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(72) Inventors MARION LIPSCOMB BROWN JR., ALBERT WISE
GREEN and ELMER LADELLE BLANTON

(54) METHOD OF PRODUCING CONCENTRATED SOLUTIONS
OF MIXED AMMONIUM SALTS OF BORIC, PHOSPHORIC
AND SULPHURIC ACIDS

(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:—

This invention relates to a method of producing concentrated solutions of a mixture of the ammonium salts of boric, phosphoric and sulphuric acids, more particularly by the addition of boric acid to a concentrated solution of ammonium salts of phosphoric and sulphuric acids, free from phosphoric acid, followed by the addition of sufficient ammonia to produce a final solution in which at least most of the ammonium phosphate is diammonium phosphate.

The sensitivity of ammonium nitrate to II—IV and III—IV crystal transitions can be reduced by including in the liquid from which the solid ammonium nitrate is to be obtained a mixture of ammonium salts of boric, phosphoric and sulphuric acids. It is desirable to reduce such transitions since they result in physical breakdown of the granules or prills which are a convenient form for ammonium nitrate for various purposes e.g. as a fertilizer.

In ammonium nitrate production the ammonium salts of boric, sulphuric and phosphoric acids cannot be added satisfactorily in dry form to the liquid containing the ammonium nitrate since the dry mixture cannot readily be distributed uniformly in the liquid and since if the ammonium salts are added in the dry form the orifices used in forming ammonium nitrate prills tend to become fouled. For these reasons it is more satisfactory to have the ammonium salts of boric, phosphoric and sulphuric acids in the

form of an aqueous solution prepared by dissolving the salts together or separately in that order. Unfortunately solutions obtained in this way are relatively dilute and thus their use increases the load on the evaporators employed in an ammonium nitrate plant. This is undesirable since the capacity of such a plant may be determined by the capacity of its evaporators and, in a high density ammonium nitrate plant, the water content of dilute solutions might preclude their use.

The problem associated with the addition of dilute solutions of the ammonium salts cannot of course be avoided simply by making the dilute solutions and then concentrating them by evaporation since this would require the use of further evaporators. Furthermore concentrated solutions of the mixed ammonium salts cannot be obtained by adding ammonia to a mixture of the three free acids since this results in the formation of insoluble precipitates. The same problem arises if sulphuric and boric acids are first converted to their ammonium salts and phosphoric acid then added. Nor is it satisfactory to form the ammonium phosphate separately and then add it to the other ammonium salts since this requires the use of an extra tank, pump and ancillary equipment.

Attempts to produce concentrated solutions of the mixed ammonium salts of boric, phosphoric and sulphuric acids in which most of the ammonium phosphate was present as monoammonium phosphate have resulted in the formation of slurries of precipitated solids which were difficult to handle and to maintain in a homogeneous state. Also when solutions have been obtained solids have tended to precipitate from them on standing even at very high temperatures, e.g. 256—311° F.

The process according to the present invention involves the addition of boric acid to a concentrated solution, free from phosphoric acid, of a mixture of the ammonium salts of

[Price 25p]

phosphoric and sulphuric acids. The solution to which the boric acid is added contains less than 55% by weight water and often less than 50% by weight water, e.g. from 30 to 50% by weight of water, thus the concentration of the ammonium salts of sulphuric and phosphoric acids in the solution is preferably at least 50% by weight. The weight of ratio of ammonium salt of phosphoric acid to ammonium salt of sulphuric acid in the solution is at least 5:1, preferably from 10:1 to 30:1 but may be up to 100:1 or higher.

Such a solution is preferably prepared by ammoniation, preferably with anhydrous but optionally with aqueous ammonia, of a mixture of phosphoric and sulphuric acids. Preferably sufficient ammonia is added so that a portion, e.g., 25 percent and desirably from 30—80 percent by weight, of the phosphoric acid is converted to diammonium phosphate, to ensure that no free phosphoric acid is present in the mixture when the boric acid is added. The water content of the acid mixture is preferably less than 55 percent and more preferably 30 to 50 percent. If aqueous ammonia is used, the acids should be of correspondingly higher concentration so that the water content of the final solution is less than 55 percent. Cooling means should be provided to maintain the temperature of the solution below 190° F. The weight ratio of phosphoric acid to sulfuric acid in the mixture of starting acids is at least 5:1, e.g., up to 100:1 or higher but preferably from 10:1 to 30:1.

The ammonia is preferably bubbled well below the surface of the mixture of acids, which should be well stirred during the addition, thereby minimizing any ammonia losses. The amount which should be added can be determined on a weight basis; by the pH of the solution, which should be at least about 4 but no more than 8; or by the odor of ammonia, which tends to build up after all the phosphoric acid has been converted to monoammonium phosphate. The precise amount of ammonia which has been added can be calculated by adding at least enough ammonia to convert all the free acid to ammonium salts, withdrawing an aliquot sample, determining the amount of standard acid required to bring the pH to 4 and then the amount of standard base required to bring the pH to 8. The proportion of the added acid to base is the proportion of phosphoric acid present as diammonium phosphate.

It will be apparent the amount of ammonia which must be added is influenced by the amount of sulphuric acid present in the mixture. However, in the preferred mixtures, only about 1/10th to 1/30th as much sulphuric acid is present as phosphoric acid, an amount of ammonia such that at least the total amount of ammonia added.

Boric acid is added to the solution of mixed ammonium salts in a weight proportion

of at least 5:1 based on the sulphuric acid, e.g., up to 100:1 or higher but preferably from 10:1 to 30:1. Desirably, the molar ratio of boric acid to phosphoric acid is from 0.5:1 to 2:1, preferably 0.5:1 to 1.1:1.

The boric acid can be added as solid, e.g., crystals or powder, or as a hot concentrated aqueous solution. Powdered boric acid is preferred. As in the preceding step, the mixture should be thoroughly stirred, the temperature kept below 190° F. Care should be taken to ensure the boric acid is uniformly distributed without lumping in the solution. If aqueous boric acid is used, preferably the amount of water thus added to the mixture is no more than that required to maintain the total moisture content of the solution below 55 percent.

In the next step, ammonia is added, in the manner described above, in an amount such that most, e.g., at least 70 percent by weight and preferably at least 80 percent by weight of the phosphoric acid is present as diammonium phosphate. Such solutions have much lower freezing points than corresponding solutions of the same concentration in which less than 70 percent of the phosphoric acid is in the form of diammonium phosphate. The amount which should be added can be determined in the same manner as described above. The pH of the solution should be about 7 to 8. Thus, all acid present in the mixture is in the form of ammonium salts thereof.

The resulting solution has a relatively low freezing point, e.g., 60 to 130° F. It can be pumped into ammonium nitrate plants by means of proportioning pumps or other methods. The solution can be fed into ammonium nitrate solution or melt at one of the following several points:

- A. Into the melt or solution in the pipeline leading to the prilling sprays;
- B. Into the pump suction tanks which feed the prilling towers;
- C. Into the solution feeding to the evaporators;
- D. Into head tanks which feed to prilling tower sprays; and
- E. Into ammonium nitrate-ammonia-water solutions used in granulation of complete fertilizers.

It will be apparent to those familiar with the art there are also other possible points of introducing the additive batch mixture into the ammonium nitrate.

EXAMPLE.

Add 3400 pounds of water to a batch weight tank. Start mechanical agitation of the water. Add 2230 pounds of phosphoric acid (75 percent by weight H_3PO_4) to the batch weight tank followed by 106 pounds of

5 sulphuric acid (98.0 percent by weight H_2SO_4). Add anhydrous ammonia to the solution in the tank until the molar ratio of NH_3 to H_3PO_4 of 1.3:1 (or higher) is obtained. This ought to require about 414 pounds of ammonia based on all the sulphuric acid being converted to diammonium sulphate and 30 percent of the phosphoric acid being converted to diammonium phosphate. The molar ratio of the batch can be checked by conventional laboratory titration procedure, e.g., back titrate an aliquot sample with standard acid to pH4 and then to pH8 with standard base. Add 2000 pounds of boric acid (powdered form) to the batch tank. Next, add ammonia to the batch solution to bring the molar ratio of NH_3 to H_3PO_4 to 1.8:1 to 2.0:1. This ought require 284 to 340 pounds anhydrous ammonia, based on all the boric acid being converted to ammonium salt and all the phosphoric acid to diammonium phosphate. Final pH should be about 8. Maintain the temperature in the batch tank at no greater than

190° F. at all times. The batch, which is about 60—65 percent solids, can then be agitated until used in the plant. It is quite fluid at 70° F. and can be stored for long periods of time.

With a proportioning pump, pump the resulting solution to molten ammonium nitrate at the prilling tower of a high density nitrate plant at a rate of about ten pounds per ton of ammonium nitrate, which incorporates about 0.2 percent diammonium phosphate, about 0.01 percent diammonium sulphate and about 0.18 percent boric acid (equiv.) into the ammonium nitrate. Prill in the conventional manner.

The following table illustrates the marked increase in freezing point of mixtures of ammonium salts of boric, sulphuric acid when the $NH_3:H_3PO_4$ ratio is less than 1.7, i.e., when less than 70 percent of the ammonium phosphate is in the form of diammonium phosphate. All the following percentages are by weight.

Percent H_3BO_3 (equiv.)	Percent DAS*	Percent DAP/MAP**	Percent H_2O	Mole Ratio NH_3/H_3PO_4	Freezing Point
19.6	2.2	31.7	46.5	2.01	60°F.
30.3	2.0	30.3	32.4	1.17	115°F.
33.0	1.75	30.8	33.0	1.24	171°F.
30.2	3.2	32.9	33.7	1.64	168°F.

*diammonium sulphate

**diammonium phosphate/monoammonium phosphate

The above solutions can also be pumped to the prilling tower of a low density plant or to the granulating equipment of a mixed fertilizer plant.

WHAT WE CLAIM IS:—

1. A method of producing a concentrated aqueous solution of mixed ammonium salts of boric, phosphoric and sulfuric acids which comprises the steps of (a) adding boric acid to an aqueous solution containing less than 55% by weight of water, and ammonium salts of phosphoric and sulphuric acids, which solution is free from phosphoric acid and in which the weight ratio of ammonium salt of phosphoric acid to ammonium salt of sulphuric acid is at least 5 to 1, and the weight ratio of boric acid to ammonium salt of sulphuric acid is at least 5 to 1; and (b) then adding an amount of ammonia such that at least the major portion of the ammonium salt of phosphoric acid is diammonium phosphate.
2. A method according to claim 1 wherein anhydrous ammonia is employed in step (b) and the starting solution of mixed ammonium salts has a water content of from 30 to 50 percent by weight.
3. A method according to either preceding claim wherein at least a portion of the ammonium salt of phosphoric acid in the solu-

tion to which the boric acid is added is diammonium phosphate.

4. A method according to any preceding claim which includes the step of forming the starting solution of mixed ammonium salts by adding ammonia to a mixture of phosphoric and sulphuric acids of a weight ratio of at least 5 to 1 and of a water content of less than 55 percent by weight until the solution is free of phosphoric acid.

5. A method according to claim 4 wherein the ratios of the boric acid and of the phosphoric acid (in the ammonium salts) to the sulphuric acid (in the ammonium salts) both are from 10 to 1 to 30 to 1.

6. A method according to claim 4 or claim 5 wherein sufficient ammonia is added to the starting mixture of phosphoric and sulphuric acids to convert at least 25 percent by weight of the phosphoric acid to diammonium phosphate.

7. A method according to any preceding claim wherein the amount of ammonia added in step (b) is such that at least 80 percent by weight of the ammonium salt of phosphoric

5 sulphuric acid (98.0 percent by weight H_2SO_4). Add anhydrous ammonia to the solution in the tank until the molar ratio of NH_3 to H_3PO_4 of 1.3:1 (or higher) is obtained. This ought to require about 414 pounds of ammonia based on all the sulphuric acid being converted to diammonium sulphate and 30 percent of the phosphoric acid being converted to diammonium phosphate. The molar ratio of the batch can be checked by conventional laboratory titration procedure, e.g., back titrate an aliquot sample with standard acid to pH4 and then to pH8 with standard base. Add 2000 pounds of boric acid (powdered form) to the batch tank. Next, add ammonia to the batch solution to bring the molar ratio of NH_3 to H_3PO_4 to 1.8:1 to 2.0:1. This ought require 284 to 340 pounds anhydrous ammonia, based on all the boric acid being converted to ammonium salt and all the phosphoric acid to diammonium phosphate. Final pH should be about 8. Maintain the temperature in the batch tank at no greater than

190° F. at all times. The batch, which is about 60—65 percent solids, can then be agitated until used in the plant. It is quite fluid at 70° F. and can be stored for long periods of time.

With a proportioning pump, pump the resulting solution to molten ammonium nitrate at the prilling tower of a high density nitrate plant at a rate of about ten pounds per ton of ammonium nitrate, which incorporates about 0.2 percent diammonium phosphate, about 0.01 percent diammonium sulphate and about 0.18 percent boric acid (equiv.) into the ammonium nitrate. Prill in the conventional manner.

The following table illustrates the marked increase in freezing point of mixtures of ammonium salts of boric, sulphuric acid when the $NH_3:H_3PO_4$ ratio is less than 1.7, i.e., when less than 70 percent of the ammonium phosphate is in the form of diammonium phosphate. All the following percentages are by weight.

Percent H_3BO_3 (equiv.)	Percent DAS*	Percent DAP/MAP**	Percent H_2O	Mole Ratio NH_3/H_3PO_4	Freezing Point
19.6	2.2	31.7	46.5	2.01	60°F.
30.3	2.0	30.3	32.4	1.17	115°F.
33.0	1.75	30.8	33.0	1.24	171°F.
30.2	3.2	32.9	33.7	1.64	168°F.

*diammonium sulphate

**diammonium phosphate/monoammonium phosphate

The above solutions can also be pumped to the prilling tower of a low density plant or to the granulating equipment of a mixed fertilizer plant.

WHAT WE CLAIM IS:—

1. A method of producing a concentrated aqueous solution of mixed ammonium salts of boric, phosphoric and sulphuric acids which comprises the steps of (a) adding boric acid to an aqueous solution containing less than 55% by weight of water, and ammonium salts of phosphoric and sulphuric acids, which solution is free from phosphoric acid and in which the weight ratio of ammonium salt of phosphoric acid to ammonium salt of sulphuric acid is at least 5 to 1, and the weight ratio of boric acid to ammonium salt of sulphuric acid is at least 5 to 1; and (b) then adding an amount of ammonia such that at least the major portion of the ammonium salt of phosphoric acid is diammonium phosphate.
2. A method according to claim 1 wherein anhydrous ammonia is employed in step (b) and the starting solution of mixed ammonium salts has a water content of from 30 to 50 percent by weight.
3. A method according to either preceding claim wherein at least a portion of the ammonium salt of phosphoric acid in the solu-

tion to which the boric acid is added is diammonium phosphate.

4. A method according to any preceding claim which includes the step of forming the starting solution of mixed ammonium salts by adding ammonia to a mixture of phosphoric and sulphuric acids of a weight ratio of at least 5 to 1 and of a water content of less than 55 percent by weight until the solution is free of phosphoric acid.

5. A method according to claim 4 wherein the ratios of the boric acid and of the phosphoric acid (in the ammonium salts) to the sulphuric acid (in the ammonium salts) both are from 10 to 1 to 30 to 1.

6. A method according to claim 4 or claim 5 wherein sufficient ammonia is added to the starting mixture of phosphoric and sulphuric acids to convert at least 25 percent by weight of the phosphoric acid to diammonium phosphate.

7. A method according to any preceding claim wherein the amount of ammonia added in step (b) is such that at least 80 percent by weight of the ammonium salt of phosphoric



acid is diammonium phosphate.

8. A method according to claim 5 wherein (a) anhydrous ammonia is employed and the starting solution of mixed ammonium salts has a water content of from 30 to 50 percent; (b) the boric acid is added as a powder; (c) sufficient ammonia is added to the starting mixture of phosphonic and sulphuric acids to convert at least 30 percent of the phosphoric acid to diammonium phosphate; and (d) the amount of ammonia added following the boric acid is such that at least 80 percent of the ammonium salt of phosphonic acid is diammonium phosphate.
9. A method according to claim 1 substantially as described herein with reference to the Example.

For the Applicants,
R. G. C. JENKINS & CO.,
Chancery House, 53/64, Chancery Lane,
London, WC2A 1QU.

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