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(54) Title: UREA COMPOSITION HAVING REDUCED COMPRESSIBILITY, CAKING AND DUST FORMATION, AND PROCESS FOR ITS PREPARATION

(57) Abstract: Colourfast urea composition having reduced compressibility, cake formation and tendency of re-crystallization of the urea granulate, wherein the granulate further contains at least two different biodegradable polymers, of which at least one polymer is preferably a polyalkenyl amine compound. The other polymer is preferably polyaspartic acid or polyvinyl alcohol. The invention further relates to a process for the preparation of such a urea composition.



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Title: Urea composition having reduced compressibility, cake formation and dust formation, and process for the preparation thereof

Introduction

It is common knowledge that urea granulates are subject to crushing during production, storage and transport. Up to 25% b.w. of the urea granulate may be crushed when the urea granulate is stored or transported by ship at a relatively high temperature of, for example, more than 40°C. Although the urea granulate as such absorbs little moisture and is in fact per se not sensitive to caking, high percentages of crushed granules result in dust problems with a strong tendency of caking.

Besides, the problem of caking of granules occurs in particular during transport of bulk amounts of urea in tropical areas, due to migration of residual moisture from the granules as a result of the pressure being present at the bottom of the bulk amount of urea.

It is also known that a number of chemical compositions can be used as additive to improve the crushing strength, the tendency of caking and the resistance against moisture.

Formaldehyde, hexamethylene tetramine and formaldehyde/urea condensation products can be added as improvers of the crushing strength, while the combination of poly(vinyl acetate)/surfactant (see US 4 812 158) is used to reduce the tendency of caking. However, these additives must be added in relatively large amounts, or the poisonous properties thereof make them difficult to handle. Moreover, the presence of a surfactant component, such as in the combination of poly(vinyl acetate)/surfactant, results in a larger foam formation when the urea is used in industrial applications, such as the resin production, while formaldehyde derivatives are unsuitable in the case of melamine production.

There is also an important difference with respect to the way of adding the additives. Formaldehyde derivatives as well

as the compositions according to the invention are mixed with an urea melt. However, the combination of polyvinyl acetate/surfactant is sprayed on a preformed granule.

5 GB-A-1 217 106 describes a process for reducing the caking of urea by using a poly(vinyl alcohol) having a high molecular weight as an additive to prevent caking. More particularly, according to this process, an aqueous solution of the additive is mixed with an aqueous solution of urea. Preferably, an amount of additive of 0.005 to 5% b.w., based
10 on the weight of the urea, is admixed. The concentration of the aqueous urea solution is initially 80%, according to the given example; after admixing the solution of the additive, concentration up to 95% takes place at increased temperature, after which one lets the urea crystallize by cooling. Practice
15 has learned that the presence of polyvinyl alcohol in urea results in dust formation, probably as a result of internal moisture migration.

WO02/20471 mentions a process wherein a combination of a polyvinyl compound and inorganic salts are mixed with a urea
20 melt. The crushing strength as well as the impact resistance of the obtained granulate prove to be improved in comparison with untreated urea. Besides, the compressibility of the urea proved to be decreased considerably. This last observation could be an advantage because the urea granulates will be less
25 sensitive to deformation during storage. However, adding inorganic salts, such as aluminium sulphate, in urea results in a strong decrease of the pH when dissolving the urea in water. This is a great disadvantage in the use of this urea for technical applications, such as the production of resins.

30 US 4 063 919 describes a fertilizer composition containing a polyvinyl alcohol polymer, and a plasticizer for the polyvinyl alcohol, wherein this plasticizer is preferably chosen from glycerol, sorbitol, glycol, polyglycols having 4-20 C-atoms, and mixtures thereof. Additionally, mannitol and
35 sucrose are mentioned as plasticizers in this publication. Although sorbitol, mannitol and sucrose are sugars, they are referred to as polyglycols in this publication. It is a disadvantage that sugars will colour at higher temperatures (> 100°C), the so-called caramelizing. Also the presence of

small polar compounds may result in higher hygroscopicity of urea, as a result of which which re-crystallization can take place and consequently the dust formation will increase drastically.

5 US 5 766 302 mentions compositions of a fertilizer, such as urea, a polyvinyl alcohol, and an alkali metal lignosulfonate. However, it is commonly known to the expert, that lignosulfonates give urea a brown colour. This is not desired in many applications of urea, for example in the production of
10 melamine. In the compositions according to the invention, the lignosulfonates are therefore excluded; the compositions according to the invention, on the other hand, are colourfast because they are, as is assumed, inert to urea and/or thermal decomposition and therefore do not give any colouring
15 reaction.

Object of the invention

Therefore, it is an object of the invention to provide a urea composition having a low compressibility, low tendency of
20 cake formation as well as low moisture sensitivity and with which the above-mentioned disadvantages are overcome.

Description of the invention

Applicant found, surprisingly, that the addition to the
25 urea melt of at least two different polymers, of which at least one is a poly-alkenyl compound, results in a significant decrease of the compressibility and the tendency of caking of the urea granulate formed thereafter. Moreover, the urea granulate is not sensitive to re-crystallization by moisture
30 absorption during storage and handling. The polymers can either be added separately to the molten urea or together with the polyalkenyl compound, whether or not as an aqueous mixture or solution. According to a preferred embodiment, the total added amount of the polymer mixture is at most 10% b.w., based
35 on the total amount of urea. The present use relates to an intimate mixture of urea, a first polymer in the form of a polyalkenyl compound and a second polymer containing hydroxyl, carboxylic acid, amine and/or amide groups, causing the tendency of caking, the compressibility and dust formation by

re-crystallization of the composition to be substantially lower than of untreated urea and known forms of treatment. Preferably, the first polymer particularly is a polyalkenyl compound, such as a polyalkenyl amine, preferably a polyvinyl amine, polyvinyl formamide or polyallyl amine, while the second polymer preferably is polyvinyl alcohol or polyaspartic acid.

The new additive according to this invention preferably is a mixture of a nitrogen containing polyalkenyl compound with the general formula $(C-CX)_n(C-CY)_m$, wherein $n=2$ to 2,000,000 and $m=0$ to 2,000,000 and wherein X and Y, independently of each other, are part of the group consisting of NH_2 , $(CH_2)_nNH_2$, $NH_2.HCl$, $(CH_2)_nNHR$, $(CH_2)_nNH_2.HCl$, $NH-HC=O$, $NH-RC=O$, while Y can further be H, wherein R consist of alkyl or alkenyl having 1-30 C-atoms and $n=1$ to 5. These polymers are preferably mixed with polyaspartic acid or a polyvinyl compound with the general formula of $(CHX-CHY)_n$, wherein n is an integer from 4 to 10,000 and X and Y, independently of one another, are chosen from a hydrogen atom, a carboxylic acid-, ester-, hydroxyl-, amine- and amide group, preferably a polyvinyl alcohol.

The dose of the different, biodegradable polymers is from 50-10,000 ppm, preferably 500-3,000 ppm, based on the weight of the urea, wherein water is preferably used as a solvent.

The temperature at which the treatment is performed, is usually from 10-160°C, preferably at 80-140°C.

Further preferred embodiments are reflected in the subclaims.

Granulation additives for urea on the basis of polyvinyl compounds $(CHX-CHY)_n$ are claimed by the Applicant in WO02/20471.

In the PCT publication WO02/20471 it has been reported that polyaspartic acid does not offer a considerable improvement to the hardness of urea.

Surprisingly, Applicant has now found that the combination of at least two specific polymers has a synergetic effect on the physical properties of urea.

Moreover, adding polyaspartic acid to urea is interesting, because this biopolymer may increase the productivity of plants (see US 5 861 356).

Advantages of polyvinyl alcohols, polyalkenyl amines and polyaspartic acid are the good biodegradability, relatively low toxicity and good miscibility with water. Use of these products as granulation additive for urea will result in a much lower burden to the environment relative to the current situation, which gives toxic formaldehyde products.

The invention therefore relates to a urea composition as defined in the accompanying claims, which composition has a reduced compressibility, tendency of cake formation and dust formation by re-crystallization, compared with a usual urea composition.

The invention will be explained below with a number of examples, with the use of a method which is representative for the production and testing of the quality of the urea granulate formed. These examples exclusively serve to explain and not to limit the claimed protective scope of the present invention.

Preparation method

An aqueous solution of the additive (with the concentrations given in the examples) was added to a urea melt consisting of 99.7% w/w of urea p.a. and 0.3% w/w of water. Thereafter, the urea pellets were formed by separately dropping the molten urea drops from a height of 1 cm onto a glass plate. After solidifying, the pellets were scraped from the glass plate and the fine dust was removed by means of a sieve. The pellets were collected and kept in an air tight flask until the compressibility and tendency of cake formation were measured.

Process for determining the compressibility and cake formation

A transparent round tube with an internal diameter of 3 cm was filled with 40 g of urea pellets. On top of that, a plunger was arranged, causing a pressure of about 600 kPa to

be exerted on the sample. Directly after applying the overpressure and again after 24 hours, the height of the urea column was measured. The relative difference in height, which is a measure for the compressibility, was calculated from these two values (Δ height (%)).

The degree of cake formation can be determined by measuring the breaking strength of the compressed urea sample.

Process for determining the degree of re-crystallization by moisture absorption

A Petri dish with a diameter of about 8.5 cm was filled with 15.0 g urea pellets. This was subsequently placed in a climate chamber with a relative air humidity of 80% and a temperature of 20°C. After 24 hours, the increase in weight as a result of moisture absorption by the granulate was measured, after which the Petri dish was closed with the corresponding cover. The dish was put aside in the dark at room temperature. After two weeks, the content of the dish was examined by looking at the granulate under a loupe.

The abbreviation ghk stands for no re-crystallization, whereas hk stand for re-crystallization after moisture absorption and drying.

Example 1

A number of polymers were tested as granulation additive for urea as a solution or mixture in water. The polymers are shown in Table 1. The results obtained with the aqueous solutions are presented in Table 2.

Table 1

Active compound	Dissolved percentage (w/w%)	Molecular mass (gram / mol)	Degree of hydrolysis (%)
Polyvinyl alcohol	12	$\pm 15,000$	>80
Polyallyl amine	10	$\pm 15,000$	-
Polyallyl amine HCl salt	50	$\pm 15,000$	-
Polyallyl amine/	40	$\pm 70,000$	-

diallyl amine copolymer			
Polyvinyl amine 1	45	$\pm 10,000$	> 90
Polyvinyl amine 2	36	$\pm 45,000$	> 90
Polyvinyl amine 3	30	$\pm 340,000$	> 90
Polyvinyl formamide	22	$\pm 340,000$	30
Polyaspartic acid	40	$\pm 2,500$	-

Table 2

Raw material	Dose (ppm)	Compressi- bility (%)	Tendency of cake formation (N)	Appearance after moisture absorption
Blank	0	10	9.0	ghk
Urea-formaldehyde (80%)	3000	2	0.7	ghk
Polyvinyl alcohol (aq)	1000	5	3.8	hk
Polyallyl amine	1000	3	5.7	hk
Polyallyl amine HCl salt	1000	5	4.3	hk
Polyallyl amine/ diallyl amine copolymer	1000	4	3.9	hk
Polyvinyl amine 1	1000	5	0.8	ghk
Polyvinyl amine 2	1000	7	3.9	ghk
Polyvinyl amine 3	1000	5	3.1	ghk
Polyvinyl formamide	1000	5	7.0	ghk
Polyaspartic acid	1000	11	8.5	ghk

- 5 It can be concluded from the above table that almost all tested polymers have a positive influence on reduction of the compressibility and the cake formation. There are also a number of compounds which are able to counteract re-crystallization of urea granulate after moisture absorption.
- 10 However, the tested compounds can not approach the quality of urea granulate which was treated with urea-formaldehyde.

Example 2

Subsequently, several mixtures were composed on the basis of polyvinyl alcohol and polyvinyl amine/polyvinyl formamide.

- 5 One started from a 12 w/w% solution of polyvinyl alcohol (>80% hydrolysed, molar weight about 15,000 g/mol), to which 5.0 w/w% nitrogen-containing polymer (see Table 1 for the concentrations) was added. The results are shown in Table 3.

10 *Table 3*

Polymer	Dose (ppm)	Compressibility (%)	Tendency of cake formation (N)	Appearance after moisture absorption
Polyvinyl amine 1	1000	2	0	hk
Polyvinyl amine 2	1000	2	0.1	hk
Polyvinyl amine 3	1000	3	0.5	ghk
Polyvinyl formamide	1000	2	0.5	hk
Polyallyl amine	1000	3	0.7	hk

- It can be concluded from the results that there is synergism between polyvinyl alcohol and nitrogen-containing polymers, such as polyvinyl amine, polyvinyl formamide and polyallyl amine, for the preparation of high-quality urea granulate. Use of the combination polyvinyl alcohol and high molecular weight polyvinyl amine additionally makes urea insensitive to re-crystallization after moisture absorption.

20

Example 3

- Since polyaspartic acid can have a favourable influence on plant growth, a number of mixtures on the basis of 80% w/w polyaspartic acid (40% w/w active) and 20% w/w polyvinyl amine, polyvinyl formamide or polyvinyl alcohol (for concentrations, see Table 1) were tested. The results are shown in Table 4.

25

Table 4

Polymer	Dose of the total mixture (ppm)	Compressibility (%)	Tendency of cake formation (N)	Appearance after moisture absorption
Polyvinyl amine 1	1000	3	0.2	ghk
Polyvinyl amine 2	1000	2	0.3	ghk
Polyvinyl amine 3	1000	2	0.6	ghk
Polyvinyl formamide	1000	3	0.8	ghk
Polyallyl amine	1000	2	0.3	ghk
Polyvinyl alcohol*	1000	3	0.9	hk

*Polyaspartic acid and a polyvinyl alcohol separately dosed

5 The above experiment has shown that an additive on the basis of polyaspartic acid and a polar polyalkenyl compound gives urea granulate excellent physical properties.

Example 4

10 It has also been examined whether the addition of three different polymers to the urea melt has a positive effect on the properties of the resulting granulate. In order to examine this, one started from a mixture of 80% w/w polyvinyl alcohol (12% w/w active, >80% hydrolysed) and 20% w/w polyvinyl amine
 15 1 (45% w/w active, >90% hydrolysed). This mixture was added to the urea melt in a dose of 700 ppm. Subsequently, 300 ppm of another type of polymer, mentioned in table 5, was dosed (for concentrations, see Table 1). The results are shown in Table
 5.

20 Table 5

Polymer	Compressibility (%)	Tendency of cake formation (N)	Appearance after moisture absorption
Polyvinyl formamide	2	0.2	ghk
Polyallyl amine	2	0.2	ghk
Polyaspartic acid	1	0	ghk

Use of a mixture of three polymers as additive for the production of urea granulate results in high-quality urea granulate.

CLAIMS

1. A colourfast urea composition, consisting of a mixture of urea and at least two different, biodegradable polymers, of which at least one is a polyalkenyl compound.

2. Urea composition according to claim 1, wherein the polyalkenyl compound is nitrogenous, preferably a polyalkenyl amine.

3. Urea composition according to claim 1 or 2, wherein the alkenyl group of the polyalkenyl amine contains 1-6 C-atoms, preferably 2-4 C-atoms.

4. Urea composition according to claims 1 to 3, wherein the polyalkenyl amine is comprised in the formula

$(C-CX)_n(C-CY)_m$, wherein

$n = 2$ to 2,000,000, $m = 0$ to 2,000,000

$X = NH_2, CH_2NH_2, NH-HC=O, NH-RC=O, CH_2NHR,$

$Y = H, NH_2, CH_2NH_2, NH-HC=O, NH-RC=O, CH_2NHR,$

$R = \text{alkyl- or alkenyl group having 1-30 C-atoms.}$

5. Urea composition according to claim 4, wherein $m=0$ and $n=2$ to 2,000,000, preferably $n=100$ to 20,000.

6. Urea composition according to one or more of the claims 1 to 5, wherein the polyalkenyl amine is chosen from the group consisting of polyvinyl amine, polyvinyl formamide, polyallyl amine, preferably polyvinyl amine or polyallyl amine.

7. Urea composition according to one or more of the claims 1 to 6, wherein the second polymer complies with the general formula $(CHX-CHY)_n$, wherein n is an integer from 4 to 10,000, and X and Y , independently from one another, are chosen from a hydrogen atom, a carboxylic acid-, ester-, hydroxyl-, amine-, or amide-group.

8. Urea composition according to one or more of the claims 1 to 6, wherein the second polymer consists of polyvinyl alcohol, having a degree of hydrolysis of $\geq 70\%$, preferably $\geq 80\%$.

5

9. Urea composition according to one or more of the claims 1 to 7, wherein the second polymer is polyaspartic acid.

10. Process for the preparation of a colourfast urea composition according to one or more of the claims 1 to 9, wherein one mixes a solution of at least two different, biodegradable polymers with urea, in a dose of 50-10,000 ppm, preferably 500-3,000 ppm, based on the weight of urea, and thereafter, according to a way known per se, one removes the solvent in order to obtain the said urea composition.

15

11. Process according to claim 10, wherein the solvent is a polar solvent, preferably water.

20 12. Process according to claims 10 and 11, wherein one performs the process at a temperature from 10° - 160°C , preferably at 80° - 140°C .

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER
 INV. C05C9/00 C05G3/00

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 C05G

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 766 302 A (LEFROY ET AL) 16 June 1998 (1998-06-16) claims	1,10-12
X	DATABASE WPI Section Ch, Week 197729 Derwent Publications Ltd., London, GB; Class A97, AN 1977-51233Y XP002360524 & JP 52 068715 A (HAYASHI KAGAKU KOGY) 7 June 1977 (1977-06-07) abstract ----- -/--	1,2,6,7, 10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *&* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199645 Derwent Publications Ltd., London, GB; Class C04, AN 1996-450885 XP002360525 & JP 08 225387 A (MITSUBISHI CHEM CORP) 3 September 1996 (1996-09-03) abstract -----	1,7, 10-12
X	GB 1 479 455 A (FISONS LTD) 13 July 1977 (1977-07-13) the whole document -----	1,7, 10-12
A	WO 98/30100 A (DONLAR CORPORATION) 16 July 1998 (1998-07-16) claims -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2006/000023

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5766302	A	16-06-1998	WO 9426680 A1 BR 9406680 A EP 0701543 A1	24-11-1994 23-01-1996 20-03-1996
JP 52068715	A	07-06-1977	JP 933395 C JP 53011778 B	14-11-1978 24-04-1978
JP 8225387	A	03-09-1996	NONE	
GB 1479455	A	13-07-1977	BE 817891 A1	20-01-1975
WO 9830100	A	16-07-1998	AU 6021098 A ZA 9800038 A	03-08-1998 08-07-1998