0 and 7.0 (as an 8 percent by weight solution). The second is the ratio of boric acid to diammonium sulphate and the ratio of di-

ammonium phosphate to diammonium sulphate. The third factor is the manner in which the additives composition is formed and added to the mixture. When using a combination of boric acid, phosphoric acid and sulphuric acid to form the additives, the phosphoric acid must be converted to an ammonium salt before being mixed with free boric acid. A preferred technique involves ammoniating a mixture of phosphoric acid and sulphuric acid in the selected proportion until a pH is reached whereby all the phosphoric and sulphuric acid is converted to an ammonium salt. Boric acid is then added thereto and the mixture again ammoniated to a pH above 5.0. If concentrated acids are used, e.g., 93 percent sulphuric and 85 percent phosphoric, the resulting mixture is a slurry which can be pumped into the ammonium nitrate composition to be stabilized. This procedure is particularly advantageous with prilled ammonium nitrate because it does not increase the load on the evaporators and thus does not adversely affect plant capacity.

In areas having high boron content, it is desirable to employ as little boric acid as possible to stabilize the ammonium nitrate. A surprising degree of stability can be achieved with very low amounts of boric acid or ammonium salt thereof calculated as boric acid, e.g., 0.04 to 0.075 percent by weight, by employing from 0.002 to 0.01 percent by weight diammonium sulphate and from 0.04 to 0.2 percent by weight diammonium phosphate, where boric acid content is critical. Outstanding results are obtained with from 0.1 to 0.135 e.g., 0.125 to 0.135 percent by weight of boric acid or ammonium salt thereof calculated as boric acid by employing from 0.005 to 0.0125 e.g., 0.01 to 0.0125 percent by weight of diammonium sulphate and from 0.1 to 0.2 e.g. 0.15 to 0.2 percent by weight diammonium phosphate.

The following examples further describe and illustrates the invention. Percentages and parts are by weight.

EXAMPLES 1-10 Ammonium Nitrate Prills
 NH_4NO_3 prills (0.2 percent H_2O) were melted and various percentages of diammonium phosphate (DAP), boric acid, and diammonium sulphate (DAS) were blended in the melt. The molten mixture was then dropped with a dropper onto a Teflon sheet to form prills and cooled. These prills were tested for resistance to breakage from cycling through the III—IV (90° F.) transition. In the III—IV transition tests, prills were heated at 110° F. for two hours and then cooled to about 78° F. for two hours. The percent prills cracked in each test were recorded after each cycle. These data are tabulated in Table I.

TABLE I

AMMONIUM NITRATE COMPOSITIONS
Percent Prills Cracked by 90° F. Thermal Shock

No. of Transitions	1	2	3	4	5	6	7	8	9	10
Example										
% H ₂ BO ₃	0.04	0.06	0.065	0.075	0.1	0.10	0.10	0.125	0.125	0.135
% 2DAS	0.002	0.003	0.01	0.0125	0.005	0.01	0.0065	0.0075	0.0125	0.01
% DAP	0.04	0.06	0.20	0.15	0.1	0.13	0.20	0.15	0.15	0.20
DAP/DAS	20	20	20	12	20	13	31	20	12	20
B/DAS	20	20	6.5	6	20	10	15.4	16.7	10	13.5
DAP/B	1	1	3.1	2	1	1.3	2	1.2	1.2	1.5
10	0	0	0	0	0	0	0	0	0	0
50	0	0	0	0	0	0	0	0	0	0
200	0	0	0	0	0	0	0	0	0	0
250	0	0	0	0	0	0	0	0	0	0
300	0	0	0	0	0	0	0	0	0	0
350	4	0	0	0	0	0	0	0	0	0
400	4	0	0	0	0	0	0	0	0	0
450	4	0	0	0	0	0	0	0	0	0
500	4	0	0	0	0	0	0	0	0	0
510	20	4	0	0	0	0	0	0	0	0
520	32	8	0	0	0	0	0	0	0	0
530	36	12	0	0	0	0	0	0	0	0
540	40	16	0	0	0	0	0	0	0	0
550	40	16	4	0	0	0	0	0	0	0
560	44	48	4	0	0	0	0	0	0	0
570	56	60	4	0	0	0	0	0	0	0
580	54	68	8	0	0	0	0	4	0	0
590	72	72	0	0	0	0	0	4	0	0
600	72	72	0	0	0	0	0	8	0	0
610	88	80	0	0	0	0	0	8	0	0
620	88	84	0	0	0	0	0	8	0	0
630	100	96	0	0	0	0	0	12	0	0
640		100	0	0	0	0	0	12	0	0
700			8	8		0	0		0*	0**

* passed through over 1200 transitions with no breakage

** passed through over 1400 transitions with no breakage

**WHAT WE CLAIM IS:—**

1. Particulate crystalline ammonium nitrate in which the crystals comprise, in addition to ammonium nitrate, boric acid or an ammonium salt thereof, diammonium phosphate and diammonium sulphate and the weight percentage of the boric acid or ammonium salt thereof, calculated as boric acid, is 0.015 to 0.15, the weight percentage of diammonium phosphate is 0.03 to 0.2, the weight percentage of diammonium sulphate is 0.0015 to 0.015, the weight ratio of diammonium sulphate to boric acid or ammonium salt thereof calculated as boric acid is from 0.05 to 0.2 and the weight ratio of diammonium phosphate to boric acid or ammonium salt thereof calculated as boric acid is from 1 to 3.5, at least one of (i) the weight ratio of diammonium phosphate to diammonium sulphate and (ii) twice the weight ratio of boric acid or ammonium salt thereof calculated as boric acid to diammonium phosphate being other than 20.
2. Particulate crystalline ammonium nitrate according to claim 1 containing at least 97% by weight of ammonium nitrate.
3. Particulate crystalline ammonium nitrate according to either preceding claim containing 0.125 to 0.135% by weight of boric acid or ammonium salt thereof calculated as boric acid, 0.15 to 0.2% by weight of diammonium phosphate and 0.01 to 0.0125% by weight of diammonium sulphate.

4. Particulate crystalline ammonium nitrate according to claim 1 or claim 2 containing 0.04 to 0.075% by weight of boric acid or ammonium salt thereof calculated as boric acid, 0.04 to 0.2% by weight of diammonium phosphate and 0.002 to 0.01% by weight of diammonium sulphate.
5. Particulate crystalline ammonium nitrate according to claim 1 substantially as described herein with reference to any of the Examples.
6. A method of making particulate crystalline ammonium nitrate according to claim 1 comprising crystallising ammonium nitrate from a liquid mixture comprising, in addition to ammonium nitrate, boric acid or ammonium salt thereof, diammonium phosphate and diammonium sulphate in the amounts and relative proportions specified in claim 1.
7. A method according to claim 6 substantially as described herein with reference to any of the Examples.
8. Particulate crystalline ammonium nitrate prepared by a method according to claim 7.

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