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- (54) **Title:** UREA FERTILISER HAVING IMPROVED HARDNESS
- (57) **Abstract:** The present invention discloses a urea fertiliser having a lignin compound and elemental sulphur dispersed throughout the fertiliser and having improved hardness.

UREA FERTILISER HAVING IMPROVED HARDNESS

Field of the Invention

The present invention provides a urea fertiliser having improved physical properties, particularly having improved hardness and desirably also improved abrasion resistance and impact resistance.

Background of the Invention

Urea is commonly used as a fertiliser, supplying nitrogen to plants. Urea granules are often friable, breaking into smaller particles and creating substantial amounts of dust during storage, transport and use.

US 4,587,358 discloses that the physical properties of urea particles can be improved by incorporating formaldehyde, or, more desirably from a safety perspective, by incorporating a lignosulphonate such as calcium lignosulphonate. US 4,676,821 discloses urea particles that contain calcium lignosulphonate and that additionally have a coating of elemental sulphur. The sulphur coating enables a controlled dissolution rate of the urea fertiliser.

The present inventors have sought to prepare a urea fertiliser having improved physical properties, in particular improved hardness.

Summary of the Invention

Accordingly, the present invention provides the use of a lignin compound and elemental sulphur to prepare a urea fertiliser having the lignin compound and the elemental sulphur dispersed throughout the fertiliser and having improved hardness.

The invention further provides a urea-sulphur fertiliser composition comprising from 50 to 99wt% urea,

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from 1 to 25wt% elemental sulphur and from 0.1 to 5wt% of a lignin compound, wherein the weight percentages are based upon the weight of the fertiliser composition, and wherein the lignin compound and the sulphur are dispersed throughout the fertiliser.

The present inventors have recognised that the combination of sulphur and lignin compound, dispersed throughout a urea fertiliser, can improve the physical properties of the fertiliser, particularly when the components are present in an amount of from 50 to 99wt% urea, from 1 to 25wt% of elemental sulphur and from 0.1 to 5wt% of a lignin compound.

Detailed Description of the Invention

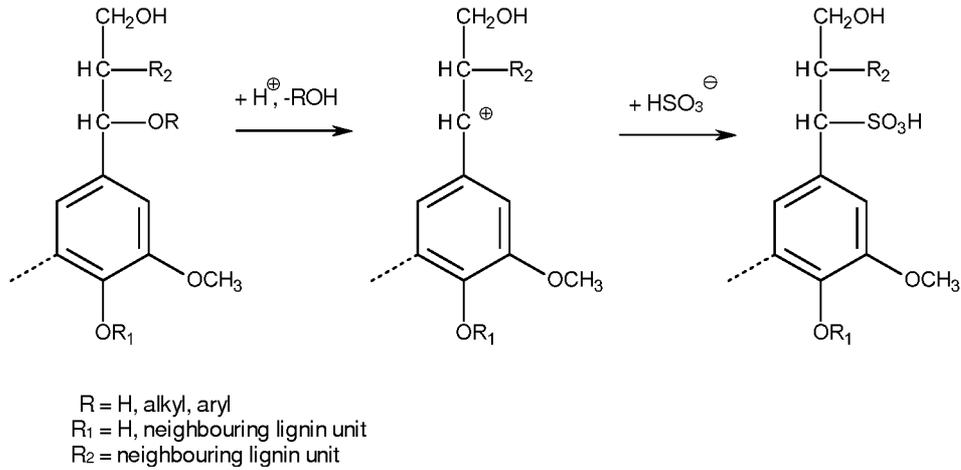
In the present invention, a lignin compound is incorporated into a urea-sulphur fertiliser.

The lignin compound is suitably a lignosulphonate. Examples of lignosulphonates include ammonium lignosulphonate, sodium lignosulphonate, calcium lignosulphonate and potassium lignosulphonate. Preferably, the lignosulphonate is calcium lignosulphonate.

Lignin compounds are derived from lignin, which is found in the cellular material of plants, e.g. trees.

Lignins comprise polymeric propylphenol substituted moieties which are interconnected at various positions on the carbon skeleton through a phenoxy group. Lignosulphonate may be produced from lignin by a sulphite process, in which suitable feedstock such as wood is digested at 140-170°C with an aqueous solution of calcium bisulphite in acidic conditions. A benzylic cation is formed under the stated conditions, which is quenched by the sulphite ion to produce a sulphonated derivative which is separated.

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Details of this process are described, for example, in *Monomers, Polymers and Composites from Renewable Resources*; M. N. Belgacem, A. Gandini; Elsevier, 2008, 225-241.

5 Depending on the nature of the reaction conditions the liginosulphonate produced can contain carbohydrate components which are chemically linked to the liginosulphonate molecular framework. This material finds commercial applications as sugared liginosulphonate, which may for example have a carbohydrate content as high as
 10 35wt% depending on manufacturing conditions. Alcoholic fermentation of a sugared liginosulphonate mixture or selective chemical treatment by ultrafiltration can be used to remove sugar content to produce a de-sugared
 15 calcium liginosulphonate.

Liginosulphonates useful as in the present invention may be sugared liginosulphonates or de-sugared liginosulphonates and may be derived from softwood or hardwood feedstocks.

20 For example, sugared liginosulphonates derived from hardwood and de-sugared liginosulphonates derived from softwood have been found to be of particular use.

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Preferably, the carbohydrate content of the lignosulphonates, as determined by TAPPI test method T 249 cm-85 (involves an acid treatment followed by gas chromatography analysis), may be at most 35wt%, more preferably at most 15wt%, even more preferably at most 5wt%.

The molecular weight of the lignosulphonate may vary considerably and may be, for example, in the range of from 7000 to 35000 Daltons, preferably 12,000 to 28,000 Daltons.

The term lignosulphonate also encompasses mixed salts of different ions such as potassium/sodium lignosulphonate or potassium/calcium lignosulphonate.

The amount of lignin compound in the fertiliser is suitably at least 0.05wt% based upon the weight of the urea fertiliser composition, preferably at least 0.1wt%, more preferably at least 0.25wt% and most preferably 0.75wt%. The amount of lignin compound is suitably less than 10wt%, more preferably less than 5wt% and most preferably less than 1.5wt%.

The amount of urea in the fertiliser is suitably at least 50wt% based upon the weight of the urea fertiliser composition, preferably at least 60wt% and more preferably 75wt%. The amount of urea is suitably less than 99wt% and more preferably less than 95wt%.

The elemental sulphur in the urea-sulphur fertiliser may be high purity (> 99.9% S) chemical sulphur as obtained from the Claus process. However, elemental sulphur of significantly lower purity can also be used. Examples of such elemental sulphur are sulphur filter cake as obtained from sulphur melting and filtration operations and sulphur obtained from a various chemical and biological H₂S gas removal processes. Typically, such

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5 sulphur sources may contain anywhere in the range of from 30 to 99.9 wt.%, preferably from 50 to 99.5 wt.%, more preferably from 60 to 99.0 wt.%, sulphur, with the balance comprising lime, gypsum, silica, iron and other trace materials.

10 The amount of elemental sulphur in the fertiliser is suitably at least 1wt% based upon the weight of the urea-sulphur fertiliser composition, and preferably at least 3wt%. The amount of sulphur is suitably less than 50wt%, more preferably less than 25wt% and most preferably less than 7wt%.

15 The preferred amounts of lignin compound and sulphur are determined by considering how much of these components are required to improve the hardness of the urea fertiliser versus the cost of these components.

20 The lignin compound and the elemental sulphur are dispersed throughout the fertiliser. By "dispersed throughout" the fertiliser the inventors mean that the lignin compound and the elemental sulphur are homogeneously dispersed throughout all of the fertiliser, i.e. not just at the surface, nor only at the core of the fertiliser particles. It is not desirable that the sulphur is coated onto the surface of the urea. The present inventors believe that sulphur dispersed
25 throughout the urea matrix creates disruptions in the urea crystal structure, thereby decreasing brittleness and improving hardness. The average particle size of the elemental sulphur is suitably less than 50µm, and preferably less than 20µm. Suitably the average particle
30 size of the elemental sulphur is more than 2µm, and preferably more than 5µm.

The urea fertiliser may comprise additional plant nutrients. Such plant nutrients may be selected, but not

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limited to potassium, phosphorus, nitrogen, boron, selenium, sodium, zinc, manganese, iron, copper, molybdenum, cobalt, calcium, magnesium and combinations thereof. These nutrients may be supplied in elemental
5 form or in the form of salts such as oxides, hydroxides, sulphates, nitrates, halides or phosphates. The amount of additional plant micronutrients depends on the type of fertiliser needed and is typically in the range of from 0.1 to 30wt%, based on the total weight of the
10 fertiliser, preferably in the range of from 0.5 to 20wt%.

The fertiliser may be made by a process comprising steps of:

- (a) providing a first stream which comprises liquid urea;
- 15 (b) providing a second stream comprising liquid elemental sulphur;
- (c) mixing the first stream and the second stream in a mixing device in the presence of a lignin compound to form an emulsion comprising micro-encapsulated elemental
20 sulphur particles which are coated with a layer of the lignin compound, whereby a temperature is applied of more than 135 °C which maintains the elemental sulphur and the urea substantially in the liquid form in the mixing device; and
- 25 (d) subjecting the emulsion as obtained in step (c) to one or more further processing steps to obtain the urea-sulphur fertiliser.

In step (c) use is made of a mixing device. The mixing device to be used in step (c) can suitably be a
30 dispersion mill wherein a rotor turns within a slotted stator or a static mixer. Preferably, the mixing device is a dispersion mill.

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In step (c) one or more additional plant nutrients can be added and/or a defoamer may be added.

In step (d) the emulsion as obtained in step (c) is subjected to one or more further processing steps to obtain the urea-sulphur fertiliser. The one or more further processing steps comprise subjecting the emulsion to a forming process to obtain the urea-sulphur fertiliser. The forming process can suitably be a granulating process, a prilling process, a compaction process, a tablet forming process, or a compressing process.

The emulsion of elemental sulphur particles as obtained in step (c) can be combined with one or more further components to obtain a mixture of the emulsion and the one or more further components, and this can be subjected to a forming process in step (d). The one or more further components could be other fertiliser products. For example, phosphate rock could be added to the emulsion of elemental sulphur particles before it is supplied to the forming process in step (d), thereby providing a urea-sulphur-phosphate rock fertiliser. Alternatively, potassium chloride could be added to the emulsion of elemental sulphur particles before it is supplied to the forming process in step (d), thereby providing a urea-sulphur-KCl fertiliser. In one embodiment, phosphoric acid could be added to the emulsion of elemental sulphur particles whilst it is hot and before it is supplied to the forming process in step (d). The phosphoric acid would react with the urea, thereby providing a urea-phosphate-sulphur fertiliser. In another embodiment, the urea-sulphur emulsion or the formed urea-sulphur fertiliser can be combined with NPK fertilisers, either by adding the urea-sulphur emulsion

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into the NPK fertiliser production process (prior to the forming of the fertiliser) or by blending granules of urea-sulphur fertiliser with granules of NPK fertiliser.

5 Another material that could be incorporated into the urea-sulphur fertiliser is a clay such as bentonite. Suitably the clay could be added to the emulsion of elemental sulphur particles before it is supplied to the forming process in step (d).

10 The present invention enables the skilled person to prepare a fertiliser having improved hardness, i.e. by using a lignin compound and elemental sulphur to prepare a urea fertiliser having the lignin compound and the elemental sulphur dispersed throughout the fertiliser, the skilled person can prepare a fertiliser that is
15 harder than a fertiliser that is otherwise the same but not does not have the lignin compound and elemental sulphur dispersed throughout the fertiliser. Hardness may be measured using the IFDC S-115 test (as described in the Manual for Determining Physical Properties of
20 Fertilizer from the International Fertilizer Development Center). The fertilisers prepared according to the invention may also have improved abrasion resistance (measured using the IFDC S-116 and S-117 tests), improved impact resistance (measured using the IFDC S-118 test)
25 and improved caking tendency (measured using the IFDC S-105 and S-106 tests).

The invention will now be demonstrated by means of an example which is not intended to be limiting of the invention.

30 Example

The drum granulation pilot plant of the International Fertilizer development Center (IFDC) located in Muscle Shoals, Alabama was used to granulate

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different fertilisers from freshly remelted urea, freshly melted elemental sulphur, and various additives.

Freshly molten urea (from PCS sourced urea microprilled), freshly molten sulphur (from commercial pastillated Canadian sulphur) and a commercial calcium lignosulphonate product were pumped into a mixing device to produce a stable emulsion of molten sulphur in molten urea. The stabilized emulsion was mixed with a granulation aid and granulated using a standard drum granulation plant consisting of a drum granulator, a rotating cooler, a series of screens and crushers, a product export belt and an internal solids recycle belt.

Various combinations of sulphur, urea, and calcium lignosulphonate were produced, and various physical properties of the granulated product were assessed by IFDC laboratories using standard IFDC procedures from the IFDC Manual for Determining Physical Properties of Fertilizer (IFDC R-10). The results are shown in Table 1:

Table 1

	Comparative Example 1	Comparative Example 2	Example 1
Chemical Composition	N	47%	40%
	S (elemental)	0%	14%
	Calcium Lignosulphonate	0.0%	0.2%
Crushing Strength	Crushing Strength Average, kg/granule	2.43	2.88
	Range, kg/granule	1.00 - 4.00	1.70 - 4.70
Moisture Absorption/ Penetration	Moisture Absorption, mg/cm ²	256	311
	Moisture Penetration, cm	12.0	7.2
	Moisture Holding Capacity, mg/cm ³	21	43
	Moisture Holding Capacity, %	3.3	5.9
	Granule Integrity, wet	good	poor

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The addition of finely divided elemental sulphur to urea granules, without the presence of calcium lignosulphonate does had some positive and some negative impacts on the fertiliser physical properties compared to urea. For example, the moisture absorption, the moisture penetration, as well as the moisture holding capacity of Comparative Example 2 are superior to those of Comparative Example 1, but its crushing strength, and its granule integrity, wet, are worse than those of Comparative Example 1. Based on the above, it cannot be clearly demonstrated that finely dispersed sulphur alone increases or decreases the quality of urea's physical properties.

The addition of finely divided elemental sulphur to urea granules in the presence of a lignin additive leads to a granule of superior physical properties to those of pure urea. All the studied physical properties are superior in Example 1 compared to those of Comparative Example 1, and are equal or superior to those of Comparative Example 2. The present inventors have found that the combination of sulphur and lignin compound, dispersed throughout a urea fertiliser, can improve the physical properties of the fertiliser.

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C L A I M S

1. Use of a lignin compound and elemental sulphur to prepare a urea fertiliser having the lignin compound and the elemental sulphur dispersed throughout the fertiliser and having improved hardness.
- 5 2. Use of a lignin compound and elemental sulphur according to claim 1, wherein the lignin compound is a lignosulphonate.
3. Use of a lignin compound and elemental sulphur according to claim 2, wherein the lignin compound is
10 calcium lignosulphonate.
4. Use of a lignin compound and elemental sulphur according to any preceding claim, wherein the lignin compound is present in amount of at least 0.25wt% based upon the weight of the urea fertiliser.
- 15 5. Use of a lignin compound and elemental sulphur according to claim 4, wherein the lignin compound is present in amount of at least 0.75wt% based upon the weight of the urea fertiliser.
6. Use of a lignin compound and elemental sulphur
20 according to any preceding claim, wherein the urea fertiliser comprises from 50 to 99wt% urea and from 1 to 25wt% elemental sulphur, based upon the weight of the urea fertiliser.
7. Use of a lignin compound and elemental sulphur
25 according to any preceding claim, wherein the urea fertiliser comprises one or more additional fertiliser components chosen from potassium, phosphorus, nitrogen, boron, selenium, sodium, zinc, manganese, iron, copper, molybdenum, cobalt, calcium, magnesium and combinations
30 thereof.

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8. A urea-sulphur fertiliser composition comprising
from 50 to 99wt% urea, from 1 to 25wt% elemental sulphur
and from 0.1 to 5wt% of a lignin compound, wherein the
weight percentages are based upon the weight of the
5 fertiliser composition, and wherein the lignin compound
and the elemental sulphur are dispersed throughout the
fertiliser.

9. A fertiliser composition according to claim 8,
comprising one or more additional fertiliser components
10 chosen from potassium, phosphorus, nitrogen, boron,
selenium, sodium, zinc, manganese, iron, copper,
molybdenum, cobalt, calcium, magnesium and combinations
thereof.