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(54) Title: A UREASE DEGRADATION RESISTANT LIQUID PRODUCT AND A METHOD FOR MAKING SAME

(57) Abstract

The urease resistant product of the invention is made in an aqueous reaction comprising urea, a hexose sugar source and an acid to obtain a liquid urea fertilizer product which is urease hydrolysis resistant. During the reaction, the following are balanced: the rate of combining (speed of mixing) the urea, the hexose sugar source and acid where the urea is in molar excess of the hexose sugar source, the pH of the reaction mixture provided by the acid and the time and temperature at which the acid, the hexose sugar and the urea are held. The resulting urea fertilizer product has at least about 12 weight percent nitrogen from urea (based upon the weight of the liquid product), and a range of from about 12 to about 30 weight percent nitrogen from urea and at least about 34 weight percent of the urea nitrogen in the product being urease hydrolysis resistant.

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A UREASE DEGRADATION RESISTANT LIQUID PRODUCT AND A METHOD FOR MAKING SAME

BACKGROUND OF THE INVENTION

Urea is a preferred form of nitrogen fertilizer because it is inexpensive and high in its nitrogen analysis. It is susceptible to volatilization, however, after its hydrolysis to NH_2 by the action of the enzyme urease which is commonly found in soil. A substantial fraction of the nitrogen in urea can be lost to volatilization with 3 days of application. Up to 50% of the nitrogen can be lost to volatilization when urea is applied to a surface and not incorporated as in the case of turf use (Joo et al., 1992; Crop Sci. 32:1397-1401). Loss of nitrogen to volatilization as ammonia will continue even after incorporation. When soil conditions are favorable for nitrification, a significant fraction of urea-nitrogen can be lost to leaching in the form of NO_2. The leaching loss beyond the reach of plant roots is a more severe problem in sandy soils. Urea-nitrogen can also be lost in the form of nitrogen gas (N_2), nitric oxide (NO), or nitrous oxide (N_2O) due to the action of denitrifying bacteria on NO_2 derived from urea.

Coating "granulated" urea with commercially available resins such as Osmocote® or sulfur to physically restrict the release of nitrogen into the soil and decreasing water solubility of urea by reaction with aldehydes have been utilized to reduce the rapid loss of urea to hydrolysis. Urease inhibiting compounds [such as N-(n-butyl) thiophosphoric triamide and phenylphosphoro-diamidate] also have been known as fertilizer amendments. No one approach, however, appears to have been adequate to overcome the loss of urea-nitrogen to volatilization as NH_2 or to leaching as NO_2.

SUMMARY OF THE INVENTION

The present invention generally provides an inexpensive enzyme degradation resistant liquid product which provides plants with a slow release urea nitrogen and a method for producing the degradation resistant product. The urea nitrogen containing product of the invention, which exhibits resistance to degradation (hydrolysis) by urease enzymes, can be applied to soil and other plant growth mediums in solid or liquid forms for use as a slow release or slow performance nitrogen fertilizer for plants. The product can be used alone, or in combination with one or more other powder, granular or liquid fertilizers. The liquid product exhibits resistance to degradation by urease, an enzyme present in plant growth mediums which disadvantageously rapidly hydrolyzes urea present in fertilizers, and causes a loss of the beneficial nitrogen by volatilization of ammonia (NH_3). The hydrolyzed urea nitrogen can also be lost in the form of NO_3 due to leaching. Thus, the urea containing product of the invention advantageously degrades very slowly in plant growth mediums and supplements the mediums with valuable nitrogen.

In its broadest aspect, the method of the present invention balances the following in an aqueous reaction mixture comprising urea, a hexose sugar source and an acid to obtain a liquid urea fertilizer product which is urease hydrolysis resistant: the rate of combining (speed of mixing) the urea, the hexose sugar source and acid where the urea is in molar excess of the hexose sugar source, the pH of the reaction mixture provided by the acid and the time and temperature at which the acid, the hexose sugar and the urea are held to provide a liquid urea fertilizer product which has at least about 12 weight percent nitrogen from urea (based upon the weight of the liquid product), and a range of from about 12 to about 30 weight percent nitrogen from urea and at least

about 34 weight percent of the urea nitrogen in the product being urease hydrolysis resistant.

In an important aspect, the method of the present invention which provides the degradation resistant liquid urea product comprises combining a hexose sugar source, an acid source and urea in an aqueous reaction mixture, the urea and the hexose sugar source being combined at a gradual rate, the urea being in molar excess of the hexose sugar after the combining the urea and hexose sugar in the hexose sugar source, the water in the reaction mixture, the hexose sugar source in the reaction mixture and urea in the reaction mixture being held at a time and temperature, the acid source effective for supplying a pH, all of which are effective for providing a liquid urea fertilizer product which is urease hydrolysis resistant and which has a urea nitrogen content of at least about 12 weight percent (based upon the weight of the liquid fertilizer product), and a range of from about 12 to about 30 weight percent urea nitrogen, and a urease hydrolysis resistant urea nitrogen content, based upon the weight of the urea nitrogen in the fertilizer product, of at least about 34 weight percent. In another important aspect, the fertilizer product will have a urea nitrogen content of about 16 to about 17 weight percent.

The method of the invention is particularly effective and efficient in its use of hexose sugar from the sugar source, such as glucose, for providing a hydrolysis resistant product. The urea is in molar excess of the hexose sugar source such that the molar ratio of the hexose sugar to the urea is not more than about 0.35. Moreover, the molar ratio of hexose sugar to the resulting urease hydrolysis resistant urea product is not more than about 1.0. In another important aspect the acid source is in an amount for providing an aqueous blend of the urea and hexose sugar source with an initial pH of not more than about 2. In a very important aspect, the hexose sugar is glucose.

It also has been discovered that as a result of the presence in the aqueous urea-sugar-acid reaction mixture of small quantities of a water soluble source of metal 2+ ions selected from the group consisting of Mn^{2+}, Zn^{2+}, Cu^{2+} ions and mixtures thereof, during the process unexpectedly results in a significant increase in the percent of urease resistant urea nitrogen reaction product which is obtained over that which is obtained when the water soluble metal 2+ ion source is not added during the process. In this aspect of the invention which provides the degradation resistant liquid product, the method comprises combining as an aqueous blend, a water soluble metal 2+ ion source, a hexose sugar source, an acid source and urea, the urea, the metal 2+ ion source and the hexose sugar source being combined in relative amounts such that urea is in molar excess of hexose sugar from the hexose sugar source, the water in the aqueous blend, the metal 2+ ion source, the hexose sugar source and the urea being held at a time and temperature, the acid source effective for supplying a pH, all of which are effective for providing a liquid fertilizer product has urea nitrogen which is urease hydrolysis resistant. This urease hydrolysis resistant product has a urea nitrogen content (nitrogen from urea) of at least about 12 weight percent, and a range of from about 12 to about 30 weight percent, and a urease hydrolysis resistant nitrogen content (nitrogen from urea which is hydrolysis resistant), based upon the weight of the urea-nitrogen in the fertilizer product of at least about 50 weight percent. In an important aspect, the method of the invention provides a urease hydrolysis resistant urea nitrogen of at least about 80 weight percent with the process effective for providing yields of hydrolysis resistant urea nitrogen of up to about 100 percent. This aspect of the invention also is particularly effective and efficient in its use of the hexose sugar, such as glucose, for providing a product having hydrolysis resistant urea nitrogen such that the

molar ratio of hexose sugar to urea is not more than about 0.35 and molar ratio of hexose sugar to the resulting urea product having urease hydrolysis resistant urea is not more than about 1.0. Also it is important in this aspect of the invention that the acid source is in an amount for providing a blend of the urea, hexose sugar source and water with an initial pH of not more than about 2. In an important aspect of the invention, the metal 2+ ion is Cu^{2+} and in a very important aspect of the method of the invention, it has been discovered that the presence of a water soluble Cu^{2+} ion source coupled with the incremental or gradual mixing of the urea with the hexose sugar source, such as glucose, water and acid source in the blend results in a very significant increase in the yield of the urease resistant urea nitrogen reaction product, such as at least about 75 weight percent up to about 100 percent.

In an important aspect, the method of the invention comprises: (a) mixing from about 15 to about 50 weight percent water, from about 4 to about 40 weight percent of a hexose sugar hexose source, from about 0.1 to about 1.0 weight percent of a Cu^{2+} ions and from about 10 to about 45 weight percent of urea at a temperature of from about 15°C to about 100°C for a period of time which is effective for dissolving the hexose sugar source and the urea; and (b) maintaining the resulting mixture at a temperature from about 15°C to about 100°C for a period of time which is effective for converting at least about 34 weight percent of the urea in the mixture to a urease-resistant nitrogen.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

As used herein, the phrase "acid source" means any source of an acid which at the concentration described herein is not toxic to, or otherwise detrimental to the growth of, plants and includes, for example, sulfuric

acid, phosphoric acid, citric acid, hydrochloric acid, nitric acid and mixtures of any combination of the foregoing acids. In an important aspect, the acid source employed in the present invention is a mixture of sulfuric acid and phosphoric acid.

As used herein, the phrase "water soluble source of metal 2+ ions" means any source of Mn^{2+}, Zn^{2+}, Cu^{2+} ions which is water soluble and supplies a Cu (II) or Cu $^{++}$ ion, Mn (II) or Mn^{2+} ion, and Zn (II) or Zn^{2+} ion or mixtures of these ions and is not toxic to, or otherwise detrimental to the growth of, plants. Sources of these ions include, for example, copper sulfate or zinc sulfate, copper or zinc nitrate, copper or zinc chloride and mixtures of any combination of the foregoing sources of ions. Water soluble means that the metal 2+ ion source is sufficiently soluble in the water, urea and sugar source blend to provide at least about 0.1 weight percent metal 2+ ions. In an important aspect, the metal 2+ ion is copper and the copper ion source employed in the present invention is copper sulfate.

As used herein with respect to the mixing of ingredients, the terms "incrementally" and "incremental mixing" and "gradual mixing" and "combining at a gradual rate" mean that a material, such as a hexose sugar source and urea, are mixed together and optionally with other ingredients in a series of two or more separate, consecutive additions, in one or more gradual, continuous additions over a period of time, or in a combination of the foregoing types of additions, over the entire period of performing the process for producing nitrogen which exhibits resistance to degradation by urease enzymes, or over any portion of such period. In an important aspect, the addition of the hexose sugar source and/or urea in the method of the present invention is performed by one continuous addition of the material over the period of the entire process.

Urease-resistant urea nitrogen is a fraction of the total nitrogen from urea in the product which is made by

the method of the invention that is not hydrolyzed to ammonia when subjected to the urease enzyme. Urease susceptible urea nitrogen is determined by subjecting a sample to the urease enzyme and by quantifying the ammonia that subsequently is liberated. The procedure is outlined in AOAC official methods 941.04 (1955).

Non-protein urea nitrogen (NPN) is nitrogen from urea.

As used herein, the phrase "hexose sugar source" means any source of a sweet carbohydrate hexose sugar and includes, for example, milk sugar, cane sugar, molasses (beet, cane, corn, wood, citrus, refinery, commingled, inert, discard, solidified, sorgo, sand other types of molasses), corn syrup, maple syrup, the monosaccharides or disaccharides glucose, galactose, sucrose, saccharose, mannose, maltose, lactose, dextrose, fructose, inositol, levulose, raffinose, and mixtures of any combination of the foregoing sources of sugar, such as a mixture of glucose and molasses. In an important aspect, the sugar source employed in the present invention is substantially glucose.

EXAMPLE I

Urease-resistant nitrogen is produced according to the following procedure using the ingredients, and weight percents thereof, described herein below.

The glucose and/or cane molasses is slowly mixed with the water and stirred until it is completely dissolved. Urea is mixed with the resulting glucose solution and heated with stirring to bring the temperature to 130°F (54°C) and until the urea is completely dissolved. The temperature is raised to 130°F in order to dissolve the urea more quickly. The sulfuric acid then is mixed with the solution, and the solution is stirred. The indicated amount of phosphoric acid is mixed with the solution, and the solution is stirred. The resulting solution is transferred to a 1000 mL sealable plastic container which is incubated in a 180°F

(82.22°C) water bath for 8 hours. Some foaming typically occurs causing the plastic container to expand. For this reason, the reaction container should be filled to no more than about 50% full to accommodate the foaming which occurs during the reaction. While the container is incubated, it is shaken every 15 minutes and the pressure released from the container by opening the container cap. After 8 hours, the container is removed from the water bath and allowed to cool to room temperature.

The pH of the mixtures placed into the sealed containers is measured prior to placing the containers into the water bath and after the sealed containers have remained in the water bath for 8 hours. After the containers have cooled to room temperature, the contents of the containers are each analyzed for weight percent total nitrogen (TN), weight percent non-protein urea nitrogen (NPN), weight percent urease-resistant urea nitrogen (URN) and percent urease-resistant urea nitrogen (URN) of the total nitrogen.

Solution 1, Solution 2 and Solution 3 of Table 1 are the same with the exception that the pH of Solution 3 is maintained at 2.0 throughout the entire process by mixing additional acid with the reaction mixture while the mixture is being heated in the water bath. The solutions which do not have their pH maintained had pHs which rise.

Solution 4 has a larger weight percent of glucose and a smaller weight percent of water in comparison with Solution 1, but has a molar excess of urea (more moles of urea than glucose).

Solution 5 is similar to Solution 1 but has 0.4% by weight copper sulfate mixed with the reaction mixture, resulting in 1000 parts per million (ppm) of soluble copper Cu (II) ions being present in the mixture.

Solution 6 has a molar excess of urea, is acidic, but has no phosphoric acid added to the reaction mixture.

Solution 7 is similar to Solution 5, except that more (0.8% by weight) copper sulfate is mixed with the

reaction mixture, resulting in 2000 ppm of soluble copper being present in the mixture.

Solution 8 is the same as Solution 7, except that the solution is never heated (i.e., it is maintained at room temperature).

Various fractions of the nitrogen are analyzed in each of the solutions to determine if degradation of the urea occurs. Solutions 3, 4, 5, 6, 7, and 8 represent a control of conditions such as acidity, molar excess of urea or the use of Cu(II) ions that illustrate the method of the invention which provides at least about 34 weight percent urease hydrolysis resistant urea nitrogen, based upon the weight of urea nitrogen in the product.

The results of these experiments are presented below and reflect values obtained at the end of the process.

TABLE 1

Ingredient	Sol 1	Sol 2	Sol 3	Sol 4	Sol 5	Sol 6	Sol 7	Sol 8
Percent, w/w								
Glucose (dry)	34.1	34.1	34.1	39.1	33.8	36.2	33.5	33.5
Urea (granular)	34.7	34.7	34.7	34.7	34.7	34.7	34.7	34.7
Phosphoric Acid (75%)	3.0	3.0	3.0	3.0	3.0	0.0	3.0	3.0
Sulfuric Acid (98%)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Water	24.1	24.1	24.1	19.1	24.0	25.0	23.9	23.9
Copper Sulfate	0.0	0.0	0.0	0.0	0.4	0.0	0.8	0.8
TOTAL	100	100	100	100	100	100	100	100
Results								
Total N, % w/w	16.95	16.4	17.2	16.1	16.8	17.1	16.8	16.7
NPN, % w/w	11.67	11.3	11.4	10.5	3.6	11.2	2.4	0.0
URN, % w/w	5.28	5.1	5.7	5.6	13.1	5.9	14.3	16.7
URN, % of total N	31.16	31.1	33.6	34.7	78.2	34.4	85.2	100
Carbon Dioxide	5%	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ammonia N, % w/w	11.98	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Water Activity	0.703	0.70	0.70	0.68	0.71	0.73	0.71	0.71
Urea Nitrogen	60.94	N/A	N/A	N/A	N/A	N/A	N/A	N/A

NPN - non-protein nitrogen; URN - urease-resistant nitrogen

Example II

Solutions 1 through 6 of Table 2 are prepared according to the procedure of Example I unless otherwise noted, at the given weight percents, described hereinbelow.

Solution 1 is a baseline solution having 40% wt glucose, 10.43% wt urea, a relatively low urea content, 5% wt sulfuric acid and 44.57% wt water.

Solution 2 and Solution 3 are similar to Solution 1, but contain no urea. Solutions 2 and 3 have nitrogen in the form of ammonium sulfate, instead of urea. Solution 2 has 5% wt sulfuric acid, whereas Solution 3 has no acid.

Solutions 4 and 5 differ from Solution 1 and have a molar excess of urea. The composition of Solution 4 and Solution 5 are the same, but the two solutions are prepared differently. Solution 4 is prepared by first mixing with water the ingredients listed in the table below, except for glucose, according to the procedure of Example I, followed by gradual mixing of glucose with the water over an 8-hour cook period. Solution 5 is prepared by first mixing with water the ingredients listed in the table below, except for urea, according to the procedure of Example I, followed by gradual mixing of urea with the water over an 8-hour cook period.

Solution 6 is the same as Solution 5, except that a fraction of the glucose is replaced with cane molasses as a hexose sugar source. The relative amount of hexose sugar, however, is too low. Additionally, Solution 6 contains no water.

The results of these experiments are presented below and reflect measurements obtained at the end of the process. Solutions 4 and 5 represent a process with excess urea, a sufficient urea nitrogen content, acidity and slow mixing which provide a high urease resistant nitrogen.

Table 2

Ingredient	Sol 1	Sol 2	Sol 3	Sol 4	Sol 5	Sol 6
	Percent, w/w					
Glucose (dry)	40.0	40.0	40.0	39.1	39.1	20.0
Urea (granular)	10.4	0.0	0.0	34.7	34.7	34.7
Phosphoric Acid	0.0	0.0	0.0	3.0	3.0	3.0
Sulfuric Acid	5.0	5.0	0.0	4.0	4.0	4.0
Ammonium Sulfate	0.0	22.4	22.4	0.0	0.0	0.0
Water	44.5	32.3	37.3	19.1	19.1	0.0
Cane Molasses (75 DM)	0.0	0.0	0.0	0.0	0.0	38.2
TOTAL	100	100	100	100	100	100
	Results					
Total N, % w/w	5.03	4.9	4.9	16.9	16.4	16.3
NPN, % w/w	1.44	4.8	4.7	10.6	9.8	12.4
URN, % w/w	3.59	0.0	0.2	6.3	6.6	3.9
URN, % of total N	71.33	1.7	4.1	37.1	41.2	23.7

NPN = non-protein nitrogen; URN = urease-resistant nitrogen.

What is claimed is:

1. A method for producing a urease enzyme degradation resistant fertilizer product, the method comprising:
combining a hexose sugar source, an acid source, water and urea to provide an aqueous mixture, the urea and the hexose sugar source being combined at a gradual rate, the water, hexose sugar source and urea being held at a time and temperature, the acid source effective for supplying a pH, all of which are effective for providing a liquid fertilizer product which is urease hydrolysis resistant which has a nonprotein urea nitrogen content of at least about 12 weight percent and a urease hydrolysis resistant urea nitrogen content, based upon the weight of the nitrogen in the fertilizer product, of at least about 34 weight percent, and wherein the molar ratio of hexose sugar to urea is not more than about 0.35.

2. A method as recited in claim 1, wherein the acid source is in an amount which is effective for providing the mixture of the water, hexose sugar source and urea with an initial pH of about 2 or less.

3. A method as recited in claims 1 or 2 wherein the hexose sugar source, water, acid source and urea are gradually or incrementally mixed.

4. The method of claim 3, wherein the hexose sugar source is glucose.

5. The method of claim 2, wherein the acid source is a mixture of sulfuric and phosphoric acids.

6. The method of claim 4, wherein the acid source is a mixture of sulfuric and phosphoric acids.

7. The method of claim 2, wherein the mixture is maintained at a temperature of from about 15°C to about 100°C for a period of from about 3 to about 8 hours.

8. The method of claim 6, wherein the mixture is maintained at a temperature of from about 15°C to about 100°C for a period of from about 3 to about 8 hours.

9. A method for producing a urease enzyme degradation resistant fertilizer product, the method comprising:
combining water, a water soluble source of metal 2+ ions selected from the group consisting of Mn^{2+}, Zn^{2+}, Cu^{2+} ions and mixtures thereof, a hexose sugar source, an acid source and urea to provide an aqueous mixture, the urea, the ion source and the hexose sugar source being combined in relative amounts, the water, ion source, hexose sugar source and urea being held at a time and temperature, the acid source effective for supplying a pH, all of which are effective for providing a liquid fertilizer product which is urease hydrolysis resistant which has a nonprotein urea nitrogen content of at least about 12 weight and a urease hydrolysis resistant urea nitrogen content, based upon the weight of the urea nitrogen in the fertilizer product, of at least about 50 weight percent.

10. A method as recited in claim 9 wherein the ion source is sufficiently water soluble to provide the mixture with at least about 0.1 weight percent metal 2+ ions in the mixture.

11. A method as recited in claims 9 or 10 wherein the molar ratio of hexose sugar to the resulting urease degradation resistant urea product is not more than about 1.0.

12. A method as recited in claim 11, wherein the acid source is in an amount which is effective for providing the mixture of the water, hexose sugar source and urea with an initial pH of about 2 or less.

13. A method as recited in claim 12 wherein the hexose sugar source, water, acid source and urea are gradually or incrementally mixed.

14. The method of claim 12, wherein the hexose sugar source is glucose.

15. The method of claim 12, wherein the acid source is a mixture of sulfuric and phosphoric acids.

16. The method of claim 14, wherein the acid source is a mixture of sulfuric and phosphoric acids.

17. The method of claim 16, wherein the mixture is maintained at a temperature of from about 15°C to about 100°C for a period of from about 3 to about 8 hours.

18. The method as recited in claim 9 wherein the molar ratio of the hexose sugar to urea is not more than about 0.35.

19. The method as recited in claims 9, 10 or 18 wherein the metal 2+ ion is copper (II).

20. A method for producing a reaction product of a hexose sugar source and a urea which exhibits resistance to hydrolysis by urease enzymes, comprising:

(a) mixing from about 15 to about 50 weight percent water, from about 4 to about 40 weight percent of a hexose sugar source, from about 0.1 to about 1.0 weight percent of a water soluble source of Cu^{2+} ions and from about 10 to about 45 weight percent of urea and an acid source in an amount to provide the mixture with an

initial pH of less than about 2, then mixing at a temperature of from about 15°C to about 100°C for a period of time which is effective for dissolving the hexose sugar source and the urea; and

(b) maintaining the resulting mixture at a temperature from about 15°C to about 100°C for a period of time which is effective for converting at least about 50 weight percent of the nonprotein urea nitrogen present in the mixture to a liquid urease-resistant urea nitrogen.

21. The method as recited in claim 20, wherein the ratio of the hexose sugar to the resulting hydrolysis resistant urea product is not more than about 1.0.

22. The method of claims 20 or 21, wherein the hexose sugar source is glucose, sucrose or fructose.

23. The method of claim 22, wherein the acid source is a mixture of sulfuric and phosphoric acids.

24. The method of claim 23, wherein the Cu^{2+} ion source is copper sulfate.

25. The method of claim 24, wherein from about 30 to about 40 weight percent of the glucose, sucrose or fructose is mixed with the water, copper sulfate and urea.

26. The method of claim 25, wherein the hexose sugar source is glucose.

27. The method of claim 24, wherein from about 0.6 to about 1.0 weight percent copper sulfate is mixed with the water, glucose and urea.

28. The method of claim 20, wherein the mixture is maintained at a temperature of from about 15°C to about 100°C for a period of from about 2 to about 24 hours.

29. The method of claim 22, wherein the mixture is maintained at a temperature of from about 15°C to about 100°C for a period of from about 3 to about 8 hours.

30. The method of claim 29, wherein the glucose is added to the water, the urea and the copper sulfate incrementally.

31. A reaction product of a hexose sugar source and a urea which exhibits resistance to hydrolysis by urease enzymes produced by the method comprising:

(a) mixing from about 15 to about 50 weight percent water, from about 4 to about 40 weight percent of a hexose sugar source, from about 0.1 to about 1.0 weight percent of a water soluble source of metal 2+ ions selected from the group consisting of Mn^{2+}, Zn^{2+}, Cu^{2+} ions and mixtures thereof, from about 10 to about 45 weight percent of urea and an acid source in an amount to provide an acidified blend with an initial pH of less than about 2, the molar ratio of hexose sugar to urea being not more than about 0.35;

(b) dissolving and mixing the acidified blend at a temperature of from about 15°C to about 100°C for a period of time which is effective for dissolving the hexose sugar source and the urea to provide a resulting mixture; and

(c) maintaining the resulting mixture at a temperature from about 15°C to about 100°C for a period of time which is effective for converting at least about 50 weight percent of the nonprotein urea nitrogen present in the acidified blend to a liquid urease-resistant urea nitrogen in the fertilizer product, of at least about 34 weight percent, and wherein the ratio of hexose sugar to the resulting hydrolysis resistant urea product is not more than about 1.0.

32. The reaction product of Claim 31 wherein the metal 2+ ion source is a source for Cu (II) ions.

33. The reaction product of Claim 32, wherein the acid source is a mixture of sulfuric and phosphoric acids and from about 4 to about 7 weight percent of the mixture of sulfuric and phosphoric acids is added to the mixture to initially adjust the pH of the mixture to about 2.0 or below, the hexose sugar source is glucose, the copper source is copper sulfate, the mixing is performed at a temperature of from about 20°C to about 24°C, and the mixture is maintained at a temperature of from about 20°C to about 24°C for a period of from about 3 to about 8 hours.

34. The reaction product of Claim 33, wherein the glucose is added to the water, the urea and the copper sulfate incrementally.

35. A method for producing a urease enzyme degradation resistant fertilizer product, the method comprising controlling in an aqueous reaction mixture comprising urea, hexose sugar source and an acid to obtain a liquid urea fertilizer product which is urease hydrolysis resistant: the speed of mixing the urea, the hexose sugar source and acid where the molar ratio of the hexose to urea is not more than about 0.35, the pH of the reaction mixture provided by the acid and the time and temperature at which the acid, the hexose sugar and the urea are held to provide a urea fertilizer product which has at least about 12 weight percent nitrogen from urea, and at least about 34 weight percent urease hydrolysis resistant urea nitrogen.

36. A method as recited in claim 35 where the pH of the reaction mixture is controlled by maintaining it less than about 2.

37. A method as recited in claims 35 or 36 where the speed of mixing is controlled by gradually mixing the urea, hexose sugar source and acid.

38. A method as recited in claim 37 wherein the ratio of hexose sugar source to the resulting urease enzyme degradation resistant urea fertilizer product is not more than about 1.0.

39. A method for producing urease enzyme degradation resistant urea nitrogen in a fertilizer product having at least about 12 weight percent nitrogen from urea, the method using an aqueous reaction mixture comprising urea, a hexose sugar source and an acid source, the urea being in molar excess of the hexose sugar and being in an amount which is effective to provide the fertilizer product with at least about 12 weight percent nitrogen from urea, the method comprising:

combining the urea, the hexose sugar source and acid source to provide the aqueous reaction mixture, the acid source providing a pH;

controlling the rate of combining the urea, hexose sugar source and acid source, the pH of the aqueous reaction mixture provided by the acid source; and

providing a time and a temperature at which the acid source, the hexose sugar and the urea are held, the controlling the rate of combining and the pH and the time and temperature at which the hexose sugar source and the urea are held in the aqueous reaction mixture, the control effective providing a reaction for rendering at least about 34 weight percent of the urea nitrogen in the fertilizer product urease hydrolysis resistant nitrogen.

40. A method as recited in claim 39, wherein the acid source is in an amount which is effective for providing the mixture of the hexose sugar source and urea with an initial pH of about 2 or less and maintaining the pH to about 2 or less throughout the time of the reaction.

41. A method as recited in claims 39 or 40 wherein the hexose sugar source, water, acid source and urea are gradually or incrementally mixed.

42. The method of claim 41, wherein the hexose sugar source is glucose.

43. The method of claim, 41, wherein the acid source is a mixture of sulfuric and phosphoric acids.

44. The method of claim 43, wherein the mixture is maintained at a temperature of from about 15°C to about 100°C for a period of from about 3 to about 8 hours.

45. The method of claim 39, wherein the molar ratio of hexose sugar to urea is not more than about 0.35.

46. The product made in accordance with the method of claim 1.

47. The product made in accordance with the method of claims 9 or 18.

48. The product made in accordance with the method of claims 39 or 40.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/06613

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) :C05C 9/00; CO5 5/00
US CL :71/28, 64.1
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 71/28, 64.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Chemical Abstracts

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,328,497 A (HAZLETT) 12 JULY 1994 (12-07-94), see col. 2, line 3 to col. 6, line 58.	1, 2, 9, 10, 18, 20, 21, 28-36, 39, 40, 45, 46
A	US 4,336,052 A (CHEN et al) 22 JUNE 1982 (22-06-82), see col. 1, line 41 to col. 2, line 10.	1, 2, 9, 10, 18, 20, 21, 28-36, 39, 40, 45, 46
A	US 5,443,613 A (ROBINSON) 22 AUGUST 1995 (2-08-95), see col. 2, line 46 to col. 7, line 43.	1, 2, 9, 10, 18, 20, 21, 28-36, 39, 40, 45, 46

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
01 JUNE 2000	22 JUN 2000

Name and mailing address of the ISA/US	Authorized officer
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Form PCT/ISA/210 (second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/06613

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,388,989 A (SOR) 18 JUNE 1968 (18-06-68), see col. 2, line 60 to col. 5, line 35.	1, 2, 9, 10, 18, 20, 21, 28-36, 39, 40, 45, 46
A	US 3,195,999 A (CHANCE) 20 JULY 1965 (20-07-65), see col. 1, line 63 to col. 2, line 71.	1, 2, 9, 10, 18, 20, 1, 28-36, 39, 40, 45, 46

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/06613

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 3-8, 11-17, 19, 22-27, 37, 38, 41-44, 47 and 48
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.