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(54) Title: PROCESS FOR MANUFACTURING FREE-FLOWING GRANULATE PARTICLES OF A PLANT AUXILIARY AGENT

(57) Abstract: The invention relates to a free-flowing granulate of a plant auxiliary agent, and to a process for manufacturing such a free-flowing granulate. In the process, the granulate is mixed at a temperature in the range of 0 - 2000C with a waste flow from a natural source, preferably of vegetable origin. The invention relates to the use in an intimate mixture, produced from the melt, as well as to externally applying the product. The compounds of which these additives consist, are dissolved in a polar solvent, if desired. This solvent, if present, is to be removed according to a way known per se after applying the additive solution. More particularly, the additives consist of a waste flow of natural origin containing nitrogen. Caking of plant auxiliary agents can, if desired, be further reduced by adding a polyalkylene amine compound or an alkyl alcohol. In order to reduce the moisture absorption of granulate, preferably an organic compound containing polyoxyethylene is added, which has an HLB value between 2 and 11.

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Title: **Process for manufacturing free-flowing granulate particles of a plant auxiliary agent**

Introduction

Very many inorganic salts are produced and marketed world wide. Salts are used, inter alia, as fertilizer and drying agent or as additive for foods, cleaning agents and the production of glass and porcelain.

Before it reaches its final use, inorganic salts often undergo a long-term storage and/or intercontinental transport. Therefore, granulate should not cake together, absorb moisture and/or form dust. In order to obtain robust granulates, small amounts of chemicals are added to the salts. A known example is prussiate of potash for sodium chloride (see e.g. US 3.174.825).

Coatings

In the fertilizer industry, nearly always use is made of coatings based on a fatty amine (C12-C22), which is dissolved in a mixture of oil and paraffins. These compositions, possibly in combination with talc, can prevent cake formation of salts (see e.g. US 4.150.965) and, after addition of alkyl phosphate esters, can also strongly reduce moisture absorption (see e.g. EP 0 113 687 and WO 03/006399). These mixtures are mostly applied on the fertilizer via a coating drum or via a spraying system at a conveyor belt. Because of this, a thin film layer is formed around the granulate, by which it is (partially) protected against external influences. Coatings on the basis of oil and paraffins have been examined very intensively and several compositions are claimed (see e.g. WO 03/006399 and references therein). The power is that these coatings mostly give an excellent performance in very low doses. Commonly used amounts are between 0.05 and 0.15 percent by weight, based on the weight of the treated fertilizer.

The legislation in Europe in the field of the treatment of salts, in particular fertilizer, becomes increasingly stringent. In Germany, for example, it is no longer allowed to process mineral oil as additive for fertilizer, soil auxiliary agents, agri-cultural substrates and plant auxiliary agents as of 4 December 2006 (Düngemittelverordnung - DüMV of 26 November 2003, published in Bundesgesetzblatt Jahrgang 2003 Teil I No. 57, 2373-2437). It means that there is a need for environmentally friendly products that give plant auxiliary agents such a protection, that they can be stored and processed without problems.

Cake formation of ammonium nitrate-containing fertilizers can be reduced by using polyalkylene glycols as coating (GB 1.026.023). Most polyalkylene glycols are soluble in water, low-toxic and biodegradable. The optimum dose is between 0.3 and 1.0 percent by weight, based on the weight of the treated fertilizer. This is considerably higher than common with oil-paraffin-containing products.

Several water-soluble biodegradable polymers can be used, inter alia, as coating for the so-called "slow-release" fertilizers, i.e. that the plant nutrients are released slowly to the soil through slow decomposition of the coating (DE 198 20 297-A1). The effect is only realized when relatively large amounts of coating (1-10% based on the weight of the treated fertilizer) are applied. Cake formation of the final product can be limited by adding inert powder, such as talc. Another process for obtaining "slow release" fertilizers has been reported in JP 8-277191. Herein, after applying to the granulate, initially water-soluble coatings are made insoluble by heating at 200°C. Because of that, cross-linking of the polymers takes place (cross-linking). Due to the required heating (and the subsequent cooling), this process is not profitable for bulk processes.

Another approach for preventing lump formation of salts and fertilizer is the use of alkyl amine - alkyl naftalene sulfonate mixtures (US 4.374.039) and alkyl sulfates (US 4.772.308). Practice has proven that these products can give a maximum reduction of cake formation of 50%. Moreover, fertilizers which have been treated with sulfonates or sulfates show cake and dust formation after long-term storage. Due to moisture absorption of the fertilizer, the strong surface active alkyl naftalene sulfonates or alkyl sulfates dissolve a part of the fertilizer, as a result of which the fertilizers can easily cake together and form dust particles.

The caking tendency of sodium chloride can be reduced strongly by treating it with metal complexes of hydroxyl poly carboxylic acids, preferably an iron complex of *meso*-tartaric acid (WO 00/59828). These compounds prove not to satisfy as treating agent for granulate with a strong tendency of lump formation and/or moisture absorption, such as most kinds of fertilizer, for example NPK's, urea and ammonium nitrates.

Another approach has been reported in WO 01/38263 and WO 02/090295. In this case, a part of the paraffin and oil has been replaced by natural oils, such as rapeseed oil. The products are inherently biodegradable, but still contain mineral oil or derivatives thereof. Moreover, natural oils are sensitive to polymerization and oxidation, causing it to be only limitly imperishable.

Granulation additives

It is common knowledge that granulates are subject to crushing during production, storage and transport. High percentages of crushed granules result in dust problems with a strong tendency of caking, because the reactive surface is strongly enlarged. Several 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 of urea. These additives must however be added in relatively large amounts, or the poisonous properties thereof make them difficult to handle. Moreover, formaldehyde derivatives are unsuitable when the urea is used for the production of melamine.

GB-A-1 217 106 describes a process for reducing of caking of urea by using a polyvinyl alcohol having a high molecular weight as an additive in order 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 % by weight, based on the weight of the urea, is admixed. The concentration of the aqueous urea solution is initially 80%, according to the example given; after admixing the solution of the additive, concentration to 95% takes place at increased temperature, after which one lets the urea crystallize through cooling. Practice has shown that the presence of polyvinyl alcohol in urea results in dust formation, probably due to internal moisture migration.

WO 02/20471 mentions a process wherein a combination of a polyvinyl compound and inorganic salts are mixed with urea 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 reduced considerably. This last observation could be an advantage because the urea granulates will be less sensitive to deformation in 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 in technical applications, such as the production of resins.

US 4,063,919 describes a fertilizer composition containing a polyvinyl alcohol 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. Besides, mannitol and 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 increased temperatures (> 100°C), the so-called caramelizing. Also the presence of small polar substances can result in higher hygroscopicity of urea, as a result of which recrystallization can take place and consequently the dust formation will increase drastically.

Object of the invention

Due to the increasingly stringent legislation with respect to the treatment of salts, in particular plant auxiliary agents, such as fertilizer, there will be an increasing demand for a product that can be used as an additive in order to reduce the caking tendency, the moisture absorption of the granules, the dust formation (small particles which already float in case of small air turbulence) and/or the compressibility. This product should be added in a small amount, be cheap, free of paraffin, free of oil and environmentally friendly.

Therefore the object of the invention is to provide a free-flowing, mineral oil-free granulate of a plant auxiliary agent, as well as a process for manufacturing the same.

Another object of the invention is the use of residual flows of natural origin, preferably vegetable waste flows, such as corn and wheat residues, as additive for plant auxiliary agents, such as fertilizer. The products can be added in the melting phase of the granulation process or on the produced granules after the granulation.

Another object of the invention is the use of a particular polyoxy ethylene-containing organic component having an HLB value between 2 and 11 as additive for plant auxiliary agents, such as fertilizer.

Description of the invention

The invention relates to free-flowing, mineral oil-free, granulate particles of a plant auxiliary agent, consisting of the reaction product of a nitrogen-, phosphor- and/or potassium-containing plant auxiliary agent and a nitrogen compound(s)-containing waste flow of natural material. The plant auxiliary agent is preferably a urea- or ammonium nitrate-containing fertilizer; whereas the waste flow preferably originates from the starch preparation from products such as corn, wheat, soy, barley and potatoes. If desired, the protein and/or amino acid content of the waste stream to be used can be supplemented with a protein-rich or amino acid-rich source, such as soy protein, or chicken egg protein.

The invention also relates to the preparation of said granulate particles by treating the granules with a nitrogen-rich additive of natural origin at increased temperature. The additive(s) is (are) mixed in a polar solvent, if desired. If desired, this solvent, if present, can be removed after adding the additive solution according to a way known per se.

It is noted that the treatment according to the invention can be applied for crystals, granules and prills; for simplification, the invention is explained by means of granules.

Preferably, the new additive is a natural waste flow of vegetable origin from the group of corn, potatoes, wheat, barley, soy, which preferably has a protein and amino acid content of more than 10% (w/w), in particular granular corn derivatives. In a preferred embodiment, the nitrogen content can be raised, if desired, by means of adding extra protein, or (co)polymers on the basis of 1-alkenes having the general formula CHX=CHY, wherein X and Y, independently of each other, are part of the group consisting of NH_2, $NH_2.HCl$, $(CH_2)_nNHR$ (n = 1 to 5), $(CH_2)_nNH_2.HCl$, $(CH_2)_nNH_2$, NH-HC=O, NH-RC=O, while Y can further be H, wherein R consists of alkyl or alkenyl having 1 - 30 C-atoms. The (co)polymer is preferably synthesized of 2 to 2,000,000 units.

Coatings

If desired, the tendency of lump formation can be further reduced by adding (preferably) linear alkyl alcohols (C10-C30), preferably C16-C22 alcohols to the granulate of a plant auxiliary agent.

To reduce the moisture absorption by the granulate, if desired, a biodegradable ethoxylated organic component can be added, which has a HLB value between 2 and 11.

The moisture absorption by granulate particles can be further reduced by adding a linear alkane having an alkyl chain length between C16 and C40, which has a solidification range between 50 and 10°C.

Although Applicant does not wish to be bound to any theory, it is assumed that the presence of a nitrogen-containing (in the form of amine and/or amide groups) natural product on the granulate particles of a plant auxiliary agent results in the formation of an adduct with these particles, causing (the outside of) the granulate to become less sensitive to interaction with surrounding granulate particles, as a result of which the tendency of caking is strongly reduced. Depending on the type of additive, also influence on the dissolving rate of the plant auxiliary agent in water has been observed.

Further preferred embodiments are reflected in the sub-claims.

Coatings on the basis of natural waste flows are known per se and are used for example in the paper industry (see US 2002/0121222). Besides, corn products can serve as coating for tableware and cutlery (CN 1458189).

Vegetable waste flows are in some cases used as a fertilizer. In that way, maize gluten promote the growth of grass, but inhibit the formation of weed (US 5030268).

Some fertilizers can be treated with coatings on the basss of vegetable residues. Patent GB 8150829 claims an effect of a protein-rich polymer as a treating agent for fertilizer. In this embodiment, the fertilizer is first provided with an inorganic layer.

Patent GB 2110518 mentions the use of a water-soluble protein of natural origin and a metal salt as part of a hydrophilic, water-insoluble bioactive coating for the protection of plants and seeds.

The Japanese patent JP 6144981 describes a composition for an improved degradable coating for granular fertilizer, consisting of a biodegradable powder, such as starch, mixed with an auto oxidating organic compound having at least one double C=C bond, possibly supplemented with olefin (co)polymers and vinyl chloride (co)polymers.

Further, polyvinyl amine can be used as part of laminating films (EP 0 644 247). Compositions with polyvinyl amine-graft polymers are claimed as treating agent for textile (WO 02/095122). Polyvinyl amine can even be added as polyelectrolyte to fertilizer in order to condition soil (GB 734 504). Polyallyl amine can be used as coating on e.g. textile in order to absorb harmful gases (WO 93/17760). Resins on the basis of polyallyl amine or polyvinyl amine having an unsaturated C=C bond at the end of the chain can be used as protective films for all kinds of substrates, for example the inert materials glass and wood (EP 0 294 506).

Polyaspartic acid can serve as a surface coating for medicines and food (US 5.175.285). Besides, polyaspartic acid, in combination with fertilizer, can enhance the productivity of the plant (US 5,861,356).

Advantages of polyalkenyl amines and polyaspartic acid are the good biodegradability, relatively low toxicity and good miscibility with water. Use of these products as additive for salts will therefore result in a much lower burden for the environment relative to the current situation: badly water-soluble, toxic fatty amines in oil and/or paraffins.

Coating products on the basis of (modified) polyalkylene alcohols are known per se. In this context, GB 1 383 444 describes the use of mixtures of polyalkylene alcohols and a surface active substance as coating for fertilizer for reducing lump and dust formation during storage and handling.

For the protection against moisture absorption by the present granulate particles, preferably a biodegradable ethoxylated organic component is added, which has a HLB value between 2 and 11.

The use of polyoxy ethylenes on fertilizer has been reported (DE 2330847) per se. However, these compounds are mixed with mineral oil, of which the use can however be overcome by the present invention. Polyoxy ethylenes are also used as a part of compositions for coatings, which can establish controlled release of particular agrochemicals in fertilizers (see e.g. JP 2003081705).

The moisture absorption of inorganic salts can be further reduced by coating the granules with a mixture consisting of residue flows of natural origin and linear alkanes. Adding linear alkanes to salt granulate is known per se

(WO03/006399), but then it relates to a fully apolar medium, consisting of paraffin and oil. However, no combinations with natural residue products are claimed.

Granulation additives

Furthermore, Applicant surprisingly found that adding a waste material of natural origin to the molten plant auxiliary agent results in a significant decrease of the compressibility and the tendency of caking of the granulate being formed thereafter. Moreover, the granulate is not sensitive to recrystallization by moisture absorption during storage and handling. The natural waste materials can be added to the molten plant auxiliary agent either separately 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 natural waste material is at most 10% b.w., based on the total amount of plant auxiliary agent.

It is noted that the treatment according to the invention can be applied to all kinds of grains, such as crystals, granules or prills.

Preferably, the new additive is a waste flow of natural origin, particularly of vegetable origin, such as maize, potatoes, wheat, barley, soy, which preferably has a protein and/or amino acid content of more than 10% (w/w), in particular granular maize derivatives. In a preferred embodiment, the granulate properties can be optimized, if desired, by means of adding (co)polymers on the basis of 1-alkenes having the general formula of CHX=CHY, wherein X and Y, independently of each other, are part of the group consisting of OH, O(RC=O), COOH, NH_2, $NH_2.HCl$, $(CH_2)_nNHR$, $(CH_2)_nNH_2$, $(CH_2)_nNH_2.HCl$, NH-HC=O, NH-RC=O, while Y can further be H, wherein R consists of alkyl or alkenyl having 1-30 C-atoms and n = 1 to 5. The (co)polymer is preferably synthesized of 2 to 2,000,000 units.

Preferably, use is made of polyvinyl alcohol and/or polyvinyl amine and/or polyaspartic acid.

Further preferred embodiments are reflected in the sub-claims.

It has been reported in the PCT publication WO 02/20471 that polyaspartic acid does not offer a considerable improvement to the hardness of urea. Adding polyaspartic acid to urea is interesting, because this biopolymer can enhance the productivity of plants (see US 5,861,356). It has however been found that polyaspartic acid in combination with vegetable residues can act indeed as good granulation additive for urea.

Advantages of the use of natural residues are recycling of raw materials, the good biodegradability, low toxicity, ample availability and the very favourable price. Use of these products as granulation additive for plant auxiliary agents will result in a much lower burden for 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 has a reduced compressibility, tendency of cake formation and dust formation through recrystallization, compared with a common urea composition.

The invention will be explained hereafter by means of a number of examples, by using methods which are representative for the production and testing of the quality of the obtained granulates. These examples exclusively serve to explain and not to limit the claimed protective scope of the present invention.

Process for applying the coating

Before applying the coating, the granulate (1.0 kilogram per sample) is kept in sealed plastic jars in an oven at 35°C for 16 hours. The treatment takes place as follows: the granulate is brought into a rotating coating drum, which has a temperature of about 50°C. Thereafter, 0-5000 ppm of a coating is dripped onto the granulate, followed by rotating the drum for yet another 5 minutes. The thus treated granulate is dumped into a broad plastic tank, where the granulate can "evaporate" for 5 minutes. Subsequently, the treated granulate is transferred into a plastic jar. After sealing the jar, the grains are allowed to cool to room temperature over a period of 24 hours.

Preparation method of an intimate mixture through the melt

An aqueous solution of the additive (having the concentrations indicated in the examples) is added to a urea melt (T = approx. 133°C) consisting of 99.7 % w/w urea p.a. and 0.3 % w/w water. Thereafter, urea pellets were formed by dropping the molten urea drops separately from a height of 1 cm onto a glass plate. After solidification, the pellets were scraped off 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 urea pellets. On top of that a plunger was arranged, which caused a pressure of about 600 kPa to be exerted on the sample. Directly after applying the gauge pressure 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 (expressed in kilograms) of the compressed urea sample.

Process for determining the tendency of baking

A representative test for simulating caking of granulate was performed as follows. Polyethylene tube foil was closed on one side by means of sealing (70 mm wide, 300 mm long). At the bottom of the formed pouch, a plastic chip (48 mm diameter) was brought. The pouch was filled with 125 gram granulate. Subsequently, another plastic chip was put on the granulate.

The pouch was evacuated and closed by a seal. The obtained pouch was suspended from a metal pin. This procedure was repeated twice for the same sample. All sealed pouches with granulate were subsequently placed in an autoclave. The samples were kept for a week at 2 bar gauge pressure at a temperature of 35 or 50°C. Subsequently the pouches were carefully cut open. The hardness of the baked sample was measured in a breaking apparatus. The force required to break the sample was read electronically. The obtained values (expressed in kilograms) were the average of at least three samples

Process for determining the moisture absorption

Two plastic beakers of 200 ml were filled with 160 gram (blank or treated) fertilizer. The weights of the beakers as well as the fertilizer are measured with an analytical balance. The total weight is calculated (m_{tot}). The beakers are placed in a climate chamber with the following conditions: 80% relative air humidity and a temperature of 20°C. After 72 hours, the samples are removed from this climate chamber and subsequently the weight is determined (m_{na}) and the appearance is examined. Thereafter, the moisture absorption can be calculated as follows:

$$\text{Moisture absorption} = m_{na} - m_{tot}$$

Process for determining the degree of recrystallization by moisture absorption

A Petri dish with a diameter of approximately 8.5 cm was filled with 15.0 gram 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 recrystallization, whereas hk stands for recrystallization after moisture absorption and drying.

Process for determining the dust content

The relative amount of dust particles of the granulates, mentioned in this document was determined as follows. 40 grams (accurately weighed) of fertilizer was brought into a three-neck round-bottom flask of 500 ml. The flask was provided with a glass column and a gas capillary, connected with a compressed air cylinder. The end of the gas capillary was placed in the granulate. Air (2 bar gauge pressure) was blown through the granulate for 75 seconds, by which a fluidised bed system was created. The weight of the remaining granulate was determined accurately on an analytical balance. The loss in weight is a measure for the amount of free dust particles and the dust particles created by friction. The determinations were at least performed twice.

Coatings

Example 1

A number of residues of natural origin is applied as coating to Calcium Ammonium Nitrate granules (CAN, 27% N). The baking tendency of the thus coated material is determined. The different natural residue products are shown in Table 1. The protein and amino acid contents relate to the dry matter. The obtained results are presented in Table 2.

Table 1

Active matter	Dry matter content (%)	Protein content (%)	Amino acid content (%)
Grain maize residue (Maize steep liquid)	51	43	10
Soy milk residue	10	30	8,5
Liquid wheat starch	16	27	1,5

residue			
Sugar-rich wheat residue	23	22	14,7
Pig bones residue	40	70	<1

It is noted that the used grain maize residue consists of the steep liquid resulting from the extraction of starch from grain maize, possibly after concentration of the slurry for restricting the added amount of liquid.

Table 2

Coating	Dose (ppm)	Baking tendency at 35°C (kg)
Blank (without coating)	-	11,7
Grain maize residue	1500	1,9
Soy milk residue	1500	8,2
Liquid wheat starch residue	1500	6,2
Sugar-rich wheat residue	1500	3,5
Pig bones residue	1500	2,5

The above example proves that waste flows from natural origin can considerably reduce the baking tendency of granulate, such as CAN.

Example 2

It can be deduced from example 1 that natural proteins provide the decrease of caking. In order to further substantiate this, the protein concentration of the grain maize residue has been increased by adding 5 to 15% w/w very fine (< 60 micron) soy protein powder. The obtained mixtures were applied as coating to Calcium Ammonium Nitrate granules (CAN, 27% N). The baking tendency of the thus coated material has been determined (Table 3).

Table 3

Coating	Dose (ppm)	Baking tendency at 35°C (kg)
Blank (without coating)	-	10,8
Grain maize residue	1500	1,8
Grain maize residue plus 5% (w/w) soy protein powder	1500	1,4
Grain maize residue plus 10% (w/w) soy protein powder	1500	1,0
Grain maize residue plus 15% (w/w) soy protein powder	1500	1,3

The above example shows that adding extra protein to natural residue products results in a good coating for preventing lump formation of plant auxiliary agents.

Example 3

Another plant auxiliary agent often used is urea, which can as such be sensitive to caking. Waste materials of natural origin could reduce that baking tendency. In order to test this, a number of products of natural origin was applied as a coating to urea prills (46% N, without internal additive). The baking tendency of the coated material has been determined. The results are mentioned in Table 4.

Table 4

Coating	Dose (ppm)	Baking tendency at 35°C (kg)
Blank (without coating)	-	0,6
Standard coating for urea[1]	400	0,2
Grain maize residue	400	0,2
Pig bones residue	400	0,2

[1] Mixture as described in US 4,812,158, consisting of 67% (w/w) water, 11% (w/w) polyvinyl acetate and 22% (w/w) alkyl sulphate.

It proves from the experiment that residue products of natural origin can act as additive for preventing lump formation of urea grains.

Example 4

The natural residue products mentioned in Example 1, were tested as suspension in water. Since the presence of water in case of hygroscopic granulate often causes accellerated cake formation, it has been checked whether the use of other solvents resulted in improvement of the anti-baking properties. In order to investigate this, 20% w/w very fine (< 60 micron) soy protein powder was mixed with several polar solvents. The obtained slurries were applied to calcium ammonium nitrate, CAN (27% N) via the coating process. Subsequently, the baking tendency of the treated grains was determined.

Table 5

Solvent	Dose (ppm)	Baking tendency at 35°C (kg)
Blank (without coating)		8,9
Water	1000	2,7
Glycerol	1000	2,0
Diethylene glycol	1000	1,9
Polyethylene glycol 200	1000	1,3
Polyethylene glycol 400	1000	1,2

It proves from this experiment that, in a coating on the basis of natural residue products, replacing water by another polar solvent results in an improved functioning with respect to the tendency of lump formation of plant auxiliary agents.

Example 5

For a stronger reduction of the caking of granulate, 2% (w/w) polyvinyl amine (molecular mass 10,000 g/mol, hydrolysis degree > 90%) was added to the natural waste material. The obtained mixtures were coated onto calcium ammonium nitrate, CAN (27% N), by means of spraying. As reference, a paraffin product **A** has been taken in the test. It had the following properties: solidification point 45°C, viscosity 7 mPa.s (80°C). The composition is as follows: tallow fat amine content 7.0% w/w, mineral oil 20% w/w and 73% w/w low-melting paraffin wax.

Table 6

Coating	Dose (ppm)	Baking tendency at 35°C (kg)
Blank (without coating)	-	11,7
Paraffin product **A**	1500	0,6
Grain maize residue + 2% polyvinyl amine	1500	0,7
Sugar-rich wheat residue + 2% polyvinyl amine	1500	1,5

The above example proves that adding a small amount of polyvinyl amine to vegetable waste flows results in a performance as coating which is similar to classic paraffin products.

Example 6

Another process for reducing the caking of granulate is adding a fatty alcohol (C10-C30) to the vegetable waste material. In this experiment, 5% (w/w) has been mixed with grain maize residue at a temperature of approx. 60°C. The obtained mixtures were coated onto calcium ammonium nitrate granules (27% N). As reference, paraffin-containing product **A** has been taken in the test. In this experiment, also the dust-binding properties of the formulations have been observed.

Table 7

Coating	Dose (ppm)	Baking tendency at 35°C (kg)	Dust (ppm)
Blank (without coating)	-	12,9	238
Paraffin product **A**	1500	0,7	42
Grain maize residue plus 5% Hexadecyl alcohol (C16)	1500	0,9	53
Grain maize residue plus 5% Docosyl alcohol (C22)	1500	0,7	48

The above example proves that adding a small amount of fatty alcohol (C10-C30) to vegetable waste flows results in a performance as coating, which is similar to classic paraffin products, both in the field of cake formation and binding of dust particles.

Example 7

Several salts, including fertilizers, can be sensitive to moisture absorption. Excessive moisture absorption by salts can result in undesired phenomena such as dust formation and caking. The natural residue substances show per se a low hydrophobic effect. In order to reduce the moisture absorption by salts, a number of moisture resistant substances are added to the formulations, with a baking tendency reducing effect. The examined moisture resistant compounds are shown in Table 8. These compounds are well biodegradable.

Table 8

Active compound	Unsaturated alkyl chain	Alkyl chain length (number of C-atoms)	Number of oxyethylene groups	HLB value
Polyoxyethylene (2) stearyl ether	No	18	2	4

Polyoxyethylene (2) oleyl ether	Yes	18	2	4

The formulations in Table 9 consist of 95% grain maize residue and 5% moisture resistant active compound. These formulations (temperature approx. 60°C) were applied to calcium ammonium nitrate (CAN, 27% N).

Table 9

Active compound	Dose (ppm)	Moisture absorption (g)	Baking tendency (35°C) (kg)
Blank (without coating)	-	9,9	11,7
Paraffin product **A**	1500	7,5	0,6
Formulation without moisture resistant compound	1500	9,8	1,9
Polyoxyethylene (2) stearyl ether (+ grain maize residue)	1720	6,2	0,8
Polyoxyethylene (2) oleyl ether (+ grain maize residue)	1600	6,9	1,1

The above experiment proves that applying coatings on vegetable basis, which are provided with ethoxylated alkyl compounds, results in a decrease of the moisture absorption of the treated fertilizer. Moreover, the tendency of caking remains low. A performance can be realized which is equivalent to or better than coatings on paraffin basis.

Example 8

The protection against moisture absorption has been further examined on very moisture-sensitive ammonium nitrate (33.5% N, stabilized with dolomite and magnesium nitrate). A formulation **B** has been made, having the following composition: 85% (w/w) aqueous grain maize residue, 10% (w/w) polyoxyethylene (2) stearyl ether and 5% (w/w) tallow fat alcohol. This mixture has been applied as coating in different doses. As reference, a moisture resistant coating **C** has been taken, in accordance with WO 03/006399 (7.5% (w/w) tallow fat amine (C16-C18), 7.5% (w/w) 2-ethyl hexyl phosphate acid ester, 85% (w/w) paraffin wax (> 50% linear alkane), melting point 45°C). The results are mentioned in Table 10.

Table 10

	Dose (ppm)	Moisture absorption (g) after 72 hours
Blank (without coating)	-	11,7
Paraffin coating **C**	700	5,8
B	300	6,4
B	600	5,9
B	1000	5,9

It has proven from this experiment that already with a dose of 300 ppm of a coating in accordance with the invention, a good protection against moisture action on very hydroscopic salts can be established.

Example 9

The reduction of moisture absorption by inorganic salts with coatings on the basis of residues of natural origin can also be established by adding linear alkanes. In order to examine this, a number of mixtures (temperature approx. 60°C) has been made on the basis of aqueous grain maize residue and a linear alkane mixture. This product was obtained through a Fischer-Tropsch process (solidification range 45-20°C, C16-C40 alkanes). The coatings were tested on calcium ammonium nitrate

(27% N). As reference, coating **C** was used. The results are mentioned in Table 11.

Table 11

	Dose (ppm)	Moisture absorption (g) after 72 hours
Blank (without coating)	-	6,9
Paraffin coating **C**	1200	3,2
Grain maize residue/ Linear alkane = 90/10	1000	4,6
Grain maize residue/ Linear alkane = 80/20	1000	4,1
Grain maize residue/ Linear alkane = 70/30	1000	3,6

The protection against moisture absorption of moisture-sensitive inorganic salts can therefore also be established by applying mixtures on the basis of natural residue products and linear alkanes.

The following examples relate to the use of vegetable waste flows as granulation additive, to the urea melt.

Example 10

Furthermore, a number of aqueous waste flows of natural origin has also been tested as granulation additive for urea. In this case, the additive is added to urea in molten state (T = approx. 133°C), after which granulation takes place by means of the formation of pellets. The compressibility and the baking tendency of the thus obtained material has been determined after compression. Moreover, the appearance of the granulate after moisture absorption (24 hours, 20°C, 80% RH) has been examined. As references, a blank as well as a urea-formaldehyde and polyvinyl alcohol were taken. The obtained results are mentioned in Table 12.

Table 12

Raw material	Dose (ppm)	Compressibility (%)	Tendency of caking (N)	Appearance after moisture absorption
Blank	0	10	9,0	ghk
Urea-formaldehyde (80%)	3000	2	0,7	ghk
12% Polyvinyl alcohol (aq)	1000	5	3,8	hk
Grain maize residue	3000	2	0,8	ghk
Soy milk residue	4000	5	2,8	hk
Liquid wheat starch residue	4000	4	1,9	hk
Sugar-rich wheat residue	4000	2	0,5	hk

ghk = no recrystallization after moisture absorption and drying

hk = recrystallization after moisture absorption and drying

The above example proves that waste flows of natural origin have a positive influence on decreasing the compressibility and the cake formation. The grain maize residue gives a performance which is at least equivalent to urea treated with urea-formaldehyde in all measured properties.

Example 11

Subsequently, several mixtures were composed on the basis of the grain maize residue and a number of polymers. One started from a mixture consisting of 80% w/w grain maize residue and 20% w/w polymer. The examined polymers are shown in Table 13. The results are mentioned in Table 14.

Table 13

Active compound	Dissolved percentage (w/w%)	Molecular mass (gram/mol)	Degree of hydrolysis (%)
Polyvinyl alcohol	12	± 15.000	>80
Polyallyl amine/ diallyl amine copolymer	40	± 70.000	-
Polyvinyl amine	45	± 10.000	> 90
Polyvinyl formamide	22	± 340.000	30
Polyaspartic acid	40	± 2.500	-

Table 14

Polymer	Dose of the total mixture (ppm)	Compressibility (%)	Tendency of caking (N)	Appearance after moisture absorption
Polyvinyl alcohol	1200	3	1,8	ghk
Polyvinyl alcohol	3000	3	0	ghk
Polyallyl amine/ diallyl amine copolymer	3000	3	0,8	ghk
Polyvinyl amine	3000	2	0,5	ghk
Polyvinyl formamide	3200	3	0,7	ghk
Polyaspartic acid	3000	2	0,8	ghk

It can be concluded from the results that adding polymers provided with polar groups to a natural residue flow as urea additive can result in the production of very high-quality urea granulate.

CLAIMS

1. Free-flowing, mineral oil-free granulate particles of a plant auxiliary agent, consisting of the reaction product of a plant auxiliary agent containing nitrogen, phosphor and/or potassium and a waste flow of natural material containing nitrogen compound(s).

2. Free-flowing, mineral oil-free granulate particles according to claim 1, wherein the plant auxiliary agent is a fertilizer containing urea or ammonium nitrate.

3. Free-flowing, mineral oil-free granulate particles according to claims 1 or 2, wherein the natural material is of vegetable or animal origin.

4. Free-flowing, mineral oil-free granulate particles according to one or more of the claims 1 - 3, wherein the waste flow of vegetable material is a by-product of the starch preparation from maize, wheat, soy, barley or potatoes, preferably maize or wheat.

5. Free-flowing, mineral oil-free granulate particles according to claim 4, wherein the waste flow originates from the starch preparation from grain maize, preferably consisting of maize steep liquid.

6. Free-flowing, mineral oil-free granulate particles according to one or more of the claims 1 - 5, wherein the waste flow has a protein and/or amino acid content of at least 10% (w/w).

7. Free-flowing, mineral oil-free granulate particles according to claim 6, wherein the protein and/or amino acid being present at least partially originates from a protein- and/or amino acid-rich supplement.

8. Free-flowing, mineral oil-free granulate particles according to one or more of the claims 1 - 7, wherein the plant auxiliary agent further contains a (co)polymer containing polar groups, in particular a (co)polymer on the basis of 1-alkenes having the general formula CHX=CHY, wherein X and Y, independently of one another, are part of the group consisting of OH, O(RC=O), COOH, NH_2, NH_2.HCl, $(CH_2)_nNHR$, $(CH_2)_nNH_2$, $(CH_2)_nNH_2$.HCl, NH-HC=O, NH-RC=O, while Y can further be H, wherein R consists of alkyl or alkenyl having 1 - 30 C-atoms and n = 1 to 5.

9. Free-flowing, mineral oil-free granulate particles according to claim 8, wherein the polymer is chosen from the group consisting of polyvinyl alcohol, polyvinyl acetate, polyvinyl amine, polyvinyl formamide, polyallyl amine and polyaspartic acid, preferably polyvinyl amine or polyallyl amine.

10. Free-flowing, mineral-oil free granulate particles according to one ore more of the claims 1 - 9, wherein the plant auxiliary agent further contains a C_{10}-C_{30} alkyl alcohol, preferably a C_{16}-C_{22} alkyl alcohol.

11. Free-flowing, mineral oil-free granulate particles according to one ore more of the claims 1 - 10, wherein the plant auxiliary agent further contains a compound containing polyoxyethylene group(s), having an HLB value of 2-11.

12. Free-flowing, mineral oil-free granulate particles according to claim 11, wherein the compound containing polyoxyethylene group(s) has an HLB value between 3 and 6.

13. Free-flowing, mineral oil-free granulate particles according to claim 11 or 12, wherein the compound containing polyoxyethylene group(s) consists of a polyoxyethylene-alkyl, a polyoxyethylene-alkenyl, a polyoxyethylene sorbitan alkylate or a polyoxyethylene sorbitan alkenylate, wherein the alkyl or alkenyl group has 10 to 30 carbon atoms.

14. Free-flowing, mineral oil-free granulate particles according to one or more of the claims 11 to 13, wherein the compound containing polyoxyethylene group(s) has 1 to 10 oxyethylene groups, preferably 2 to 5 oxyethylene groups.

15. Free-flowing granulate particles of a plant auxiliary agent, consisting of the reaction product of the plant auxiliary agent containing nitrogen, phosphor, or potassium, preferably chosen from urea and a fertilizer containing ammonium nitrate, and a waste flow of natural material of vegetable or animal origin containing nitrogen, as well as a linear C16-C40 alkane having a solidification temperature between 10° and 50°C.

16. Process for preparing free-flowing, mineral oil-free granulate particles of a plant auxiliary agent, wherein one lets particles of a plant auxiliary agent, whether or not in molten state at a temperature between 10 and 200°C, react with a waste flow of natural material containing a nitrogen compound(s), if desired in the presence of a suitable solvent, after which one removes the solvent, if present, according to a way known per se, for forming particles of the plant auxiliary agent which are at least partially converted with the nitrogen compound(s), and thereafter the particles are granulated, if desired.

17. Process according to claim 16, wherein the plant auxiliary agent is at least a compound containing nitrogen, phosphor and/or potassium.

18. Process according to claim 16 or 17, wherein the plant auxiliary agent consists of a fertilizer containing urea or ammonium nitrate.

19. Process according to one or more of the claims 16 to 18, wherein the solvent is a polar solvent, preferably polyethylene glycol, glycerol or water.

20. Process according to one or more of the claims 16 to 19, wherein the natural waste flow originates from plants, or bones.

21. Process according to one or more of the claims 16 to 20, wherein the vegetable waste flow originates from maize, wheat, soy, barley, potatoes, preferably maize or wheat.

22. Process according to one or more of the claims 16 to 21, wherein the vegetable waste flow originates from grain maize, preferably maize steep water.

23. Process according to one or more of the claims 16 to 22, wherein the waste flow has a protein- and/or amino acid-content of at least 10% (w/w).

24. Process according to one or more of the claims 16 to 23, wherein the waste flow is at least partially provided and/or supplemented with an protein- and/or amino acid-rich supplement.

25. Process according to one or more of the claims 16 to 24, wherein the waste flow of natural material is further provided with a (co)polymer containing polar groups, in particular a (co)polymer on the basis of 1-alkenes having the general formula CHX=CHY, wherein X and Y, independently of each other, are part of the group consisting of OH, O(RC=O), COOH, NH_2, NH_2.HCl, $(CH_2)_nNHR$, $(CH_2)_nNH_2$, $(CH_2)_nNH_2$.HCl, NH-HC=O, NH-RC=O, while Y can further be H, wherein R consists of alkyl or alkenyl having 1 - 30 C-atoms and n = 1 to 5, in an amount of 5-95% (w/w) based on the waste flow, preferably 10-40% (w/w).

26. Process according to claim 25, wherein the polymer is chosen from the group consisting of polyvinyl alcohol, polyvinyl acetate, polyvinyl amine, polyvinyl formamide, polyallyl amine and polyaspartic acid, preferably polyvinyl amine or polyallyl amine.

27. Process according to one or more of the claims 16 to 26, wherein the waste flow is further provided with a C10-C30 alkyl alcohol, preferably a C16-C22 alkyl alcohol, particularly an amount of 0.1-50% (w/w) based on the waste flow, preferably 10-30% (w/w).

28. Process according to one or more of the claims 16 to 27, wherein the waste flow is further provided with a compound containing polyoxyethylene group(s), which has an HLB value of 2-11, preferably in an amount of 0.1-50% (w/w) based on the waste flow, preferably 10-30% (w/w).

29. Process according to claim 28, wherein the compound containing polyoxyethylene group(s) has an HLB value 3 to 6.

30. Process according to claim 28 or 29, wherein the compound containing polyoxyethylene group(s) consists of a polyoxyethylene-alkyl, a polyoxyethylene-alkenyl, a polyoxyethylene sorbitan alkylate or a polyoxyethylene sorbitan alkenylate, wherein the alkyl or alkenyl group has 10 to 30 carbon atoms.

31. Process according to any one of the claims 28 to 30, wherein the compound containing polyoxyethylene group(s) contains 1 to 10 oxyethylene groups, preferably 2 to 5 oxyethylene groups.

32. Process according to one ore more of the claims 16-31, wherein the process is performed at a temperature of 0°-150°C, preferably at 20°-90°C, particularly 30°-50°C, expediently at room temperature.

33. Process according to one or more of the claims 16-32, wherein the reaction is performed by using an aqueous suspension of the waste flow of natural material in a dose of 100-10.000 ppm total of additive, preferably 500 - 3.000 ppm, based on the weight of the plant auxiliary agent to be treated.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C05C1/02 B01J2/30

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)
B01J 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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, BIOSIS

C. 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 200526 Derwent Publications Ltd., London, GB; Class A97, AN 2005-243229 XP002383110 & CN 1 557 791 A (UNIV SHENYANG AGRIC) 29 December 2004 (2004-12-29) abstract -----	1,3,4,8, 9,16,17, 19-21, 25,26,32
X	DATABASE WPI Section Ch, Week 199911 Derwent Publications Ltd., London, GB; Class C04, AN 1999-124227 XP002383464 & JP 10 338584 A (KONOSHIMA KASEI KK) 22 December 1998 (1998-12-22) abstract ----- -/--	1,3-5, 16,17, 19-22,32

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

☒ See patent family annex.

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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