PROCESS FOR THE MANUFACTURE OF MAGNESIUM AMMONIUM PHOSPHATE MONOHYDRATE

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ABSTRACT OF THE DISCLOSURE

This invention discloses a process for the production of magnesium ammonium phosphate monohydrate comprising reacting an aqueous slurry of a substantially water insoluble magnesium compound with an excess of monoammonium dihydrogen phosphate at a temperature of from 80 to 100°C and a pH value of from about 4.6 to about 7.2, thereby precipitating magnesium ammonium phosphate monohydrate substantially free of impurities such as, e.g., magnesium ammonium phosphate hexahydrate and magnesium hydrogen phosphate.

This invention relates to a process for the manufacture of magnesium ammonium phosphate monohydrate and, more particularly, is concerned with a process for preparing in high yields magnesium ammonium phosphate monohydrate (MgNH₄PO₄·H₂O) which is substantially free of mononitriammonium phosphate hexahydrate and other reaction products, such as magnesium hydrogen phosphate (MgH₂PO₄·3H₂O) and the like. The magnesium ammonium phosphate monohydrate is preferred over the hexahydrate form. The hexahydrate is in the form of a voluminous fine meal which is heavier and thus less economical to ship than the monohydrate form. Although the monohydrate may be obtained by drying the hexahydrate to drive off five waters of hydration, this drying procedure is expensive and involves a loss of ammonia thus lowering the ultimate yield of the monohydrate product.

Until now, magnesium ammonium phosphates have been prepared by expensive processes utilizing soluble magnesium salts in alkaline solution or by the reaction of olivine rock (MgSiO₃) with orthophosphoric acid. We have unexpectedly discovered a process for preparing magnesium ammonium phosphate containing only one water of hydration from a non-alkaline solution, which is less expensive to operate than existing processes and produces nearly stoichiometric yields of the pure monohydrate compound.

Thus, it is an object of the instant invention to provide a process for preparing magnesium ammonium phosphate monohydrate from a non-alkaline solution which is more efficient, and less expensive, than processes existing heretofore.

An additional object is to provide a process which produces nearly stoichiometric quantities of a pure product consisting of the magnesium ammonium phosphate monohydrate substantially free from magnesium ammonium phosphate hexahydrate, magnesium hydrogen phosphate and the like.

Other objects and advantages of the instant process will become apparent after reading the detailed description of the invention presented hereinafter.

In accordance with the instant invention, we have discovered that by adding a substantially water-insoluble magnesium compound, for example, a slurry of magnesium hydroxide containing from about 5 to about 60 percent by weight magnesium hydroxide, a slurry of magnesium oxide in water containing from about 3.5 to about 41.5 percent magnesium oxide, or a slurry of magnesium carbonate in water containing from about 7 to about 60 percent magnesium carbonate, to an aqueous solution of from about 10 to about 63 weight percent monoammonium dihydrogen phosphate while maintaining a reaction temperature of from about 80°C to about 100°C and a preferred temperature of from about 85°C to about 95°C, and providing a pH value in the reaction mixture within the range of from about 4.6 to about 7.2, with a preferred pH value being within the range of from about 5.8 to about 6.6, substantially pure magnesium ammonium phosphate containing one molecule water of hydration (MgNH₄PO₄·H₂O) is produced.

It is to be noted that a critical feature of the present process is that the magnesium compound must be added to the aqueous solution of monoammonium dihydrogen phosphate and not vice versa if a substantially 100 percent pure monohydrate product is to be obtained. At least a 10 percent excess of monoammonium dihydrogen phosphate, and preferably an excess of from about 10 percent to about 50 percent of that stoichiometrically needed to react with the magnesium compound, should be used in the instant process to obtain a favorable yield of the desired product substantially free of the hexahydrate.

If a slurry of magnesium hydroxide is used, a mole ratio of NH₄H₂PO₄/Mg(OH)₂ within the range of from about 1.0 to about 1.3 should be maintained.

In addition, if a slurry of magnesium oxide in water or a slurry of magnesium carbonate in water or a slurry of magnesium hydroxide is used, the mole ratio of the magnesium to magnesium equivalents (hereinafter expressed as NH₄H₂PO₄/Mg) present in the reaction mixture should be maintained at a value within the range of from about 1.0 to about 1.3 so that a product of magnesium ammonium phosphate monohydrate containing about 8 percent nitrogen (N), 44 percent phosphorus, expressed as phosphorus pentoxide (P₂O₅), and about 24 percent magnesium, expressed as magnesium oxide (MgO) is produced.

The rate of formation of the precipitate of magnesium ammonium phosphate monohydrate is almost instantaneous. The time of reaction is not critical. Ordinarily to assure a substantially complete reaction, reaction times within the range of from about 1 to about 30 minutes should be employed. If longer reaction times are used, ammonia may be evolved from the system and may thus lower the ultimate yield of the monohydrate.

Utilizing magnesium carbonate as a starting material in the instant process produces essentially the same results as when the aqueous slurry of magnesium hydroxide or the magnesium oxide in water is used; however, a reaction time ranging from about 5 to about 60 minutes should be employed with this reactant.

Monoammonium dihydrogen phosphate reactant may be easily prepared by reacting an aqueous solution containing from about 5 to about 28 percent by weight of ammonia as NH₄OH with at least stoichiometric quantities of orthophosphoric acid solutions containing from about 5 to about 85 weight percent orthophosphoric acid at a temperature within the range of from about 5°C to about 95°C, and while maintaining a pH value in the reaction mixture within the range of from about 4.4 to about 4.8. The process is not limited to the use of aqueous ammonia solution, but in fact includes the addition of gaseous ammonia to an aqueous solution of orthophosphoric acid.

The instant process may be carried out in batch or continuous-type operation.

The product of the instant process, namely, magnesium ammonium phosphate monohydrate, finds utility as a high analysis, slow release-type nitrogen phosphorus fertilizer. In addition, it provides magnesium for the
s, an essential element for plant nutrition, which is becoming increasingly more deficient in soils of many sections of the United States.

The following example is merely illustrative of the process of the instant invention and in no way is intended to limit it thereto.

Example

A 31.7 percent by weight aqueous solution of monoammonium dihydrogen phosphate was prepared by mixing 103.8 grams of a 28 percent by weight aqueous solution of ammonia along with 95.3 grams of an 85 percent by weight orthophosphoric acid solution while maintaining a pH value of about 4.6 in the mixture.

155 grams of an aqueous slurry containing about 24.8 percent Mg(OH)₂ was added to 300 grams of the above solution (said 300 grams of monoammonium dihydrogen phosphate representing about 20 weight percent in excess of that stoichiometrically needed) in a reactor. The reaction was allowed to continue for about 7 minutes while maintaining a temperature within the range of from about 91° to about 94° C.

A precipitate was thereby formed and filtered from the solution on a Buchner funnel and was then washed with about 1500 milliliters of water, said wash water being maintained at a temperature ranging from about 50° to about 60° C.

The precipitate was then washed with 500 milliliters of ethyl alcohol followed by two 500 milliliter portions of diethyl ether to remove surface water.

Air was then passed through the solvent-washed precipitate for 40 minutes to remove excess solvent.

The air dried precipitate was then dedicated in an anhydrous calcium chloride desiccator for about 40 minutes.

The precipitate, which weighed 246 grams, was then analyzed for composition by X-ray diffraction and was found to be substantially 100 percent pure MgNH₄PO₄·H₂O

Following the procedure illustrated in the example, the above product is prepared using either a slurry of magnesium oxide in water or magnesium carbonate in water, with a reaction time of from about 5 to about 60 minutes for said carbonate. A substantially 100 percent pure MgNH₄PO₄·H₂O is obtained.

Various modifications can be made in the process of the instant invention without departing from the spirit or scope thereof, for it is to be understood that we limit ourselves only as defined in the appended claims.

What is claimed is:

1. A process for preparing magnesium ammonium phosphate monohydrate which comprises:
   (a) adding an aqueous slurry of a magnesium compound selected from the group consisting of magnesium hydroxide, magnesium oxide and magnesium carbonate, to an aqueous solution of monoammonium dihydrogen phosphate at a reaction temperature within the range of from about 80° to about 100° C, containing at least 10 percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with the selected magnesium compound slurry, the resulting mixture providing a mole ratio of ammonia to magnesium equivalents within the range of from about 1.0 to about 1.3, and having a pH value within the range of from about 4.6 to about 7.2, thereby precipitating magnesium ammonium phosphate monohydrate; and
   (b) separating the so-formed precipitate from said mixture.

2. The process in accordance with claim 1 wherein a pH value of from about 5.8 to about 6.6 is maintained in said reactor during the precipitation.

3. The process in accordance with claim 1 including the initial steps of preparing monoammonium dihydrogen phosphate by adding an aqueous solution containing from about 5 to about 28 weight percent NH₄OH to an aqueous solution containing from about 5 to about 85 weight percent orthophosphoric acid while maintaining a pH value within the range of from about 4.4 to about 4.8 and a temperature within the range of from about 5° to about 95° C.

4. The process in accordance with claim 1 including the initial steps of preparing monoammonium dihydrogen phosphate by adding gaseous ammonia to an aqueous solution of orthophosphoric acid while maintaining a pH within the range of from about 4.4 to about 4.8 and a temperature within the range of from about 5° to about 95° C.

5. The process in accordance with claim 1 wherein the reaction is carried out at a temperature within the range of from about 85° to about 95° C.

6. The process in accordance with claim 1 including the steps of washing and drying the so-formed precipitate.

7. A process for preparing magnesium ammonium phosphate monohydrate which comprises:
   (a) adding an aqueous slurry containing from about 7.2 to about 60 percent by weight magnesium carbonate to an aqueous solution of from about 10 to about 63 percent by weight monoammonium dihydrogen phosphate at a temperature within the range of from about 80° to about 100° C, containing at least 10 percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with the slurry of magnesium carbonate, the resulting mixture providing a mole ratio of ammonia to magnesium equivalents within the range of from about 1.0 to about 1.3, and having a pH value within the range of from about 5.8 to about 6.6 and for a reaction time within the range of from about 5 to about 60 minutes, thereby precipitating magnesium ammonium phosphate monohydrate; and
   (b) separating the so-formed precipitate from said mixture.

8. The process in accordance with claim 7 wherein the reaction is carried out at a temperature within the range of from about 85° to about 95° C.

9. A process for preparing magnesium ammonium phosphate monohydrate which comprises:
   (a) adding a slurry of magnesium oxide in water containing from about 3.5 to about 41.5 percent by weight magnesium oxide to an aqueous solution of from about 10 to about 63 percent weight monoammonium dihydrogen phosphate at a temperature within the range of from about 80° to about 100° C, containing at least 10 percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with the aqueous slurry of magnesium oxide in water, the resulting mixture providing a mole ratio of ammonia to magnesium equivalents within the range of from about 1.0 to about 1.3 while maintaining a pH value within the range of from about 5.8 to about 6.6 and for a reaction time within the range of from about 1 to about 30 minutes, thereby precipitating magnesium ammonium phosphate monohydrate; and
   (b) separating the so-formed precipitate from said mixture.

10. The process in accordance with claim 9 wherein the reaction is carried out at a temperature within the range of from about 85° to about 95° C.

11. A process for preparing magnesium ammonium phosphate monohydrate which comprises:
   (a) adding an aqueous slurry containing from about 5 to about 60 percent by weight magnesium hydroxide to an aqueous solution from about 10 to about 63 percent by weight monoammonium dihydrogen phosphate at a temperature within the range of from about 80° to about 100° C, containing at least 10 percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with the aqueous slurry of magnesium hydroxide in water, the resulting mixture providing a mole ratio of ammonia to magnesium equivalents within the range of from about 1.0 to about 1.3, and having a pH value within the range of from about 4.6 to about 7.2, thereby precipitating magnesium ammonium phosphate monohydrate; and
   (b) separating the so-formed precipitate from said mixture.
percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with the aqueous slurry of magnesium hydroxide, the resulting mixture providing a mole ratio of ammonia to magnesium equivalents within the range of from about 1.0 to about 1.3 while maintaining a pH value within the range of from about 5.8 to about 6.6, and for a reaction time within the range of from about 1 to about 30 minutes, thereby precipitating magnesium ammonium phosphate monohydrate; and

(b) separating the so-formed precipitate from said mixture.

12. The process in accordance with claim 11 wherein the reaction is carried out at a temperature within the range of from about 85° to about 95° C.

13. A process for preparing magnesium ammonium phosphate monohydrate which comprises:

(a) adding an aqueous mixture of a magnesium compound selected from the group consisting of magnesium hydroxide, magnesium oxide and magnesium carbonate, to an aqueous solution of monoammonium dihydrogen phosphate at a temperature of about 90° C. containing at least 10 percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with the selected aqueous magnesium compounds mixture, the resulting mixture providing a mole ratio of ammonia to magnesium equivalents within the range of from about 1.0 to about 1.3 while maintaining a pH value within the range of from about 5.8 to about 6.6, thereby precipitating magnesium ammonium phosphate monohydrate; and

(b) separating the so-formed precipitate from said mixture.

14. A process for preparing magnesium ammonium phosphate monohydrate which comprises:

(a) adding a slurry of magnesium hydroxide to an aqueous solution of monoammonium dihydrogen phosphate at a temperature within the range of from about 91° to about 94° C. containing about 20 percent by weight monoammonium dihydrogen phosphate in excess of that stoichiometrically needed to react with a slurry of magnesium hydroxide, the resulting mixture providing a mole ratio of

$$\text{NH}_4\text{H}_2\text{PO}_4/\text{Mg(OH)}_2$$

within the range of about 1.0 to about 1.3 and a pH value within the range of from about 5.8 to about 6.6, thereby precipitating magnesium ammonium phosphate monohydrate; and

(b) separating the so-formed precipitate from said mixture.

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