

PATENT SPECIFICATION

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(54) STABILISED NH_4NO_3 - CaCO_3 FERTILISER COMPOSITIONS

(71) We, MISSISSIPPI CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Mississippi, United States of America, 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:—

Ammonium nitrate fertilizer compositions are subject to changes in crystalline structure during production and storage as the NH_4NO_3 passes through its crystalline transition temperatures. Transitions in crystal structure result in dust and fines being produced from the breakdown of the ammonium nitrate crystal during storage and subsequent handling. Due to the hygroscopic nature of ammonium nitrate, the compositions tend to cake on standing.

Similar problems also exist with mixed ammonium nitrate fertilizer compositions containing large amounts, e.g. up to 60 percent by weight, of calcium carbonate, usually in the form of limestone. Such fertilizers are popular in some countries for the acid neutralizing properties of limestone when applied to the soil and the diluent properties of the limestone. Attempts to solve these stability problems have been made, by introducing finely divided calcium carbonate into a hot solution of ammonium nitrate in an attempt to produce a more stable product. However, the problem remains as a serious one today.

Various methods for the purpose of stabilising ammonium nitrate have been used involving the addition of various materials to increase physical stability. For instance, boric acid and its alkali-metal and ammonium salts have been used. Also a mixture with ammonium salts of phosphoric and/or sulphuric acids has been used.

Boric acid, diammonium phosphate, diammonium sulphate or a mixture thereof has

been added to molten ammonium nitrate-calcium carbonate mixed fertilizer compositions to give a product of increased stability but prills produced from the composition were swollen and soft. Also, the product still had the typical and objectionable acrid smell of ammonia, indicating loss of nitrogen values due to the known reaction of the calcium carbonate with the ammonium nitrate. This problem is well known and it has been reported that a smell of ammonia sometimes accompanies the mixed fertilizer long after production. A special procedure for removing the smell of ammonia has in fact been proposed since the presence of the ammonia is annoying and causes production problems.

Surprisingly it has now been found that, in the manufacture of particulate ammonium nitrate-calcium carbonate mixed fertilisers, a greatly improved product can be obtained if monoammonium and/or diammonium phosphate and boric acid or an ammonium or alkali metal salt thereof is mixed into the ammonium nitrate, in liquid form, before the calcium carbonate is added. The mixed fertiliser particles e.g. prills which can be made in this way are harder than those obtained by the method referred to above in which stabilising additives are added to a melt of ammonium nitrate containing calcium carbonate. By use of the method according to the invention particles e.g. prills of the fertiliser can be produced which have improved stability to thermal and mechanical shocks and which are less hygroscopic than known ammonium nitrate-calcium carbonate mixed fertilisers. Furthermore, fertilisers can be made by the use of the present method which do not smell of ammonia, nor are problems created by evolution of ammonia during carrying out the method.

The stabilising additive or additives are mixed into the ammonium nitrate whilst the ammonium nitrate is in liquid form and the calcium carbonate is only added to the mixture after the stabilising additive or additives has

been added. The ammonium nitrate may be in the form of an aqueous solution but we greatly prefer to use molten ammonium nitrate. The liquid form of the ammonium nitrate used preferably contains at least 90 weight % and more preferably at least 94 weight % of ammonium nitrate itself. The liquid form of ammonium nitrate used can be heated before the additives are added and this is, of course, necessary where a melt of ammonium nitrate is used.

Calcium carbonate, usually ground limestone, is next added, preferably in finely divided form to facilitate suspension throughout the mixture. The proportions of ammonium nitrate and calcium carbonate may be varied within wide limits. Thus, for example from 90 to 30 parts by weight of NH_4NO_3 , and from 10 to 70 parts by weight of calcium carbonate can be used. The preferred ratio of NH_4NO_3 to CaCO_3 is 3:1 by weight.

This sequence of addition of the ingredients is essential to the production of the highly stabilised fertiliser compositions of this invention.

The resulting stabilized ammonium nitrate-calcium carbonate mixed fertilizer composition is then converted to particulate form, that is in the form of separate, discrete macro-particles, such as prills, granules or pellets, and preferably prills, as opposed to powdered ammonium nitrate or solutions thereof.

The amount of ammonium phosphate which gives optimum stabilization will vary with the conditions employed. From 0.05 to 0.5 percent by weight can be used, the preferred amount being from 0.1 to 0.3 percent. Diammonium phosphate gives better results than monoammonium phosphate. The amount of boric acid or salt thereof used is generally an amount which provides 0.03 to 0.2 weight percent, preferably 0.05 to 0.15 weight percent, boric acid in the final mixture. The amount of ammonium sulfate used is usually from 0.005 to 0.5 weight percent, preferably 0.01 to 0.5 weight percent and most preferably 0.015 to 0.2 weight percent and the ammonium sulfate may be added e.g. in aqueous solution to produce this content. Generally, the total amount of additive which gives optimum results is less than 0.5 weight percent, e.g. from 0.1 to 0.4 percent by weight, calculated on the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture.

The preferred stabilizing agent is a mixture of boric acid or an ammonium or alkali-metal salt thereof, and diammonium phosphate. Best results are obtained when the percentage by weight of the above ingredients in the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture is 0.135 percent, 0.01 percent, and 0.2 percent by weight respectively. The liquid mixture is maintained at a temperature which retains it in a fluid state, and mixed until the stabilizing ingredi-

ents are thoroughly dispersed in the ammonium nitrate.

The following examples are illustrative of the process and products of this invention which is not limited thereto. All percentages are by weight, calculated on the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture.

In the examples which follow, each sample was prepared in the following manner unless otherwise indicated. Ammonium nitrate of C.P. grade, 99.7 percent was melted, the desired amounts of boric acid, ammonium phosphate, ammonium sulfate and salts thereof, herein described as additives and expressed in percentage by weight in Tables I through VII, were added to the molten ammonium nitrate. The resulting mixture was stirred until the additive was dissolved, then C.P. calcium carbonate was added in a ratio of one part of calcium carbonate to three parts of ammonium nitrate, with continued stirring. A slurry resulted after the addition of calcium carbonate. The slurry was placed in droplets on a cool sheet of polyfluorohydrocarbon and the droplets were allowed to solidify into prills (pellets). The solidified pellets were then subjected to shaking and temperature transitions in the following manner.

In each test 25 of the ammonium nitrate-calcium carbonate prills produced as described above were placed in sealed screw-top glass containers and the containers were placed in an oven for 2 hours at 110°F. The containers with contents were then removed from the oven and cooled to 70°F. During this cooling period the containers were shaken vigorously on a Burrell laboratory shaker for 30 minutes. Then the containers were maintained at 70° without shaking for 1.5 hours. At the end of this period the containers were returned to the oven maintained at 110°F. and the heating and cooling steps were repeated. Each complete cycle of heating and cooling thus involved two III—IV crystal type transitions. After each cycle (two transitions), the prills were examined for breakage. The number of prills was multiplied by a factor of 4 to give the percentage of pellets broken by thermal shock or shaker tests.

The thermal shock and shaker test is an accelerated version of the storage and handling conditions to which fertilizer is usually subjected during storage and affords an accurate method of evaluating the storage and handling properties of the fertilizer compositions.

Effect of Order of Addition

Table I shows the effects of varying the sequence of addition in the production of ammonium nitrate-calcium carbonate stabilized fertilizer compositions according to the invention. Sample A contained no additives, only ammonium nitrate and calcium carbonate.

Sample B was prepared by first mixing the calcium carbonate with the ammonium nitrate, then mixing in the additives. Note that the prills thus-produced tolerated about ten more transitions well than the untreated prills of Sample A. Samples 1 and 2 were prepared in accordance with the invention by adding the stabilizing agent to the molten ammonium nitrate before the calcium carbonate. Samples 1 and 2 also show the relative stabilizing effect of $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$.

TABLE I

Effect of Sequence of Addition
Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	B*	1**	2**
% H_3BO_3	0	0.135	0.135	0.135
% $(\text{NH}_4)_2\text{SO}_4$	0	0.01	0.01	0.01
% $(\text{NH}_4)_2\text{HPO}_4$	0	0.2	—	0.2
% $\text{NH}_4\text{H}_2\text{PO}_4$	—	—	0.2	—
No. of Transitions				
10	0	0	0	0
50	100	28	0	0
100		100 (90 trans.)	0	0
200			40	4
300			68	12
			100 (320 trans.)	24 (400 trans.)
				32 (500 trans.)
				100 (560 trans.)

* Additives added after CaCO_3 in sample.

** Additive added before CaCO_3 in sample.

Effect of Amounts of Additives

Table II shows the range and effect of different levels of boric acid, ammonium sulfate and ammonium phosphate additives.

All of the additives were effective in improving the quality of product produced without additives (Sample A).

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TABLE II

Effect of Additive Level
Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	2	3	4	5	6
% H_3BO_3	0	0.135	0.034	0.068	0.2	0.2
% $(\text{NH}_4)_2\text{SO}_4$	0	0.01	0.0025	0.005	0.2	0.1
% $(\text{NH}_4)_2\text{HPO}_4$	0	0.2	0.05	0.1	0.2	0.3
No. of Trans						
10	0	0	0	0	0	0
20	4	0	0	0	0	0
30	32	0	8	0	0	0
40	96	0	24	0	0	0
50	100	0	72	0	0	0
60	—	0	88	0	4	0
70		0	100	0	16	84
80		0	—	0	84	100
90		0		0	100	
100		0		4		
150		0		8		
200		4		12		
250		8		60		
				100 (280 trans.)		
		12 (300 trans.)				
		24 (400 trans.)				
		32 (500 trans.)				
		100 (560 trans.)				

Effect of Mixture of $(\text{NH}_4)_2\text{HPO}_4$ and H_3BO_3
Table III shows the effects of various mix-
tures of boric acid and ammonium phosphate.

The effectiveness of the mixture decreases if
the $(\text{NH}_4)_2\text{HPO}_4$ additive level exceeds about 5
0.3 percent.

TABLE III

Effect of Mixtures of H_3BO_3 and $(\text{NH}_4)_2\text{HPO}_4$

Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	7	8	9	10
% H_3BO_3	0	0.034	0.068	0.135	0.2
% $(\text{NH}_4)_2\text{SO}_4$	0	—	—	—	—
% $(\text{NH}_4)_2\text{HPO}_4$	0	0.05	0.1	0.2	0.5
No. of Trans.					
10	0	0	0	0	0
20	4	0	0	0	4
30	32	0	0	0	4
40	96	24	0	0	80
50	100	64	0	0	100
60	—	84	0	0	—
70		100	0	0	
80			0	0	
90			0	0	
100			0	0	
			8 (200 trans.)	0 (200 trans.)	
			36 (250 trans.)	0 (250 trans.)	
			100 (290 trans.)	4 (300 trans.)	

Effect of Mixtures of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ sulfate and ammonium phosphate in stabilizing ammonium nitrate-calcium carbonate fertilizer mixtures. 5

TABLE IV
Effect of Mixtures of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$
Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	11	12	13	14
% H_3BO_3	0	—	—	—	—
% $(\text{NH}_4)_2\text{SO}_4$	0	0.01	0.1	0.2	0.5
% $(\text{NH}_4)_2\text{HOP}_4$	0	0.2	0.2	0.1	0.2
No. of Trans.					
10	0	0	0	0	0
20	4	0	0	0	0
30	32	0	0	0	0
40	96	0	0	0	0
50	100	0	0	0	20
60	—	0	0	0	32
70		0	0	0	80
80		0	0	8	100
90		8	0	32	
100		12	0	84	
110		12	0	100	
120		20	0		
130		44	12		
140		88	16		
150		100	40		
		—			
190			100		

Effect of $(\text{NH}_4)_2\text{HPO}_4$
Table V shows the stabilizing effect of di-
ammonium phosphate alone.

TABLE V

Effect of $(\text{NH}_4)_2\text{HPO}_4$ Alone

Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	15	16	17
% H_3BO_3	0	—	—	—
% $(\text{NH}_4)_2\text{SO}_4$	0	—	—	—
% $(\text{NH}_4)_2\text{HPO}_4$	0	0.1	0.2	0.5
No. of Trans.				
10	0	0	0	0
20	4	4	0	0
30	32	16	0	0
40	96	72	0	0
50	100	92	0	16
60	—	100	0	36
70		—	0	100
80			0	
90			0	
100			0	
150			8	
200			52	
250			100	

Effect of Combinations of Additives
Table VI shows that certain combinations
of additives are more effective than others.

TABLE VI

Effect of H_3BO_3 , $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ Used Individually and in Combination

Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	C	D	E	F	16	11	12	9	2
% H_3BO_3	0	0.135	—	—	0.135	—	—	—	0.135	0.135
% $(\text{NH}_4)_2\text{SO}_4$	0	—	0.2	0.5	0.01	—	0.01	0.1	—	0.01
% $(\text{NH}_4)_2\text{HPO}_4$	0	—	—	—	—	0.2	0.2	0.2	0.2	0.2
No. of Trans.										
10	0	0	0	4	0	0	0	0	0	0
20	4	0	4	80	0	0	0	0	0	0
30	32	16	12	100	16	0	0	0	0	0
40	96	88	60	—	80	0	0	0	0	0
50	100	100	84		100	0	0	0	0	0
100	—	—	100 (60 trans.)		—	0	12	12 (130 trans.)	0	0
150						8	100		0	0
200						52		100 (190 trans.)	0	4
250						100			0	8
300									4	12
350										20
400									12	24
450										
500										32
550										100 (560 trans.)

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Effect of Constant pH

Because the various additives produced mixed fertilizers of different pH's, samples shown therein were prepared and the pH then adjusted so that each would have a pH of 6.8, based on an 8 percent solution. Table VII

reflects the results. It shows that even though the pH remains constant, there is a great difference in stability to the thermal shock and shaker test. Stability, therefore, is not due solely to the difference in pH of the various samples. 15

TABLE VII

Effect of Additive Composition at Constant pH

Percent Prills Broken by 90° F. Thermal Shock and Shaker Test

Sample No.	A	16	18	11	12	4	2	1
% H_3BO_3	0	—	—	—	—	0.068	0.135	0.135
% $(\text{NH}_4)_2\text{SO}_4$	0	—	0.005	0.01	0.1	0.005	0.01	0.01
% $(\text{NH}_4)_2\text{HPO}_4$	0	0.2	0.1	0.2	0.2	0.1	0.2	—
% $\text{NH}_4\text{H}_2\text{PO}_4$	—	—	—	—	—	—	—	0.2
<u>No. of Trans.</u>								
10	0	0	0	0	0	0	0	0
50	100	0	100	0	0	0	0	0
100	—	0	—	12	0	4	0	0
150		8		100	40	8	0	36
200		52			100 (190 trans.)	12	4	40
250		100				60	8	40
100 (280 trans.) 12 (300 trans.) 68 (300 trans.)								
20 (350 trans.) 100 (320 trans.)								
24 (400 trans.)								
32 (500 trans.)								
100 (560 trans.)								

Caking after Storage Test

Prills produced according to the invention were compared with samples containing no additives, e.g., Sample A of the previous tables, by subjecting them to the following procedure. Two hundred prills were placed in separate glass bottles, one inch in diameter and sealed with a screw top, and maintained at a temperature in the range of 65 to 75°F. for a period of two weeks. At the end of the two-week period, the jars were inverted to determine the extent of caking therein. Prills with additives remained free-flowing while those without additives were firmly caked together.

The jars were again inverted to their original position and placed in the same storage area at a temperature in the range of 65 to 75°F. for a period of 2.5 months. At the end of this period the samples were again examined and again the prills produced according to the invention remained free-flowing while the untreated prills did not.

The jars were returned to the same storage area and stored for an additional 3 months, under the same conditions, giving a total storage time of 6 months. The samples were again examined. Pellets without additives were found to be caked and extremely hard. Prill surfaces showed crystal growth. Samples containing additives showed no caking and remained free-flowing at the end of the 6-month storage. The surface of the prills produced according to the invention remained smooth and glossy.

WHAT WE CLAIM IS:—

1. A method of producing particulate ammonium nitrate-calcium carbonate mixed fertilisers which comprises mixing mono-ammonium phosphate and/or diammonium phosphate and boric acid or an ammonium or alkali metal salt thereof into ammonium nitrate in liquid form and then mixing the calcium carbonate into the mixture so formed.

2. A method according to claim 1 wherein the ammonium phosphate is diammonium phosphate.

3. A method according to either preceding claim in which ammonium sulphate is also added to the ammonium nitrate prior to the addition of the calcium carbonate.

4. A method according to claim 1 or claim 2 wherein the ammonium phosphate is added

in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.05 to 0.5 percent by weight of ammonium phosphate.

5. A method according to claims 1 or 3 wherein an ammonium salt of boric acid is added to the ammonium nitrate in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.03 to 0.2 percent by weight of boric acid.

6. A method according to claims 1 or 3 or claim 5 wherein diammonium phosphate is added in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.05 to 0.5 percent by weight of diammonium phosphate.

7. A method according to claim 3 wherein diammonium phosphate and boric acid are added in amounts such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.05 to 0.5 percent by weight of diammonium phosphate and from 0.03 to 0.2 percent by weight of boric acid.

8. A method according to claim 7 wherein the ammonium sulphate is added in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.01 to 0.5 percent by weight of ammonium sulphate.

9. A method according to claim 3 wherein the ammonium sulphate is added as an aqueous solution in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.005 to 0.5 percent by weight of ammonium sulphate.

10. A method according to any preceding claim in which the ammonium nitrate to which the specified compound or compounds are added is in molten form.

11. A method according to claim 1 substantially as hereinbefore described with reference to any of the Examples.

12. A particulate ammonium nitrate-calcium carbonate mixed fertiliser produced by a method according to any preceding claim.

13. A particulate mixed fertiliser according to claim 11 containing from 0.05 to 0.15 percent by weight of diammonium phosphate and from 0.05 to 0.15 percent by weight of boric acid.

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Caking after Storage Test

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1. A method of producing particulate ammonium nitrate-calcium carbonate mixed fertilisers which comprises mixing mono-ammonium phosphate and/or diammonium phosphate and boric acid or an ammonium or alkali metal salt thereof into ammonium nitrate in liquid form and then mixing the calcium carbonate into the mixture so formed.

2. A method according to claim 1 wherein the ammonium phosphate is diammonium phosphate.

3. A method according to either preceding claim in which ammonium sulphate is also added to the ammonium nitrate prior to the addition of the calcium carbonate.

4. A method according to claim 1 or claim 2 wherein the ammonium phosphate is added

in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.05 to 0.5 percent by weight of ammonium phosphate.

5. A method according to claims 1 or 3 wherein an ammonium salt of boric acid is added to the ammonium nitrate in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.03 to 0.2 percent by weight of boric acid.

6. A method according to claims 1 or 3 or claim 5 wherein diammonium phosphate is added in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.05 to 0.5 percent by weight of diammonium phosphate.

7. A method according to claim 3 wherein diammonium phosphate and boric acid are added in amounts such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.05 to 0.5 percent by weight of diammonium phosphate and from 0.03 to 0.2 percent by weight of boric acid.

8. A method according to claim 7 wherein the ammonium sulphate is added in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.01 to 0.5 percent by weight of ammonium sulphate.

9. A method according to claim 3 wherein the ammonium sulphate is added as an aqueous solution in an amount such that the final $\text{NH}_4\text{NO}_3\text{—CaCO}_3$ mixture contains from 0.005 to 0.5 percent by weight of ammonium sulphate.

10. A method according to any preceding claim in which the ammonium nitrate to which the specified compound or compounds are added is in molten form.

11. A method according to claim 1 substantially as hereinbefore described with reference to any of the Examples.

12. A particulate ammonium nitrate-calcium carbonate mixed fertiliser produced by a method according to any preceding claim.

13. A particulate mixed fertiliser according to claim 11 containing from 0.05 to 0.15 percent by weight of diammonium phosphate and from 0.05 to 0.15 percent by weight of boric acid.

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