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- (71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).
- (71) Applicant (for US only): SHELL OIL COMPANY [US/US]; Shell Plaza 1, Houston, Texas 77252-2463 (US).
- (72) Inventors: GARCIA MARTINEZ, Rafael, Alberto; 400-4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). AL-LAIS, Cyrille, Paul; Grasweg 31, NL-1031 HW Amsterdam (NL). D'MELO, Dawid, John; Shell Technology Centre Bangalore, Shell India Markets Private Limited No. 143, C-4, Bommasandra Industrial Area, Off. Hosur Road, Anekal Taluka, Bengaluru 560099 (IN). MANIKANDAN, Chithra; Shell India Markets Private Limited #143, C4 Bommasandra Industrial Area, Off Hosur Road, Bangalore 560099 (IN).
- (74) Agents: MATTHEZING, Robert, Maarten et al.; PO Box 384, NL-2501 CJ The Hague (NL).
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(54) Title: FERTILISER HAVING REDUCED BIURET CONTENT

(57) Abstract: The present invention discloses the use of a lignin compound to prepare a urea fertiliser having reduced biuret content.

FERTILISER HAVING REDUCED BIURET CONTENT

Field of the Invention

The present invention provides a fertiliser having reduced biuret content.

Background of the Invention

5 Urea is commonly used as a fertiliser, supplying nitrogen to plants. Biuret is a phytotoxin (a material that is toxic to plants) and is formed as an impurity during the production of urea fertilisers. Biuret interferes with nitrogen metabolism and protein synthesis
10 in plants.

It is desirable to reduce the amount of biuret in fertilisers. US 2009 019906 discloses a process for producing urea fertilisers wherein a centrifugal pump is employed. The use of the pump allows for the use of
15 shorter pipelines, thereby decreasing the residence time and reducing biuret formation during urea synthesis.

The present inventors have sought to prepare a urea fertiliser having reduced biuret concentration.

Summary of the Invention

20 Accordingly, the present invention provides the use of a lignin compound to prepare a urea fertiliser having reduced biuret content.

It is known to incorporate lignin compounds into urea fertilisers to improve the physical properties of
25 the fertiliser, e.g. as described in US 4,676,821. However, the present inventors have advantageously recognised that lignin compounds can be used to reduce biuret content in urea fertilisers. The inventors believe that the presence of a lignin compound during the
30 production of urea fertilisers can reduce the formation

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of biuret, particularly when the components are present in an amount of from 50 to 99.9wt% urea and from 0.01 to 0.25wt% of a lignin compound.

Detailed Description of the Invention

5 In the present invention, a lignin compound is incorporated into a urea fertiliser. The lignin compound is suitably a liginosulphonate. Examples of liginosulphonates include ammonium liginosulphonate, sodium liginosulphonate, calcium liginosulphonate and potassium

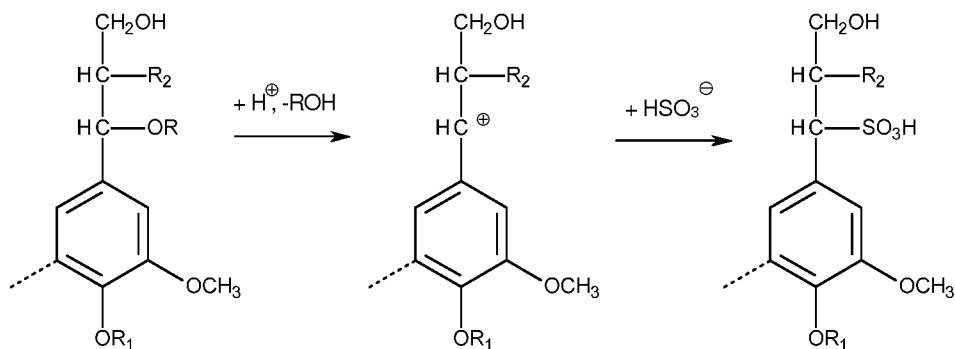
10 liginosulphonate. Preferably, the liginosulphonate is calcium liginosulphonate.

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

Lignins comprise polymeric propylphenol substituted

15 moieties which are interconnected at various positions on the carbon skeleton through a phenoxy group. Liginosulphonate 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

20 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.



R = H, alkyl, aryl
R₁ = H, neighbouring lignin unit
R₂ = neighbouring lignin unit

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

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

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

 Preferably, the carbohydrate content of the lignosulphonates, as determined by TAPPI test method T
25 249 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
30 considerably and may be, for example, in the range of from 7000 to 35000 Daltons, preferably 12,000 to 28,000 Daltons.

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

5 The amount of lignin compound in the fertiliser is suitably at least 0.01wt% based upon the weight of the urea fertiliser composition. The amount of lignin compound is suitably less than 1wt%, more preferably less than 0.5wt% and most preferably less than 0.25wt%.

10 The amount of urea in the fertiliser is suitably at least 50wt% based upon the weight of the urea fertiliser composition. The amount of urea is suitably less than 99.9wt%.

In a preferred embodiment the urea fertiliser is a urea-sulphur fertiliser, comprising both urea and
15 elemental sulphur. 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
20 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 sulphur sources may contain anywhere in the range of from 30 to 99.9 wt.%, preferably from 50 to
25 99.5 wt.%, more preferably from 60 to 99.0 wt.%, sulphur, with the balance comprising lime, gypsum, silica, iron and other trace materials.

30 The amount of elemental sulphur in the fertiliser is suitably at least 5wt% based upon the weight of the urea-sulphur fertiliser composition. The amount of sulphur is suitably less than 60wt%, more preferably less than 50wt% and most preferably less than 40wt%.

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The preferred amount of lignin compound is a balance between minimising cost (and therefore minimising the amount of lignin compound) and achieving sufficient reduction of biuret content.

5 When the fertiliser comprises both urea and sulphur, the urea and sulphur are suitably homogeneously dispersed throughout the fertiliser. It is not desirable that the sulphur is coated onto the surface of the urea. The lignin compound is suitably homogeneously dispersed
10 throughout the urea fertiliser.

The urea fertiliser may comprise additional plant nutrients. Such plant nutrients may be selected, but not limited to potassium, phosphorus, nitrogen, boron, selenium, sodium, zinc, manganese, iron, copper,
15 molybdenum, cobalt, calcium, magnesium and combinations thereof. These nutrients may be supplied in elemental 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
20 fertiliser needed and is typically in the range of from 0.1 to 30wt%, based on the total weight of the fertiliser, preferably in the range of from 0.5 to 20wt%.

The urea fertiliser may be made by a process wherein a stream which comprises liquid urea is mixed with a
25 lignin compound, and the liquid is formed into fertiliser particles.

In the preferred embodiment wherein the fertiliser is a urea-sulphur fertiliser, the fertiliser may be made by a process comprising steps of:

- 30 (a) providing a first stream which comprises liquid urea;
(b) providing a second stream comprising liquid elemental sulphur;

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(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 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

(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 dispersion mill wherein a rotor turns within a slotted stator or a static mixer. Preferably, the mixing device is a dispersion mill.

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

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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.

5 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
10 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
15 formed urea-sulphur fertiliser can be combined with NPK fertilisers, either by adding the urea-sulphur emulsion 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.

20 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).

25 Suitably the amount of biuret in the urea fertiliser is less than 1.5wt%, based upon the weight of the urea fertiliser, more preferably less than 1wt% and most preferably less than 0.75wt%.

30 The present invention enables the skilled person to prepare a urea fertiliser having reduced biuret content, i.e. the skilled person can prepare a fertiliser that has a lower biuret content than a fertiliser that is otherwise the same but does not comprise the lignin

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compound. Biuret content may be measured using the IFDC method: Biuret-Spectrophotometric TSU-AL AP-1002, 2002.

An experiment was carried out to demonstrate that a lignin compound can be used to reduce biuret content in urea.

Experiment

Three mixtures of molten urea and molten sulphur were maintained at temperatures of 135-145°C for extended periods of time until significant biuret concentration had developed. The biuret content of the mixtures was measured and commercial calcium lignosulphonate (50 %w/w), was added to the mixture to yield a final concentration of 0.1 % w/w of calcium lignosulphonate on total weight. Measurements of the biuret content of the mixture before and after the addition of the calcium lignosulphonate were taken and are shown in Table 1.

Table 1

	Biuret concentration (%)	
	Before addition of Calcium Lignosulphonate	After addition of Calcium Lignosulphonate
Mixture 1	8.80%	7.80%
Mixture 2	27.90%	20.30%
Mixture 3	13.20%	14.40%

For mixtures 1 and 2 the addition of calcium lignosulphonate led to a reduction in the biuret concentration. For mixture 3, this was not the case.

C L A I M S

1. Use of a lignin compound to prepare a urea fertiliser having reduced biuret content.
2. Use of a lignin compound according to claim 1, wherein the biuret content of the fertiliser is less than
5 1.5wt%, based upon the weight of the urea fertiliser.
3. Use of a lignin compound according to claim 1 or claim 2, wherein the lignin compound is a lignosulphonate.
4. Use of a lignin compound according to claim 3,
10 wherein the lignin compound is calcium lignosulphonate.
5. Use of a lignin compound according to any preceding claim, wherein the lignin compound is present in amount of at least 0.01wt% based upon the weight of the urea fertiliser.
- 15 6. Use of a lignin compound according to claim 5, wherein the lignin compound is present in amount of less than 1wt% based upon the weight of the urea fertiliser.
7. Use of a lignin compound according to any preceding claim, wherein the urea fertiliser comprises from 5 to
20 60wt% elemental sulphur, based upon the weight of the urea fertiliser.
8. Use of a lignin compound according to any preceding claim, wherein the urea fertiliser comprises an
25 additional fertiliser component chosen from potassium, phosphorus, nitrogen, boron, selenium, sodium, zinc, manganese, iron, copper, molybdenum, cobalt, calcium, magnesium and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/050170

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C05C9/00 C05F11/00
 ADD.
 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)
 C05C C05D C05G C05F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2014/009326 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 16 January 2014 (2014-01-16) page 9, line 9 - line 28 example 5 page 8, line 3 - line 20	1-8
X	WO 2013/098404 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 4 July 2013 (2013-07-04) page 19, line 11 - line 31 page 11, line 9 - line 19	1-8
X	US 5 032 164 A (SANFORD MICHAEL E [US] ET AL) 16 July 1991 (1991-07-16) claims	1-8
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 7 April 2015	Date of mailing of the international search report 13/04/2015
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Cardin, Aurélie
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/050170

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/000770 A1 (MELSPRING INTERNAT B V [NL]; EVERS MAURICE ALOYSIUS ANTONIU [NL]; TERL) 6 January 2005 (2005-01-06) claims	1-8
A	----- US 4 587 358 A (BLOUIN GLENN M [US]) 6 May 1986 (1986-05-06) claims	1-8
A	----- US 5 328 497 A (HAZLETT SCOTT [US]) 12 July 1994 (1994-07-12) claims -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2015/050170

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014009326	A1	16-01-2014	AU 2013289305 A1 15-01-2015 CA 2878430 A1 16-01-2014 WO 2014009326 A1 16-01-2014

WO 2013098404	A1	04-07-2013	NONE

US 5032164	A	16-07-1991	CA 2042927 A1 26-11-1991 US 5032164 A 16-07-1991

WO 2005000770	A1	06-01-2005	AU 2003304243 A1 13-01-2005 CA 2529222 A1 06-01-2005 DE 60309938 T2 24-05-2007 EP 1644302 A1 12-04-2006 ES 2277093 T3 01-07-2007 US 2007095118 A1 03-05-2007 WO 2005000770 A1 06-01-2005

US 4587358	A	06-05-1986	CA 1276803 C 27-11-1990 DE 3669873 D1 03-05-1990 EP 0216108 A1 01-04-1987 ES 2000228 A6 16-01-1988 US 4587358 A 06-05-1986

US 5328497	A	12-07-1994	NONE
