

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
5 January 2012 (05.01.2012)

(10) International Publication Number  
**WO 2012/000914 AI**

(51) International Patent Classification:

**CUD 3/33** (2006.01) **B01J 2/00** (2006.01)  
**CUD 3/37** (2006.01) **C09K 8/536** (2006.01)  
**CUD 7/32** (2006.0 1) **CUD 3/22** (2006.0 1)  
**CUD 17/00** (2006.01) **C08J 3/12** (2006.01)

(21) International Application Number:

PCT/EP201 1/060671

(22) International Filing Date:

27 June 2011 (27.06.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

101675 16.3 28 June 2010 (28.06.2010) EP  
61/359,526 29 June 2010 (29.06.2010) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: PARTICLES COATED WITH VINYL ALCOHOL (CO) POLYMER AND POLYSACCHARIDE

(57) Abstract: The present invention relates to a coated particle containing a particle and a coating, wherein the particle contains glutamic acid N,N-diacetic acid or a partial salt thereof of the formula  $H_nY_m-GLDA$ , wherein Y is a cation selected from the group of sodium, potassium, and mixtures thereof,  $n+m = 4$ , and wherein the coating contains at least one vinyl alcohol (co)polymer and at least one polysaccharide, to a process to make such particle, and to the use thereof. In addition, the invention provides a method to reduce the hygroscopicity and water uptake and/or to improve the stability and flow properties of materials.



WO 2012/000914 AI

**PARTICLES COATED WITH VINYL ALCOHOL (co) POLYMER AND POLYSACCHARIDE**

The invention relates to particles of (salts of) glutamic acid N,N-diacetic acid, a chelating agent of the formula  $\text{COOH-CH}(-\text{CH}_2-\text{CH}_2-\text{COOH})-\text{N}-(\text{CH}_2-\text{COOH})_2$ , abbreviated as GLDA, which are coated, to processes to produce said particles, and to the use of such particles.

The detergent market is currently undergoing important changes. Due to ecological and regulatory reasons the use of phosphate in high concentrations in detergent formulations is to be banned altogether or must at least be greatly reduced. The formulators of detergent products have to find alternatives to replace the phosphate compounds, with the most promising replacements being biodegradable chelating agents such as GLDA. Such chelating agents are used in a concentration from 5% to 60%. Many detergent formulations contain (co-) builders, which are typically polymers, such as e.g. polyacrylates, phosphonates, phosphates, silicates or zeolites. These co-builders are present in formulations in a concentration from 1% to 50%.

In powder or tabs detergent formulations, solid raw materials are required by the formulator. In for example automatic dishwashing (ADW) applications, the raw materials have to be in granule form to improve the tableting and solids handling of the formulation. These granules typically have a size comprised between 300 and 2,000 microns. The usual form in which glutamic acid N,N-diacetic acid (GLDA) and its salts are available is a liquid with an active content from 35% to 50%. After drying the substance (i.e. the powder or granules), especially when obtained in the amorphous state, shows hygroscopic properties to some extent, which makes it difficult to use for the ADW formulators. Moreover, the granules obtained from a granulation process (such as fluid bed granulation) are somewhat brittle and thus cannot grow easily to the required

size, resulting in slow processing and lots of fines. In addition, whether in powder or granule form, the (amorphous) chelating agent GLDA exhibits hygroscopic properties, and this will render the material sticky and thus introduce storage, handling, and manufacturing problems. Flow properties of particles are critical in many ways. During manufacture of the particles themselves, they must flow smoothly relative to one another, e.g. in a fluid bed. Additionally, they must then be successfully transported to storage and transport containers. Finally, they must again be transported from storage and fed into a powder or tablet manufacturing facility. Flow problems arise due to several causes. For chelating agents, poor flow can be due to low glass transition temperatures, tackiness, wetness, and physical entanglement of multifaceted, irregularly shaped particles.

GLDA will move into the ADW market and likely into many other fields where a strong, green chelate is needed. The term "green" here denotes materials with a high renewable carbon content, a sustainable environmentally friendly production process, and/or a positive biodegradability assessment. While the state of the art builders used in detergent formulations, such as sodium tripolyphosphate (STPP) and nitrilo triacetic acid (NTA), do not require a co-granulation or coating process, the hygroscopic, dusty, and sticky properties of solid GLDA will make co-granulation or coating highly desirable.

It may be noted that documents like WO 2006/002954, WO 2006/003434, and GB 241 5695 describe particles of other chelating agents than GLDA, such as of a methylglycine N,N-diacetic acid (MGDA) matrix encapsulated with polymeric materials such as polyethylene glycol and polyvinyl pyrrolidone. However, not only do these documents not relate to coated particles of GLDA, also no disclosure or suggestion is made of coating the chelating agent with a specific combination of coating materials. Additionally, unless very high levels of coating material are used, matrix encapsulation at best gives a partial coating layer but is known not to result in a closed coating layer.

Plain mixtures of chelating agent and additives are known in the art. Such mixtures are disclosed for example in EP 884 381, which document discloses a mixture of GLDA, an anionic surfactant, a salt of a polymer comprising carboxylic acid units and a crystalline aluminosilicate in specific proportions. EP 1803801 discloses a mixture of GLDA with at least one polyethylene glycol, a nonionic surfactant, polyvinyl alcohol, polyvinyl pyrrolidone, polyalkylene glycols or derivatives thereof. However, mixing the chelating agent and the other additives will hardly have any beneficial effect in reducing the hygroscopic behaviour of the chelating agent.

The object of the invention is to provide stable coated particles of GLDA of which the hygroscopic properties are improved but also wherein GLDA is obtained in a free-flowing form so that it can be added to dry compositions and formulations that are in a powdery form. Another object of the present invention is to provide a process to make coated particles of GLDA wherein a closed layer of coating is obtained while avoiding the use of very high levels of coating material. In addition, another object is to provide stable coated particles of other materials that are sensitive to moisture that are relatively cheap to prepare..

It has now been found that when a specific combination of materials is used as a coating, a coated particle of GLDA is acquired of which the hygroscopic properties are further improved compared to using a single material wherein the ingredients are not too expensive and wherein a preparation process is used that is relatively straightforward.

It should be noted that hygroscopicity comprises two different elements, namely a time dependent element and an amount dependent element, so a hygroscopicity improvement may be both a delay in the speed/rate with which water is taken up by a material as well as a reduction of the amount of water that will be taken up by a material

The present invention now provides coated particles containing a particle and a coating, wherein the particle contains glutamic acid N,N-diacetic acid or a partial salt thereof of the formula  $H_nY_m\text{-GLDA}$ , wherein Y is a cation that is sodium, potassium or a mixture thereof,  $n+m = 4$ , and the coating comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.

The invention further provides a process to make the above coated particles containing a particle and a coating, wherein the particle contains glutamic acid N,N-diacetic acid or a partial salt thereof of the formula  $H_nY_m\text{-GLDA}$ , wherein Y is a cation that is sodium, potassium or a mixture thereof,  $n+m = 4$ , and the coating comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide, comprising the steps of mixing the at least one vinyl alcohol (co)polymer and polysaccharide to give a coating mixture and subsequently applying the coating mixture on the particles or applying the vinyl alcohol (co)polymer and the polysaccharide at least partly one after the other on the particles to give one combined coating layer.

Moreover, the invention provides the use of the coated particles in detergents, agriculture, in oil field applications, in water treatment. Preferably, the particles are used in institutional and industrial cleaning compositions or household cleaning compositions.

Finally, the invention provides a method to reduce the hygroscopicity of materials by applying a coating thereon that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide, a method to reduce the water uptake of materials by applying a coating thereon that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide, a method to improve the flow properties of materials by applying a coating thereon that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide, and a method to improve the chemical and/or physical stability of materials by

applying a coating thereon that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide, and to coated particles obtainable by any of these processes.

The above methods of the invention provide suitable ways to treat any and all material of which the hygroscopicity, flowability, water uptake or stability (often due to water sensitivity) is considered subject to improvement, wherein such material may be a single compound or a mixture of compounds. Such materials include water-sensitive compounds from the group of bleaching agents, such as percarbonates, peroxides, hypochlorites; organic molecules, such as peptides, proteins, polynucleotides; reaction initiators; catalysts; paint components, such as dyes; medicines; and pharmaceutical preparations or components.

The coating surrounding the GLDA chelating agent or other water-sensitive material is such that it will act to sufficiently delay the core material/chelating agent from absorbing moisture, thereby reducing the rate of particles sticking together or forming a solid mass. At the same time the coating layer is sufficiently readily water-soluble to release the core material/chelating agent sufficiently rapidly in a final application wherein this is desired, this in addition without leaving a measurable amount of coating residue on the particles. Consequently, the invention provides an excellent balance between the barrier properties and the dissolution properties of the coating. Also, it was found that the coating of the invention has an improved adherence to the core and therefore the coated particles of the invention have good segregation and attrition resistance. Further, the particle once formulated will provide a stable particle size that will not change during storage or transportation (which is one element of physical stability). Further, the core material/chelating agent in the (structured) particles can be protected from the effects of UV rays, moisture, and oxygen and is therefore chemically stable. Chemical reactions between incompatible species of particles can be prevented due to the coating and the particles exhibit greatly improved storage, handling, and manufacturing

properties. The flow properties thereof are improved which basically means that the material remains free flowing for a prolonged period compared to the uncoated core material/chelating agent. Finally, the coated particles of the invention have a favourable ratio of ingredients that are active in their intended use on total ingredients.

The term "coated particles" as used throughout this application is meant to denote all particles (e.g. powder or granules) containing core material/GLDA ("the particle" or "the core") which have been encapsulated, coated, matrix coated, or matrix encapsulated, with at least one other material ("the coating"), as a consequence of which the particles have other physical characteristics than the chelating agent without this coating. Coated particles, unlike plain mixtures, have more coating material on the outer side of the coated particle and more core material on the inner side of the coated particle. Preferably, the coating is a closed layer as established by scanning electron microscopy/EDX, which is always the case if the coating is used in an amount of at least about 30 wt% when a matrix encapsulation process is used and, if the process is a fluidized bed encapsulation process, when at least 5 wt% of coating mixture is applied on the basis of the total particle. The particles can for instance have a modified colour, shape, volume, apparent density, reactivity, durability, pressure sensitivity, heat sensitivity, and photosensitivity compared to the original chelating agent. To be more specific, the coating layer serves to improve the storage stability of the granule and to preserve flowability. This is achieved as the coating layer reduces or delays the absorption of water, i.e. reduces the hygroscopicity.

Preferably, in the process to prepare coated particles in accordance with the invention, the GLDA-containing particle is in substantially dry form, wherein substantially dry means that the GLDA-containing particle has a water content of below 10 wt%, preferably of below 6 wt%, on the basis of (total) solids.

Coated particles of the invention may take several different forms depending on the processing conditions and the choice of materials.

Referring to the Figures, they provide an illustration of several particles as further described below.

Figures 1A-B depict state of the art particles that are not coated.

Figure 1A depicts schematically two different median particle sizes for a dried chelating agent. For example, 5-50  $\mu\text{m}$  particles can be made (e.g. by spray drying) or 50-500  $\mu\text{m}$  particles can be made (e.g. by fluid bed agglomeration). Figure 1B depicts schematically that when a structuring agent is used to provide more robust granules, the maximum size of the granules created (e.g. by fluid bed granulation) can be increased to 3,000  $\mu\text{m}$ .

Figures 2A-C depict coated particles of this invention.

Figure 2A depicts the particles of this invention, where small (5-50  $\mu\text{m}$ ) particles are coated in a continuous matrix of coating polymer and the matrix encapsulation coating is acquired by spray drying with a high amount of coating polymer. Figure 2B depicts a particle of this invention in which a set of larger chelating agent granules (or structured chelating agent granules) are coated with a thin layer of coating polymer. Figure 2C e.g. depicts the coating of a large-structured granule in which an exterior polymer coating is created around an inner structured core.

In a preferred embodiment of the invention, when making a cross-section of the coated particles they contain more than 50% of core material in the inner 50% (on the basis of the diameter) of the cross-section (which is roughly the case in the particle of Figure 2A), more preferably more than 80% (which is roughly the case in Figure 2B), and most preferably more than 90% (which is the case in Figure 2C).

It is known to those skilled in the art that the application of the coating material controls the particle design as e.g. shown in Figure 2, and that thus the method

to apply the coating material can lead to different particles. Each particle can exhibit the improved qualities of the current invention and will exhibit a number of different advantages. For instance, the particle depicted schematically by Figure 2C will, due to the large particle size, need the lowest amount of coating to achieve a closed layer of coating material. This particle, however, may require the use of a structuring agent to provide a robust inner structured particle. However, in cases where little structuring material is desired, a particle more similar to Figure 2A may be created.

This invention also covers the use of the coated particles in detergents, agriculture, in oil field applications, in water treatment, and other applications that require or benefit from the multiple benefits provided by this invention, i.e. the dissolution of crystals/scale, the sequestration of metal ions which can otherwise lead to precipitation, and the inhibition of scale growth. One preferred embodiment of this invention is the use of the coated particles in automatic dishwashing. Another preferred embodiment of this invention is the use of the particles in oil well completion and production operations.

Preferably, the vinyl alcohol (co)polymer has a melting point of more than 100°C. The melting point is preferably below 300 °C.

The vinyl alcohol (co)polymer preferably has a Hoppler viscosity as 4% aqueous solution of 1 to 100 mPas.

The vinyl alcohol (co)polymer suitable as coating is often a synthetically prepared polymer. The vinyl alcohol (co)polymer may be synthetically modified and besides vinyl alcohol and vinyl acetate monomers may contain other ethylenically unsaturated monomers.

The vinyl alcohol (co)polymer suitable as coating can be chosen from the group of (partially) hydrolyzed polyvinylacetates, (partially) hydrolyzed polyethylene-vinylacetates, or mixtures thereof.

The partially hydrolyzed vinyl alcohol (co)polymers and their derivatives can be modified for instance with amino groups, carboxylic acid groups and/or alkyl groups, and can have a degree of hydrolysis of preferably about 70 to 100 mol.%, in particular of about 80 to 99 mol.%, and a Hoppler viscosity in 4% aqueous solution of preferably 1 to 100 mPas, in particular of about 3 to 50 mPas (measured at **20°C** in accordance with DIN 53015). Other copolymerizates include styrene-maleic acid and/or vinyl ether-maleic acid copolymerizates. Quite especially preferred are in particular partially saponified, optionally modified, polyvinyl alcohols with a degree of hydrolysis of 80 to 99 mol.% and a Hoppler viscosity as 4% aqueous solution of 3 to 30 mPas.

Suitable polysaccharides are biopolymers and their derivatives like cold water-soluble polysaccharides and polysaccharide ethers, such as for instance cellulose ethers, starch ethers (amylose and/or amylopectin and/or their derivatives), guar ethers, dextrans and/or alginates. Also synthetic polysaccharides such as anionic, nonionic or cationic heteropolysaccharides can be used, in particular xanthan gum, welan gum and/or diutan gum. The polysaccharides can be, but do not have to be, chemically modified, for instance with carboxymethyl, carboxyethyl, hydroxyethyl, hydroxypropyl, methyl, ethyl, propyl, sulfate, phosphate and/or long-chain alkyl groups. Preferred usable peptides and/or proteins are for instance gelatine, casein and/or soy protein. Quite especially preferred biopolymers are dextrans, starches, starch ethers, casein, soy protein, gelatine, hydroxyalkyl-cellulose and/or alkyl-hydroxyalkyl-cellulose, wherein the alkyl group may be the same or different and preferably is a **C<sub>1</sub>**- to **C<sub>6</sub>**-group, in particular a methyl, ethyl, n-propyl- and/or i-propyl group.

The polysaccharide preferably is a gum like Arabic gum or xanthan gum or a cellulose ether like carboxymethylcellulose, even more preferably it is Arabic gum or carboxymethylcellulose.

The coating layer comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide, wherein the weight% of polysaccharide in the coating on dry basis in one embodiment is more than 0 but less than 50 wt%, preferably between 0.5 and 20 wt%, more preferably between 2 and 15 wt%, and most preferably between 3 and 12 wt%, and wherein the weight% of vinyl alcohol (co)polymer in the coating on dry basis in one embodiment is less than 100 but more than 50 wt%, preferably between 80 and 99.5 wt%, more preferably between 85 and 98 wt%, and most preferably between 88 and 97 wt%.

Additionally, it should be understood that the coated particles of the invention may contain other components besides the at least one polysaccharide and vinyl alcohol (co)polymer component in the coating, like for example a low amount (i.e. less than 30 wt%, preferably less than 20 wt%, more preferably less than 10 wt% on total coating) of another water-soluble polymer. Besides the embodiments wherein the coating contains other ingredients, it is also envisaged that the coating may contain two or more polysaccharides and/or two or more vinyl alcohol (co)polymers.

In addition, the coating may be applied in two or more coating layers that may be the same or different in their composition, though it is preferred to apply a mixture of vinyl alcohol (co)polymer and polysaccharide to give one coating layer comprising both ingredients.

When using two or more coating layers, one embodiment may have the polysaccharide in one layer and the vinyl alcohol (co)polymer in another layer. In such event it is preferred to have (more of) the polysaccharide in a layer

closer to the core than the vinyl alcohol (co)polymer and most preferred to have (more of) the vinyl alcohol (co)polymer in the outer layer applied on the particle.

In another embodiment in which two or more coating layers are applied it is possible to have both the polysaccharide and the vinyl alcohol (co)polymer in the same layer. In such event the outer layer of the coating preferably comprises the at least one vinyl alcohol (co)polymer and the polysaccharide.

When the coating is made of more than one layer, in yet another embodiment one of the coating layers, preferably the inner coating, may contain a compound that is functional in the end application of the particle (i.e. "functional additives"). When the end application is in a detergent composition, the inner coating more preferably contains a scale inhibitor or another building compound/chelating agent (citrate, MGDA), a pH buffer (sodium carbonate or silicate) or a hydrophobic polymer. Another preferred embodiment is one wherein an inner coating contains a salt and an outer coating comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.

In a more preferred embodiment where the coated particle will be used in a detergent composition, the inner coating layer comprises a salt that is functional in the detergent composition such as sodium carbonate, sodium citrate or sodium silicate. In an even more preferred embodiment, to give the inner coating salt layer an improved strength, the inner coating in addition contains a water-soluble polymer, a polysaccharide or a scale-inhibiting polymer.

In yet another embodiment an additional outer layer may be applied on the coated particles, which may comprise a flowing aid such as fumed silica.

It should be understood that in one embodiment the coated particles of the invention in addition to GLDA may contain another chelating agent, such as for example methylglycine N,N-diacetic acid (MGDA), ethylenediamine N,N,N',N'-

tetraacetic acid (EDTA), N-hydroxyethyl ethylenediamine N,N',N'-triacetic acid (HEDTA), diethylenetriamine penta acetic acid (DTPA), or a salt of any of these agents. This further chelating agent may be present in the core or in the coating.

In one embodiment the particle (core) of the invention may comprise further functional additives that can be chosen from the group of scale-inhibiting additives, structurants, (co)builders, and pH buffers.

Preferably, if a further additive is present in the core, the core will contain a (co)builder as a further additive. In a more preferred embodiment of the present invention, the core is structured with a suitable structurant. Accordingly, the particles of the invention may optionally comprise structurants which improve the physical strength of the particle.

The (co)builder can include several salts and/or inorganic additives which contribute to the strength of the resulting particles and which also function as sequestration materials or as builders. The building salts found to be functional as a structurant for the chelating agents are citrate, carbonate, silicate, and sulfate salts. Preferably, the sodium salts of materials are used. Of these salts, sodium carbonate, sodium citrate, and sodium silicate are preferred due to their functionality (e.g. as a scale-inhibiting additive). Alternatively, inorganic (nano-) particles, such as silica can be used.

In another embodiment the coating layer(s) may comprise further functional additives that can be chosen from the group of scale-inhibiting additives, structurants, (co)builders, nanoparticles, and pH buffers.

Examples of functional additives are salts like citrate, silicate, glycolate, oxalate, lactate, succinate, malonate, maleate, diglycolate, fumarate, stearate, chloride, nitrate, percarbonate or carbonate salt, such as the alkali metal salt of any of

these, that besides their above-indicated functionality have a pH buffering effect as well, chelating agents or scale-inhibiting polymers. Scale-inhibiting polymers can have a variety of chemical forms and are specifically selected from synthetic, natural, and hybrid scale-inhibiting polymers. The synthetic polymer includes selected levels of carboxylation, sulfonation, phosphorylation, and hydrophobicity to give good film forming and humidity resistance as well as good co-building and crystal growth inhibition properties. The natural polymers are likewise prepared with a combination of molecular weight modification, carboxylation, sulfonation, phosphorylation, and hydrophobic properties to give good co-building and crystal growth inhibition properties. The hybrid polymers combine natural and synthetic monomers and polymers to give good co-building and crystal growth inhibition properties.

The advantage of using scale-inhibiting polymers and/or salts as an additive is that these materials can be or are already used as co-builder or pH buffer in most detergent formulations and will therefore have a beneficial effect during the wash. Therefore, the current invention gives a superior product which provides other benefits such as co-builder or crystal growth inhibition. Also, such particles of the present invention have excellent flow properties.

The (structured) particles have many useful functions and can be employed in many different areas, frequently connected with applications in which the chelating agent contents of the particle have to be released into the surrounding environment under controlled conditions.

The amount of GLDA in the coated particle in an embodiment is at least 30 wt%, more preferably at least 50 wt %, even more preferably at least 60 wt%, most preferably at least 90 wt%, and up to 95 wt% on basis of the total weight of the particle.

The coated particles of the invention in one embodiment contain 15 to 95 wt% of the GLDA and optionally other chelating agents, 5 to 85 wt% of the coating, and 0 to 40 wt% of further additives. In a preferred embodiment, they contain 30 to 95 wt% of the GLDA and optionally other chelating agents, 5 to 50 wt% of the coating, and 0 to 20 wt% of further additives. Most preferably, the coated particles contain 60-95 wt% of GLDA and optionally other chelating agents, 5 to 20 wt% of the coating and 0 to 20 wt% of further additives, the total amounts of ingredients adding up to 100 wt%.

Preferably, the particle comprises  $H_nY_m$ -GLDA, wherein  $m$  is at least 1 and  $n$  is at most 3. However, particles wherein the values of  $m$  and  $n$  are different can also be used. In such event other components in the particle or in the coating may exchange protons with the GLDA (i.e. accept therefrom or provide thereto), ensuring that effectively the desired number of hydrogen atoms are exchangeably available per GLDA anion. In a more preferred embodiment of the invention  $m$  is 1.5 - 3.8, most preferably  $m$  is 2.5 - 3.6.

The particles of the invention in one embodiment have a particle size of 200 to 2,000 microns ( $\mu m$ ), most preferably 500 - 1,000 microns.

The processes of the invention to prepare coated particles containing a particle and a coating, wherein in one embodiment the particle contains glutamic acid,  $N,N$ -diacetic acid or a partial salt thereof of the formula  $H_nY_m$ -GLDA, wherein  $Y$  is a cation selected from the group of sodium, potassium, and mixtures thereof,  $n+m = 4$ , and in another embodiment the particle contains materials of which the hygroscopicity, water uptake, stability and/or flow properties are subject to improvement, and wherein the coating layer contains at least one vinyl alcohol (co)polymer and at least one polysaccharide comprises the steps of mixing the at least one vinyl alcohol (co)polymer and the polysaccharide to give a coating mixture and subsequently applying the coating mixture on the particles or

applying the vinyl alcohol (co)polymer and the polysaccharide at least partly one after the other on the particles to give one combined coating layer.

In one embodiment the process involves a step preceding applying the coating mixture or the vinyl alcohol (co)polymer and the polysaccharide at least partly one after the other on the particle, wherein a salt layer is applied on the particle, preferably a citrate, silicate, glycolate, oxalate, lactate, succinate, malonate, maleate, diglycolate, fumarate, stearate, chloride, nitrate, percarbonate or carbonate salt.

Suitable processes to apply the coating on the particle in accordance with the process of the invention are for example disclosed in the *Kirk Othmer Encyclopedia of Chemical Technology, Vol 16, Microencapsulation* pages 438 - 463 by C.Thies; John Wiley & Sons Inc. 2001 )) and include but are not limited to the following processes:

"Fluidized-bed encapsulation technology which involves spraying shell material in solution or hot melt form onto solid particles suspended in a stream of heated gas, usually air. Although several types of fluidized-bed units exist, so-called top and bottom spray units are used most often to produce microcapsules.

In top-spray units, hot melt shell materials are sprayed onto the top of a fluidized-bed of solid particles. The coated particles are subsequently cooled producing particles with a solid shell. This technology is used to prepare a variety of encapsulated ingredients. In bottom-spray or Wurster units the coating material is sprayed as a solution into the bottom of a column of fluidized particles. The freshly coated particles are carried away from the nozzle by the airstream and up into the coating chamber where the coating solidifies due to evaporation of solvent. At the top of the column or spout, the particles settle. They ultimately fall back to the bottom of the chamber where they are guided once again by the airstream past the spray nozzle and up into the coating chamber. The cycle is repeated until a desired capsule shell thickness has been

reached. Coating uniformity and final coated particle size are strongly influenced by the nozzle(s) used to apply the coating formulation. This technology is routinely used to encapsulate solids, especially pharmaceuticals (qv). It can coat a wide variety of particles, including irregularly shaped particles. The technology generally produces capsules >100 - 150 micrometer, but can produce coated particles <100 micrometer."

In yet another example of a coating process, the coated particles are prepared by spraying the coating onto the particle using a fluid bed coating process as for example described by E. Teunou, D. Poncelet, "Batch and continuous fluid bed coating review and state of the art," *J. Food Eng.* 53 (2002), 325 - 340. In the conventional fluidized bed process, the fluidized bed is a tank with a porous bottom plate. The plenum below the porous plate supplies low pressure air uniformly across the plate leading to fluidization. The process comprises the following steps:

- (a) a compound to be encapsulated in the form of a powder is fluidized with air at an air inlet temperature below the melting temperature of the powder;
- (b) a coating liquid comprising a water based coating solution is sprayed onto the powder via a nozzle, followed by subsequent evaporation of the water by using elevated temperatures in the fluid bed. This leaves behind a coating layer on the particles with the compound in the core.

The process of the present invention may involve a preceding step of preparing the particle (containing GLDA) on which in a subsequent step the coating mixture is applied.

The particle can be made by drying a solution of the core material/GLDA and the optional further additives.

Drying the solution can be done by any drying method known to the person skilled in the art, like evaporating off the water via e.g. spray drying, fluid bed spray drying, fluid bed granulation.

The dry material may optionally be further processed, for example by compacting and/or crushing the material until it has the desired shape, i.e. is in the form of core particles of the desired size.

The step of compacting includes any method wherein the particles are agglomerated by applying an external force on them, for instance by extruding, tableting or agglomerating them under a pressure of suitably from 40 to 200 MPa, preferably a pressure of from 50 to 120 MPa, most preferably of from 75 to 100 MPa.

The pressure used for compacting the material is the pressure applied at uniaxial compaction of a tablet (leading to a certain density of the compacted particle mixture). However, compacting may suitably be done by other compactors, like a roll compactor. In such cases, the pressure to be used is the pressure that results in the same density of the compact as in uniaxial compaction.

The step of crushing includes any method whereby the size of the particles is decreased and is intended to include methods like breaking, crushing, or milling.

In another more preferred embodiment of the process of the invention the coating mixture layer is applied on the material containing the chelating agent at a pH of 2 - 11, more preferably 5 - 10, most preferably 7 - 10.

In a preferred embodiment of the invention the process to prepare the coated particles encompasses the preparation of a granule that is subsequently coated in a fluid bed coating process. The granule preparation is started by dissolving the chelating agent in water together with the coating material and if required a

structurant. This mixture is sprayed into a hot spray drying chamber leading to the evaporation of water. The particles formed this way are recirculated in the spray chamber and at the same time spraying the water based mixture into the chamber is continued, due to which the particle grows and a granule is gradually formed. The composition gradient inside the granule can be modified by altering the composition of the spray mix while spraying it into the drying chamber. This means that the core of the particle can be higher in concentration of the compound, whereas the outer part of the particle is enriched with the coating material. The particle formed is described as a co-granule as it consists of the compound, the coating material, and, if required, a structurant. The obtained co-granule is subsequently coated in a fluid bed process. In this process, a powder is fluidized with warm air and a water based coating solution is sprayed onto the powder. The water is evaporated, leaving a coating on the particle surface. The amount of coating can be controlled easily by manipulating the spray on time and spray mix composition. To control the coating quality, it may be necessary to increase the temperature of the coating solution (i.e. spray mix). This will lower the spray mix viscosity, most likely leading to a better atomization and droplet formation which gives a better distribution of the coating material on the granule.

## **EXAMPLES**

### **Processes used**

#### ***Manufacture of GLDA (co-)granule/ Materials used***

Co-granules of GLDA and Alcoguard 4160 were produced in a spray granulation process. The co-granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S available from Akzo Nobel Functional Chemicals LLC, Chicago, IL, USA) and the anti-scaling polymer Alcoguard 4160 (available as a dissolved polymer solution or in dry form from AkzoNobel Surface Chemistry LLC, Chicago, IL, USA).

To produce the co-granule, GL47S and GL-Na-36S (mixed in a weight ratio of 95:5%) were mixed with Alcoguard 4160 (also abbreviated as "4160"), where the ratio of the total amounts of GLDA and Alcoguard 4160 was 80:20 in weight. This mixture was sprayed into a hot spray drying chamber, leading to the evaporation of water. The particles formed this way were recirculated into the spray chamber via cyclones and at the same time spraying the water based GLDA/4160 mixture into the chamber was continued, due to which the particle grew and a granule was gradually formed. More specifically, the mixture of GLDA and 4160 was continuously sprayed into a fluid bed spray granulator type AGT, equipped with cyclones, an external filter unit, and a scrubber. During the spray granulation process, the air flow was kept between 700 - 1,300 m<sup>3</sup>/hour and air inlet temperatures between 100 and 250°C were used. The particle formed is described as a co-granule, as it consisted of GLDA and the anti-scaling polymer. This process resulted in a free flowing powder, described as "uncoated" co-granule.

To produce the GLDA-pure granule, the same process as described for the co-granule was used, except that in this case the spray mix consisted of GL-47-S and GL-Na-36S mixed in a ratio of 85:15 wt%, hence no anti-scaling polymer was used in the particle preparation.

### ***Manufacture of coated particles***

The "uncoated" GLDA/4160 co-granule or GLDA-pure granule was subsequently coated in a fluid bed (GEA Aeromatic Strea-1) using a Wurster set-up and a two-fluid nozzle. The Wurster set-up is a draft tube positioned in the centre of the fluid bed, below which a nozzle is positioned that sprays fine droplets upwards into the tube. These droplets hit the granule surface and after drying leave behind some dry coating material. Using this set-up an even coating can be applied. The air inlet temperature used was 80 - 90°C. The air flow was chosen such that visually an even fluidization was obtained, which

implies a setting between 10 and 80% of the maximum air flow on the GEA Aeromatic Strea-1. The spray-on rate of the coating solution was chosen such that an even coating was obtained on the particles giving no particle aggregation (i.e. about 0.5 - 1 gram/minute), resulting in a particle coated with an even coating layer. Coating was continued until a predefined amount of coating was obtained on the particles.

For some coated particles, a Glatt laboratory fluid bed was used. In this equipment the air inlet temperatures were varied between 80 °C and 150°C and where not specified in below Examples a temperature of about 100°C was used. Spraying of the liquid was done via top spray using a twin fluid air assisted nozzle. Again, the spray rate was chosen such that aggregation was avoided and an even coating was obtained.

## **Test methods**

### ***Moisture absorption***

The resulting powders were poured in a 1-particle thick layer onto a petri dish and stored in a climate chamber operated at 16°C and 60% Relative Humidity. The weight increase as a function of time was measured, as a measure for the rate of absorption of moisture. The weight increase was recomputed into a % weight increase by using the following formula:

Weight % increase at time t = [Weight (at t = 0) - Weight (at time t)]/[Weight (at t= 0)].

### ***Flowability of the powder***

The flowability of a powder was determined by manually moving the petri dish stored in the climate chamber and visually estimating the number fraction of particles that did not stick to the dish but moved freely. Hence a flowability figure (%ff) of 100% means that all particles moved freely, a figure of 0% means

that all particles were sticking completely to the dish. Flowability is considered to be acceptable when at least about 90% of the particles move freely.

### ***Melting temperature of polyvinyl alcohol***

Of three polyvinyl alcohol types the melting temperature was measured using a Differential Scanning Calorimeter (make Mettler Toledo). The three types tested were Mowiol 3-85, Mowiol 4-88 (both ex Kuraray Europe GmbH), and Elvanol 71-30 (ex DuPont). The powders were used as such. All three types showed similar results, with a glass transition temperature between 38 and 45°C and a melting temperature between about 160 and 190°C.

### **Example 1 Effect of adding gum to the polyvinyl alcohol**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), Arabic gum (laboratory grade, ex Acros Organics), anti-scaling polymer Alcoguard 4160, and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First a co-granule of GLDA and Alcoguard 4160 was produced in a spray granulation process using the process as described above. The "uncoated" GLDA/4160 co-granule was subsequently coated with mixtures of Mowiol 3-85 and Arabic gum in a fluid bed (GEA Aeromatic Strea-1). The Mowiol 3-85 was dissolved in water to give a 16 wt% solution and Arabic gum powder was added, with the Mowiol/gum ratio being varied. The levels of Arabic gum (based on Mowiol 3-85 on dry basis) were: 0, 0.5, 2, 5, 10, 20, 50, and 100%. These mixtures were sprayed onto the GLDA co-granule in the fluid bed Aeromatic coater, until 10 wt% of the polyvinyl alcohol/Arabic gum mix was coated onto the co-granule.

The powders were stored at 16°C, 60% RH in a climate chamber and the moisture absorption was determined. From these curves, the time to reach a

weight increase of 10wt% was determined. The time to reach 10 wt% as a function of the level of Arabic gum is given below in Table 1 and is graphically shown in Figure 3.

Table 1 Time to reach 10wt% increase for coated co-granule

| Arabic gum wt%<br>in Mowiol/Arabic<br>gum coating [%] | Time to reach 10wt%<br>for 10% total coating<br>level [hours] |
|-------------------------------------------------------|---------------------------------------------------------------|
| Uncoated                                              | 0.9                                                           |
| 0.0 (i.e. PVOH<br>only)                               | 11                                                            |
| 0.5                                                   | 28.5                                                          |
| 2                                                     | 38                                                            |
| 5.0                                                   | 41.5                                                          |
| 10                                                    | 52                                                            |
| 20                                                    | 34                                                            |
| 50.0                                                  | 19                                                            |
| 100.0 (i.e. gum<br>only)                              | 2                                                             |

Table 1 and Figure 3 show that the Arabic gum has a synergistic effect on the Mowiol coating. By adding an optimal amount of gum to the polyvinyl alcohol the moisture barrier properties are significantly improved, with an optimum value being found. Figure 3 shows that a preferred level for Arabic gum in the coating layer is about 10% (based on polyvinyl alcohol on dry basis).

### **Example 2 Effect of adding CMC to the polyvinyl alcohol**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), anti-scaling polymer Alcoguard 4160, carboxy methyl cellulose (CMC) AF0305 (ex AkzoNobel Cellulosic Specialties), and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First a co-granule of GLDA and Alcoguard 4160 was produced in a spray granulation process using the process as described above. The "uncoated"

GLDA/41 60 co-granule was subsequently coated with mixtures of Mowiol 3-85 and CMC in a fluid bed (GEA Aeromatic Strea-1). The Mowiol 3-85 was dissolved in water and a pre-made CMC solution powder was added, with the Mowiol/CMC ratio being varied. The levels of CMC AF0305 (based on Mowiol 3-85 on dry basis) were: 0, 1, 2, 5, 7, 10, and 50%. These mixtures were sprayed onto the GLDA co-granule in the fluid bed Aeromatic coater, until 10wt% of the polyvinyl alcohol/CMC mix was coated onto the co-granule.

The powders were stored at 16°C, 60% RH in a climate chamber and the moisture absorption was determined. From these curves, the time to reach a weight increase of 5wt% was determined. The time to reach 5 wt% as a function of the level of CMC AF0305 is given below in Table 2 and is graphically shown in Figure 4.

Table 2 Time to reach 5wt% increase in moisture absorption

| Time to reach 5% weight increase |            |
|----------------------------------|------------|
| CMC AF0305 %                     | Time [hrs] |
| 0 (i.e. PVOH only)               | 4.8        |
| 1                                | 18.6       |
| 2                                | 18.6       |
| 5                                | 27         |
| 7                                | 14.2       |
| 10                               | 11         |
| 50                               | 4.8        |

Figure 4 and Table 2 show that the CMC has a synergistic effect on the Mowiol coating. By adding CMC to the polyvinyl alcohol the moisture barrier properties are significantly improved. Figure 4 shows that a preferred level for CMC in the coating layer is about 5wt% (based on polyvinyl alcohol on dry basis).

**Example 3 Effect of other polysaccharides in polyvinyl alcohol coating**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), anti-scaling polymer Alcoguard 4160, the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH) and various polysaccharides. The following polysaccharides were selected:

- Potato starch (laboratory grade ex J.T. Baker)
- Carboxy methyl cellulose (CMC) Akucell AF0305 (ex AkzoNobel Cellulosic Specialties)
- Carboxy methyl cellulose (CMC) Akucell AF2875W (ex AkzoNobel Cellulosic Specialties)
- Gelatine from bovine skin Type B, with a Bloom value of 225 (laboratory grade, ex Sigma Aldrich)
- Gelatine from bovine skin Type B, with a Bloom value of 75 (laboratory grade, ex Sigma Aldrich)
- KUW L-Arabic gum (ex IMCD Deutschland GmbH & Co., KG)
- Arabic gum (laboratory grade, ex Acros Organics)

First a co-granule of GLDA and Alcoguard 4160 was produced in a spray granulation process using the process as described above. The "uncoated" GLDA/4160 co-granule was subsequently coated with mixtures of Mowiol 3-85 and a polysaccharide selected from the list above in a fluid bed (GEA Aeromatic Strea-1). The Mowiol 3-85 was dissolved in water and the polysaccharide powder was added, with the Mowiol/polysaccharide ratio being set at 98:2 or 90:10. These mixtures were sprayed onto the GLDA co-granule in the fluid bed Aeromatic coater, until 10wt% of the polyvinyl alcohol (PVOH)/polysaccharide mix was coated onto the co-granule.

The powders were stored at 16°C, 60% RH in a climate chamber and the moisture absorption was determined. From these curves, the time to reach a weight increase of 5 wt% was determined. The table below gives the time to

reach 5 wt% increase for the various PVOH/polysaccharide combinations. This table shows that all polysaccharides give improved moisture barrier properties of the coating when compared to the Mowiol 3-85 only coating. Below, Table 3 shows that polysaccharides have a positive synergistic effect on the barrier properties for polyvinyl alcohol.

| <b><i>GLDA/4160 co-granule coated with:</i></b> | <b>Time to reach 5 wt% increase [hours]</b> |
|-------------------------------------------------|---------------------------------------------|
| 10% Mowiol 3-85                                 | <b>4.8</b>                                  |
| 10% Mowiol 3-85/Potato starch [90:10]           | 8.4                                         |
| 10% Mowiol 3-85/Gelatine (Bloom 225) [90:10]    | 21                                          |
| 10% Mowiol 3-85/Gelatine (Bloom 75) [90:10]     | 12.1                                        |
| 10% Mowiol 3-85/L-Arabic gum [90:10]            | 34.5                                        |
| 10% Mowiol 3-85/Arabic gum [90:10]              | 27.5                                        |
| 10% Mowiol 3-85/CMC AF0305 [90:10]              | 11                                          |
| 10% Mowiol 3-85/CMC 2785W [90:10]               | 11.3                                        |

Table 3

#### **Comparative Example 4 Effect of adding Arabic gum to other water-soluble polymers**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), Arabic gum (laboratory grade, ex Acros Organics), anti-scaling polymer Alcoguard 4160, and the water-soluble polymers polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH), polyvinyl pyrrolidone PVP Luvitec VA64 (available from BASF), and polyethylene glycol PEG6000 (available as laboratory grade from Fluka).

First a co-granule of GLDA and Alcoguard 4160 was produced in a spray granulation process using the process as described above. The GLDA/4160 ratio in this case was 80:20. The "uncoated" GLDA/4160 co-granule was subsequently coated with in total 10wt% of a mixture containing polymer and Arabic gum in a ratio 90:10 in a fluid bed (GEA Aeromatic Strea-1). All polymers were dissolved in water to which the Arabic gum was added and dissolved and these mixtures were sprayed onto the GLDA co-granule in the fluid bed Aeromatic coater, until 10 wt% of that mixture was coated onto the co-granule.

The powders were stored at 16°C, 60% RH in a climate chamber and the moisture absorption was determined. The results are shown below in Table 4 and Figure 5 and the results for the PVP and PEG6000 alone are also given.

Table 4 moisture uptake and flowability for GLDA/4160 co-granules coated with 10 wt% of the two polymers, with and without Arabic gum, and stored at 16°C, 60% RH.

| <b>GLDA/4160 [80:20] co-granule coated with 10 wt% of</b> |                                 |                                                    |                              |                                       |
|-----------------------------------------------------------|---------------------------------|----------------------------------------------------|------------------------------|---------------------------------------|
|                                                           | <b>PVP<br/>Luvitec<br/>VA64</b> | <b>PVP Luvitec<br/>VA64/Arabic<br/>gum [90:10]</b> |                              | <b>PEG6000/Arabic<br/>gum [90:10]</b> |
| <b>dT [hrs]</b>                                           | <b>wt% water</b>                | <b>wt% water</b>                                   | <b>PEG6000<br/>wt% water</b> | <b>wt% water</b>                      |
| 0.0                                                       | 0.00                            | 0.00                                               | 0.00                         | 0.00                                  |
| 1.0                                                       | 5.12                            | 5.31                                               | 3.67                         | 4.25                                  |
| 3.5                                                       | 15.73                           | 16.67                                              | 11.50                        | 14.06                                 |
| 5.5                                                       | 21.92                           | 23.37                                              | 16.21                        | 19.76                                 |
| 22.5                                                      | 40.85                           | 42.20                                              | 33.61                        | 36.89                                 |

Table 4 and Figure 5 show that the Arabic gum addition has no significant positive effect on improving the moisture barrier properties for PVP and PEG6000. For the PEG6000 if anything, it has even a negative effect.

**Example 5 Citrate with Arabic gum and level of Mowiol needed for flowability of co-granules**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), anti-scaling polymer Alcoguard 4160, the functional salt tri-sodium citrate (laboratory grade, ex Fisher Scientific), Arabic gum (laboratory grade, ex Acros Organics), and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First co-granules of GLDA and Alcoguard 4160 were produced in a spray granulation process using the same process as described before. The "uncoated" GLDA/4160 co-granule was subsequently coated with a mixture of citrate and Arabic gum in a Glatt batch fluid bed. This was done using a solution in water with tri-sodium citrate and Arabic gum, where the ratio citrate/gum was about 99:1. This solution was coated onto the co-granules, using a top spray two-fluid nozzle, until about 10 wt% citrate/gum was coated onto the co-granule.

The co-granule coated with citrate was subsequently coated in the Glatt fluid bed coater with Mowiol 3-85/Arabic gum in a ratio 90:10wt%.

The results of the moisture absorption and flowability measurements are given below in Table 5 and Figure 6.

Table 5 Results of moisture absorption and flowability (%ff).

| Time<br>[hrs] | co-<br>granule<br>uncoated<br>wt%<br>water | Time<br>[hrs] | co-granule +<br>10% citrate/gum<br>[99:1] |     |  | co-granule +<br>10% citrate/gum<br>[99:1] + 5%<br>Mowiol3-85/gum<br>[90:10] |     | co-granule +<br>10% citrate/gum<br>[99:1] + 10%<br>Mowiol3-85/gum<br>[90:10] |     |
|---------------|--------------------------------------------|---------------|-------------------------------------------|-----|--|-----------------------------------------------------------------------------|-----|------------------------------------------------------------------------------|-----|
|               |                                            |               | wt% water                                 | %ff |  | wt% water                                                                   | %ff | wt% water                                                                    | %ff |
| 0.00          | 0.00                                       | 0.00          | 0.00                                      | 100 |  | 0.00                                                                        | 100 | 0.00                                                                         | 100 |
| 1.00          | 11.24                                      | 1.00          | 1.61                                      | 0   |  | 0.43                                                                        | 90  | 0.34                                                                         | 100 |
| 3.67          | 26.72                                      | 3.00          | 4.24                                      | 0   |  | 0.82                                                                        | 90  | 0.56                                                                         | 100 |
| 6.00          | 33.00                                      | 5.00          | 6.55                                      | 0   |  | 1.19                                                                        | 90  | 0.76                                                                         | 100 |
| 7.50          | 36.04                                      | 6.00          | 7.58                                      | 0   |  | 1.30                                                                        | 90  | 0.83                                                                         | 100 |
| 23.25         | 45.83                                      | 23.58         | 23.65                                     | 0   |  | 4.46                                                                        | 50  | 1.97                                                                         | 100 |
| 25.25         | 45.90                                      | 27.25         | 26.02                                     | 0   |  | 5.21                                                                        | 40  | 2.26                                                                         | 100 |
| 27.58         | 46.16                                      | 30.50         | 27.77                                     | 0   |  | 5.82                                                                        | 50  | 2.52                                                                         | 100 |
| 31.83         | 46.23                                      | 48            | 32.97                                     | 0   |  | 9.50                                                                        | 60  | 3.94                                                                         | 100 |
| 49.83         | 45.70                                      |               |                                           |     |  |                                                                             |     |                                                                              |     |

*Remark: the uncoated co-granule has a flowability of 0% within about 1 hour.*

Figure 6 and Table 5 show that using citrate/Arabic gum gives a significant reduction in moisture uptake. Figure 6 also shows that the more PVOH/gum is used, the slower the moisture absorption.

For the final powder the aim is to have a good flowability for a long period of time. Table 5 shows that citrate alone is insufficient to give a good flowability. When 5% PVOH/gum is used, a good improvement is found with a flowability up to 90% for the first 6 hours. An excellent flowability is found when 10% PVOH/gum is used as an additional coating. This suggests that ideally a final PVOH/gum coating of about 5 - 10 wt% is used.

#### **Example 6 Citrate with Arabic gum and level of Mowiol needed for flowability of GLDA pure granules**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), the functional salt tri-sodium citrate (laboratory grade, ex Fisher

Scientific), Arabic gum (laboratory grade, ex Acros Organics), and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First granules of GLDA were produced in a spray granulation process using the same process as described before. The "uncoated" GLDA granule was subsequently coated with a mixture of citrate and Arabic gum in a batch fluid bed (make Glatt). This was done using a solution in water with tri-sodium citrate and Arabic gum, where the ratio citrate/gum was about 99:1. This solution was coated onto the granules, using a top spray two-fluid nozzle, until about 10 wt% citrate/gum was coated onto the co-granule.

The GLDA granule coated with citrate was subsequently coated in the Glatt fluid bed coater with Mowiol 3-85/gum in a ratio of 90:10.

The results of the moisture absorption and flowability measurements are given below in Table 6 and Figure 7.

Table 6 Results for moisture absorption and flowability for GLDA granules coated with citrate /Arabic gum and Mowiol 3-85

| Time<br>[hrs] | 10% citrate/gum [99:1] |     | 10% citrate/gum [99:1] +<br>5% Mowiol/gum [90:10] |     | 10% citrate/gum [99:1] +<br>10% Mowiol/gum [90:10] |     |
|---------------|------------------------|-----|---------------------------------------------------|-----|----------------------------------------------------|-----|
|               | wt% water              | %ff | wt% water                                         | %ff | wt% water                                          | %ff |
| 0.00          | 0.00                   | 100 | 0.00                                              | 100 | 0.00                                               | 100 |
| 1.00          | 0.36                   | 0   | 0.32                                              | 100 | 0.36                                               | 100 |
| 3.00          |                        | 0   | 0.58                                              | 100 | 0.60                                               | 100 |
| 5.00          | 0.71                   | 0   | 0.69                                              | 100 | 0.73                                               | 100 |
| 6.00          | 0.85                   | 0   | 0.72                                              | 100 | 0.75                                               | 100 |
| 23.58         | 3.63                   | 0   | 1.36                                              | 90  | 1.20                                               | 100 |
| 27.25         | 4.47                   | 0   | 1.51                                              | 90  | 1.33                                               | 100 |
| 30.50         | 5.04                   | 0   | 1.71                                              | 95  | 1.44                                               | 100 |
| 48            | 8.32                   | 0   | 2.84                                              | 90  | 2.03                                               | 98  |

Table 6 and Figure 7 show that for the GLDA granule a citrate layer gives a reduction in moisture absorption (when compared to the uncoated GLDA granules as shown in Example 5), but that the flowability is subject to

improvement after just 1 hour of storage at 16°C, 60% Relative Humidity. Table 6 shows that for the GLDA granule pre-coated with citrate/gum, already 5% Mowiol/gum is sufficient to obtain an acceptable flowability for over 48 hours after storage at 16°C, 60% Relative Humidity. When the Mowiol/gum level is raised to 10 wt%, moisture absorption is further delayed and flowability is further improved.

### **Example 7 Functional salts as an intermediate coating layer**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), functional salts, Arabic gum (laboratory grade, ex Acros Organics) and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH). The salts used were selected based on their functionality in dishwashing applications and included tri-sodium citrate (laboratory grade, ex Fisher Scientific), sodium carbonate anhydrous (laboratory grade, ex J.T. Baker), and sodium silicate H265HP (ex PQ Europe, PQ Nederland bv).

First a granule of GLDA was produced in a spray granulation process using the process as described above. In this case, GL-47-S and GL-NA-36-S were mixed in a ratio of 85:15.

The "uncoated" GLDA granule was subsequently coated with the salts in a fluid bed (GEA Aeromatic Strea-1). The salts were dissolved in water and Arabic gum was added, such that the salt/gum ratio was about 99:1. This mixture was sprayed onto the GLDA granule in the fluid bed Aeromatic coater. After that an additional polyvinyl alcohol layer was coated on, using a 16 wt% solution of Mowiol 3-85 and gum, with the Mowiol/gum ratio being 90:10. The solutions were all coated onto the co-granules, using the Aeromatic Strea-1 fluid bed coater with a Wurster set-up and a two-fluid nozzle. The air inlet temperature used was 80°C.

The following compositions were prepared using aqueous solutions of the salts, Arabic gum, and Mowiol 3-85:

- A) GLDA granule coated with 15% citrate/gum [99:1] and 10% Mowiol/gum [90:10]
- B) GLDA granule coated with 15% Na<sub>2</sub>CO<sub>3</sub>/gum [99:1], subsequently with 10% citrate/gum [99:1], and finally with 10% Mowiol/gum [90:10]
- C) GLDA granule coated with 15% Na<sub>2</sub>CO<sub>3</sub>/gum [99:1] and subsequently with 10% Mowiol/gum [90:10]
- D) GLDA granule coated with a mixture of salts containing 15, 5, 5, and 0.6% Na<sub>2</sub>CO<sub>3</sub>/silicate/citrate/gum and subsequently with 10% Mowiol/gum [90:10]

The resulting powders were all stored in a climate chamber operated at 16°C and 60% Relative Humidity. The results of the moisture absorption measurements are given below in Table 7 and Figure 8. The table also shows as a reference the moisture uptake of the uncoated GLDA granule.

Table 7 Results of the moisture absorption tests.

| GL-47S/Na36S [85:15] uncoated |           | A          |           | B          |           | C         | D         |
|-------------------------------|-----------|------------|-----------|------------|-----------|-----------|-----------|
| Time [hrs]                    | wt% water | Time [hrs] | wt% water | Time [hrs] | wt% water | wt% water | wt% water |
| 0.00                          | 0.00      | 0.00       | 0.0       | 0.00       | 0.0       | 0.0       | 0.0       |
| 1.33                          | 11.18     | 1.00       | 0.4       | 1.00       | 1.2       | 0.5       | 0.6       |
| 3.50                          | 22.36     | 2.00       | 0.6       | 3.17       | 2.5       | 0.8       | 1.1       |
| 7.33                          | 31.98     | 19.00      | 1.8       | 6.75       | 3.9       | 1.3       | 1.6       |
| 23.92                         | 43.10     | 26.00      | 2.5       | 23.83      | 9.3       | 3.1       | 3.5       |
| 25.92                         | 43.94     | 42.83      | 3.9       | 30.83      | 10.6      | 3.9       | 4.3       |
| 30.83                         | 44.13     |            |           | 47.67      | 13.2      | 5.5       | 5.9       |
| 48.67                         | 45.16     |            |           |            |           |           |           |

A GLDA-G + 15%citrate/gum [99/1] + 10% Mowiol/gum [90/10]

B GLDA-G + 15% Na<sub>2</sub>CO<sub>3</sub>/gum [99/1] + 10% citrate/gum [99/1] + 10% Mowiol/gum [90/10]

|   |                                                                                                     |
|---|-----------------------------------------------------------------------------------------------------|
| C | GLDA-G + 15% Na <sub>2</sub> CO <sub>3</sub> /gum [99/1] + 10% Mowiol/gum [90/10]                   |
| D | GLDA-G + 15/5/5/0.6% Na <sub>2</sub> CO <sub>3</sub> /silicate/citrate/gum + 10% Mowiol/gum [90/10] |

Figure 8 and Table 7 show that the use of a coating that consists of a functional salt followed by a coating of Mowiol 3-85 and a polysaccharide gives a reduction in moisture uptake. This exemplifies that various functional (in-) organic salts and combinations thereof can advantageously be used as an intermediate coating layer.

### **Example 8 Sodium silicate as intermediate layer**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), the anti-scaling polymer Alcoguard 4160, sodium silicate Crystal0265 (ex PQ Corporation, Netherlands), Arabic gum (laboratory grade, ex Acros Organics), and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First co-granules of GLDA and Alcoguard 4160 (in a ratio of 80:20) were produced in a spray granulation process using the same process as described before.

on the "uncoated" GLDA/4160 co-granule subsequently a layer of sodium silicate was applied in a fluid bed (GEA Aeromatic Strea-1). Arabic gum was added to the sodium silicate solution, such that the silicate/gum ratio was about 99:1. This mixture was sprayed onto the GLDA/4160 co-granule in the fluid bed Aeromatic coater until 13 wt% and 20 wt% was applied. On both systems 10 wt% of a polyvinyl alcohol/Arabic gum layer was applied, using a 17 wt% solution of Mowiol 3-85 and gum, with the Mowiol/gum ratio being 90:10. The solutions were all coated onto the co-granules, using the Aeromatic Strea-1 fluid bed coater with a Wurster set-up and a two-fluid nozzle. The air inlet temperature used was 80-90 °C.

The moisture absorption and flowability of these powders were determined as described above. The results of those tests are shown below in Table 8 and Figure 9, together with the data of the uncoated co-granule (as presented in Example 5).

Table 8 Results of moisture absorption and flowability (AG is an abbreviation for Arabic gum)

| [GL47S/GLNa36S (95:5)]/4160 (80:20) coated with |                                                    |     |                                                    |     |                          |     |                         |       |
|-------------------------------------------------|----------------------------------------------------|-----|----------------------------------------------------|-----|--------------------------|-----|-------------------------|-------|
| dT [hrs]                                        | 20%silicate/AG<br>[99:1] + 10% 3-<br>85/AG [90:10] |     | 13%silicate/AG<br>[99:1] + 10% 3-<br>85/AG [90:10] |     | 20%silicate/AG<br>[99:1] |     | Uncoated co-<br>granule |       |
|                                                 | wt% water                                          | %ff | wt% water                                          | %ff | wt% water                | %ff | wt%<br>dT [hrs] water   |       |
| 0.00                                            | 0.00                                               | 100 | 0.00                                               | 100 | 0.00                     | 100 | 0.00                    | 0.00  |
| 1.00                                            | 0.46                                               | 90  | 0.55                                               | 100 | 3.48                     | 0   | 1.00                    | 11.24 |
| 3.25                                            | 1.03                                               | 90  | 1.07                                               | 100 | 7.20                     | 0   | 3.67                    | 26.72 |
| 5.92                                            | 1.38                                               | 90  | 1.51                                               | 100 | 10.43                    | 0   | 6.00                    | 33.00 |
| 23.83                                           | 2.96                                               | 80  | 3.33                                               | 90  | 20.87                    | 0   | 7.50                    | 36.04 |
| 31.67                                           | 3.70                                               | 80  | 4.34                                               | 80  | 24.22                    | 0   | 23.25                   | 45.83 |
| 47.58                                           | 4.60                                               | 80  | 5.69                                               | 70  | 27.08                    | 0   | 25.25                   | 45.90 |
| 52.83                                           | 4.92                                               | 60  | 6.37                                               | 50  | 28.20                    | 0   | 27.58                   | 46.16 |
|                                                 |                                                    |     |                                                    |     |                          |     | 31.83                   | 46.23 |

Table 8 and Figure 9 show that adding a layer of sodium silicate using the process conditions of this Example only gives a reduction in the rate of moisture absorption. However, flowability of those granules can be considered still insufficient. Applying a coating with Mowiol 3-85/gum gives a further significant improvement in moisture absorption and the flowability remains acceptable for at least 24 hours for the two levels of sodium silicate that were used, i.e. 13 wt% and 20 wt%.

#### **Example 9 Addition of citrate to co-granule (three-compound co-granule)**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), the anti-scaling polymer Alcoguard 4160, the functional salt tri-

sodium citrate (laboratory grade, ex Fisher Scientific), Arabic gum (laboratory grade, ex Acros Organics), and the water-soluble polyvinyl-alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First co-granules of GLDA, Alcoguard 4160 and citrate were produced in a spray granulation process using the same process as described before. In making these granules the GLDA part consisted of GL-47-S and GL-Na36S in a ratio of 95:5. The composition of this three-compound co-granule was such that the ratio of total GLDA:41 60:citrate was 70:20:10. This was done by dissolving all compounds in the required ratio in water and using that spray mix to generate the co-granule.

The "uncoated" GLDA/41 60/citrate co-granule was subsequently coated with Mowiol 3-85 and Arabic gum in a fluid bed (Glatt lab scale) by using a 6% solution of Mowiol 3-85/Arabic gum, with the ratio of Mowiol 3-85 and Arabic gum being 90:10. This solution was coated onto the co-granules, using a top spray two-fluid nozzle, until about 10wt% of the Mowiol/Arabic gum was coated onto the co-granule.

The results of the moisture absorption and flowability measurements are given below in Table 9 and Figure 10.

Table 9 and Figure 10 show that it is possible to generate a three-compound co-granule. The co-granule as such absorbs moisture fast. When 10 wt% Mowiol/Arabic gum is used, the rate of moisture absorption is significantly reduced and flowability is acceptable for at least the first 6 hours of storage at 16°C, 60% RH.

Table 9 Results of moisture absorption and flowability (%ff)

| dT [hrs] | GLDA/4160/citrate<br>[70:20:10] |     | GLDA/4160/citrate<br>[70:20:10] + 10%<br>Mowiol/AG [90:10] |     |
|----------|---------------------------------|-----|------------------------------------------------------------|-----|
|          | wt% water                       | %ff | wt% water                                                  | %ff |
| 0.0      | 0.00                            | 100 | 0.00                                                       | 100 |
| 1.0      | 5.04                            | 0   | 0.40                                                       | 100 |
| 3.0      | 12.48                           | 0   | 0.74                                                       | 90  |
| 5.0      | 17.22                           | 0   | 1.07                                                       | 90  |
| 6.0      | 18.95                           | 0   | 1.34                                                       | 90  |
| 23.6     | 35.25                           | 0   | 6.19                                                       | 40  |
| 27.3     | 37.96                           | 0   | 7.54                                                       | 40  |
| 30.5     | 39.56                           | 0   | 8.73                                                       | 30  |
| 48.0     | 43.08                           | 0   | 15.15                                                      | 5   |

**Example 10 Effect of gum level in citrate**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), tri-sodium citrate (laboratory grade, ex Fisher Scientific), Arabic gum (laboratory grade, ex Acros Organics), and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH). First a granule of GLDA was produced in a spray granulation process using the process as described above. In this case, GL-47-S and GL-NA-36-S were mixed in a ratio of 85:15.

The "uncoated" GLDA granule was subsequently coated with a layer of citrate/Arabic gum and subsequently with a layer of Mowiol/gum in a fluid bed (GEA Aeromatic Strea-1). To study the effect of the gum level in the citrate layer, the citrate was dissolved in water and Arabic gum was added in two levels, such that the citrate/gum ratio in the final coating was about 99:1 and 83:17. These mixtures were sprayed onto the GLDA granule in the fluid bed Aeromatic coater until about 15wt% of citrate/gum coating was achieved. After that an additional polyvinyl alcohol layer was coated on using a 16 wt% solution of Mowiol 3-85 and gum, with the Mowiol/gum ratio being 95:5. The solutions were all applied using a Wurster set-up and a two-fluid nozzle. The air inlet

temperature used was 80°C. All powders were stored in two climate chambers, one operating at 16°C, 60% Relative Humidity, the other at 27°C, 80% Relative Humidity. The results of those tests are shown below in Table 10 and Figure 11.

Table 10 and Figure 11 show that both gum levels in the citrate layer give similar results, with the higher gum level of about 17% (based on dry basis for the citrate/gum layer) giving the largest reduction in the rate of moisture absorption.

Table 10 Results of moisture absorption

| 16 C / 60% RH |                                                |                                               | 27 C / 80% RH |                                                |                                               |
|---------------|------------------------------------------------|-----------------------------------------------|---------------|------------------------------------------------|-----------------------------------------------|
|               | 15%citrate/gum [83/17] + 10% Mowiol/gum [95/5] | 15%citrate/gum [99/1] + 10% Mowiol/gum [95/5] |               | 15%citrate/gum [83/17] + 10% Mowiol/gum [95/5] | 15%citrate/gum [99/1] + 10% Mowiol/gum [95/5] |
| Time [hrs]    | wt% water                                      | wt% water                                     | Time [hrs]    | wt% water                                      | wt% water                                     |
| 0,00          | 0,00                                           | 0,00                                          | 0,00          | 0,00                                           | 0,00                                          |
| 1,00          | 1,03                                           | 2,41                                          | 1,17          | 4,67                                           | 8,31                                          |
| 3,17          | 2,04                                           | 4,72                                          | 2,58          | 9,17                                           | 15,91                                         |
| 6,75          | 3,33                                           | 7,15                                          | 4,25          | 15,03                                          | 23,21                                         |
| 23,83         | 9,14                                           | 13,39                                         | 5,50          | 18,30                                          | 27,17                                         |
| 30,83         | 11,44                                          | 15,37                                         | 21,25         | 52,25                                          | 65,47                                         |
| 47,67         | 15,93                                          | 18,30                                         |               |                                                |                                               |

### **Example 11 Incorporation of anti-scaling polymer via co-granule or as coating layer**

Granules were made on the basis of GLDA (Dissolvine GL-47-S and Dissolvine GL-Na-36-S), the anti-scaling polymer Alcoguard 4160, the functional salt tri-sodium citrate (laboratory grade, ex Fisher Scientific), Arabic gum (laboratory grade, ex Acros Organics), and the water-soluble polyvinyl alcohol Mowiol 3-85 (available from Kuraray Europe GmbH).

First co-granules of GLDA and Alcoguard 4160 as well as the GLDA pure granules were produced in a spray granulation process using the same process as described before. In making the co-granules the GLDA part consisted of GL-47-S and GL-Na36S in a ratio of 95:5, with this ratio being 85:15 for the pure granules. The composition of the co-granule was such that the ratio of total GLDA:4160 was 80:20.

The GLDA/4160 co-granules were subsequently coated with 10 wt% citrate/gum, with a citrate/gum ratio of about 99:1 and thereafter the granules were coated with 5 wt% and 10 wt% Mowiol/gum, with the Mowiol/gum ratio being [90:10]. This was all done in a lab scale Glatt fluid bed coater using a top spray two-fluid nozzle.

To determine the effect of the incorporation method of the Alcoguard 4160, the GLDA pure granules were coated with 20 wt% Alcoguard 4160, to get the same composition as the GLDA/4160 co-granule. This is denoted by GLDA-G + 20% 4160. This coating was done in a lab scale Glatt fluid bed coater using a top spray two-fluid nozzle and the Alcoguard 4160 solution, as is, which has a solids content of about 41%. The GLDA-G + 20% 4160 granules were subsequently coated with 10 wt% citrate/gum, with a citrate/gum ratio of about 99:1 and after that the granules were coated with 5 wt% and 10 wt%

Mowiol/gum, with the Mowiol/gum ratio being [90:10]. This was all done in a lab scale Glatt fluid bed coater using a top spray two-fluid nozzle.

This gave the following granule systems:

- A GLDA-G + 20%4160 + 10% citrate/gum [99:1]
- B GLDA-G + 20%4160 + 10% citrate/gum [99:1] + 5% Mowiol/gum [90:10]
- C GLDA-G + 20%4160 + 10% citrate/gum [99:1] + 10% Mowiol/gum [90:10]
- D GLDA[95:5]/4160 [80:20] + 10% citrate/gum [99:1]
- E GLDA[95:5]/4160 [80:20] + 10% citrate/gum [99:1] + 5% Mowiol/gum [90:10]
- F GLDA[95:5]/4160 [80:20] + 10% citrate/gum [99:1] + 10% Mowiol/gum [90:10]

All powders were stored in a climate chamber at 16°C, 60% Relative Humidity. The results of the moisture absorption and flowability measurements are shown below in Table 11 and Figure 12.

Table 11 Results of the moisture absorption and flowability measurements

| Time<br>[hrs] | A            |     | B            |     | C            |     | D            |     | E            |     | F            |     |
|---------------|--------------|-----|--------------|-----|--------------|-----|--------------|-----|--------------|-----|--------------|-----|
|               | wt%<br>water | %ff | wt%<br>water | %ff | wt%<br>water | %ff | wt%<br>water | %ff | wt%<br>water | %ff | wt%<br>water | %ff |
| 0.00          | 0.00         | 100 | 0.00         | 100 | 0.00         | 100 | 0.00         | 100 | 0.00         | 100 | 0.00         | 100 |
| 1.00          | 0.34         | 0   | 0.44         | 100 | 0.31         | 100 | 1.61         | 0   | 0.43         | 90  | 0.34         | 100 |
| 3.00          | 0.73         | 0   | 0.67         | 95  | 0.46         | 100 | 4.24         | 0   | 0.82         | 90  | 0.56         | 100 |
| 5.00          | 1.24         | 0   | 0.81         | 95  | 0.57         | 100 | 6.55         | 0   | 1.19         | 90  | 0.76         | 100 |
| 6.00          | 1.43         | 0   | 0.86         | 95  | 0.61         | 100 | 7.58         | 0   | 1.30         | 90  | 0.83         | 100 |
| 23.58         | 7.36         | 0   | 1.91         | 50  | 1.06         | 100 | 23.65        | 0   | 4.46         | 50  | 1.97         | 100 |
| 27.25         | 8.66         | 0   | 2.23         | 40  | 1.12         | 100 | 26.02        | 0   | 5.21         | 40  | 2.26         | 100 |
| 30.50         | 9.65         | 0   | 2.50         | 40  | 1.19         | 100 | 27.77        | 0   | 5.82         | 50  | 2.52         | 100 |
| 48.00         | 15.04        | 0   | 4.24         | 40  | 1.72         | 100 | 32.97        | 0   | 9.50         | 60  | 3.94         | 100 |

- A GLDA-G [85:15] + 20%4160 + 10% citrate/gum [99:1]
- B GLDA-G [85:15] + 20%4160 + 10% citrate/gum [99:1] + 5% Mowiol/gum [90:10]
- C GLDA-G [85:15] + 20%4160 + 10% citrate/gum [99:1] + 10% Mowiol/gum [90:10]

|   |                                                                            |
|---|----------------------------------------------------------------------------|
|   | [90:10]                                                                    |
| D | GLDA [95:5]/4160 [80:20] + 10% citrate/gum [99:1]                          |
| E | GLDA [95:5]/4160 [80:20] + 10% citrate/gum [99:1] + 5% Mowiol/gum [90:10]  |
| F | GLDA [95:5]/4160 [80:20] + 10% citrate/gum [99:1] + 10% Mowiol/gum [90:10] |

The following can be concluded from Table 11 and Figure 12:

- The higher the Mowiol 3-85 level, the slower the moisture absorption.
- The slowest moisture absorption is found for the system where three consecutive layers are used: GLDA granule, coated with Alcoguard 4160, followed by citrate/gum, and finished with Mowiol 3-85/gum. This shows that for storage stability a multi-layer approach is to be preferred over a co-granule to obtain the best reduction in moisture absorption.
- The best results on flowability are obtained for both the co-granule and the GLDA-G granule when 10 wt% Mowiol/gum is used as the final outer coating layer.
- However, for the first 6 hours acceptable flowability is also obtained for the co-granule and the GLDA-G granule when 5 wt% Mowiol/gum is used. This shows that depending upon the application requirements, the Mowiol 3-85 level will preferably be between 5 wt% and 10 wt%.

## Claims:

1. Coated particle containing a particle and a coating, wherein the particle contains glutamic acid N,N-diacetic acid or a partial salt thereof of the formula  $\text{HnYm-GLDA}$ , wherein Y is a cation selected from the group of sodium, potassium, and mixtures thereof,  $n+m = 4$ , and wherein the coating contains at least one vinyl alcohol (co)polymer and at least one polysaccharide.
2. Coated particle of claim 1 wherein the vinyl alcohol (co)polymer has a melting point of more than  $100^{\circ}\text{C}$  and less than  $300^{\circ}\text{C}$ .
3. Coated particle of claim 1 or 2 wherein the vinyl alcohol (co)polymer has a Hoppler viscosity as 4% aqueous solution of 1 to 100 mPas.
4. Coated particle of any one of claims 1 to 3 wherein the vinyl alcohol (co)polymer is polyvinyl alcohol and has a degree of hydrolysis of 80 to 99 mol%.
5. Coated particle of any one of claims 1 to 4 wherein the coating forms a closed layer, as can be established by scanning electron microscopy/EDX.
6. Coated particle of any one of claims 1 to 5 wherein in the coating the weight% of polysaccharide on dry basis is between 0.5 and 20 wt%, and wherein the weight% of vinyl alcohol (co)polymer on dry basis is between 80 and 99.5 wt%.
7. Coated particle of any one of claims 1 to 6 comprising two or more coating layers that may be different or the same.

8. Coated particle of claim 7 comprising an inner coating containing a salt and an outer coating comprising at least one vinyl alcohol (co)polymer and at least one polysaccharide.
9. Coated particle of any one of claims 1 to 8 additionally comprising further additives chosen from the group of scale-inhibiting additives, structurants, (co)builders, pH buffers, chelating agents other than GLDA, flowing aids, and nanoparticles.
10. Coated particle of any one of claims 1 to 9 wherein  $m$  is at least 1 and  $n$  is at most 3,  $n+m = 4$ , and  $Y$  is a cation selected from the group of sodium, potassium, and mixtures thereof.
11. Coated particle of any one of claims 1 to 10 wherein the polysaccharide is a gum or a cellulose ether.
12. Process to prepare coated particle containing a particle and a coating, wherein the particle contains glutamic acid  $N,N$ -diacetic acid or a partial salt thereof of the formula  $H_nY_m\text{-GLDA}$ , wherein  $Y$  is a cation selected from the group of sodium, potassium, and mixtures thereof,  $n+m = 4$ , and wherein the coating contains at least one vinyl alcohol (co)polymer and at least one polysaccharide, comprising the steps of mixing the at least one vinyl alcohol (co)polymer and polysaccharide to give a coating mixture and subsequently applying the coating mixture on the particles or applying the vinyl alcohol (co)polymer and the polysaccharide at least partly one after the other on the particle to give one combined coating layer.
13. Process of claim 12 wherein in a step preceding applying the coating mixture or the vinyl alcohol (co)polymer and the polysaccharide at least partly one after the other on the particle, a salt layer is applied on the particle, preferably a citrate, silicate, glycolate, oxalate, lactate,

succinate, malonate, maleate, diglycolate, fumarate, stearate, chloride, nitrate, percarbonate or carbonate salt.

14. Use of the coated particle of any one of claims 1 to 11 in detergents, agriculture, in oil field applications, or in water treatment.
15. Method to reduce the hygroscopicity of materials by applying thereon a coating that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.
16. Method to reduce the rate of water uptake of materials by applying thereon a coating that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.
17. Method to improve the stability of materials by applying thereon a coating that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.
18. Method to improve the flow properties of materials by applying thereon a coating that comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.
19. Coated particle containing a core and a coating, wherein the coating comprises at least one vinyl alcohol (co)polymer and at least one polysaccharide.
20. Coated particle of claim 19 obtainable by the process of any one of claims 15 to 18, wherein the core contains a water-sensitive compounds from the group of bleaching agents, such as percarbonates, peroxides, hypochlorites; organic molecules, such as peptides, proteins, polynucleotides; reaction initiators; catalysts; paint components, such as dyes; medicines; and pharmaceutical preparations or components.

Figures

Figure 1

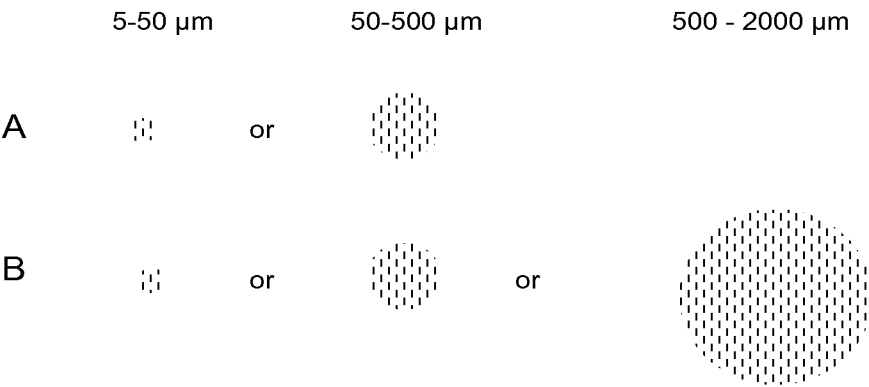


Figure 2

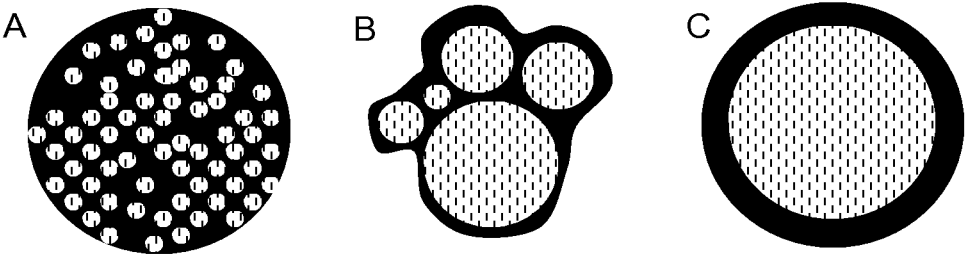


Figure 3 Graphical representation of Table 1.

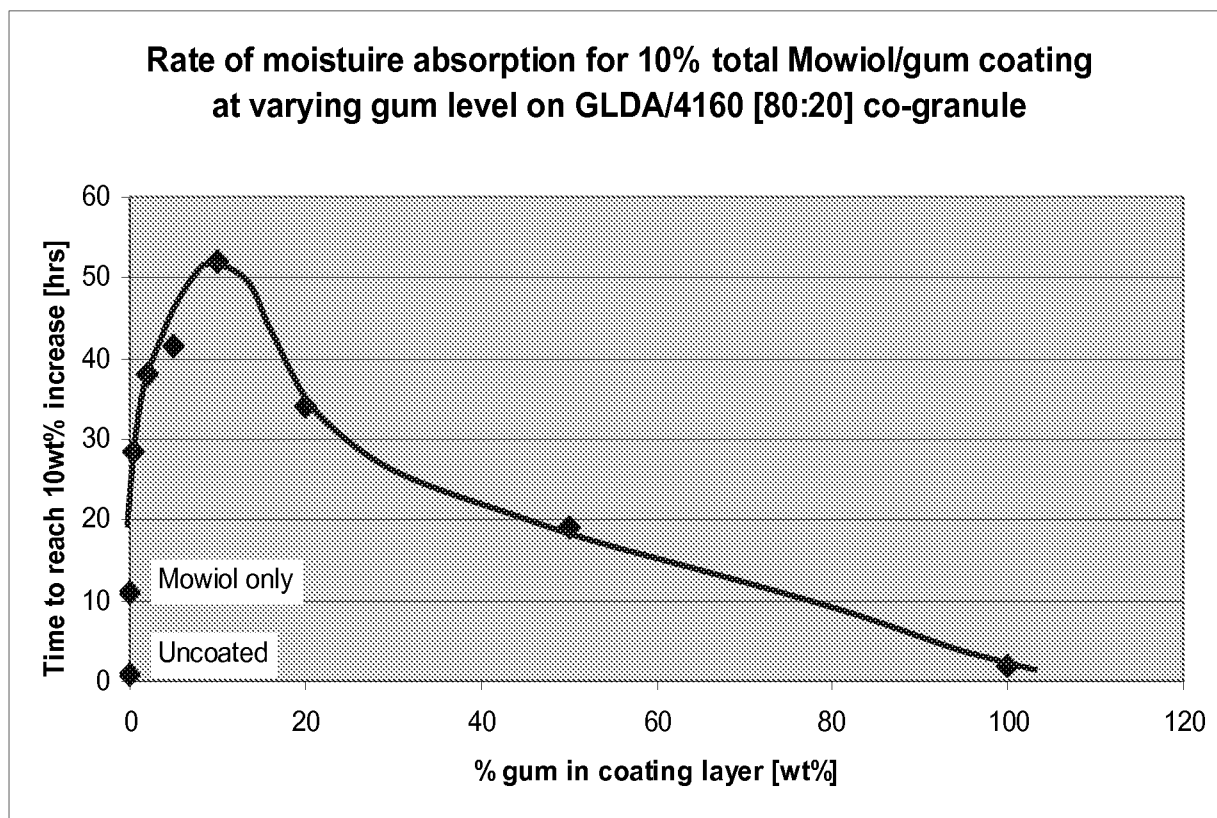


Figure 4 Graphical representation of Table 2.

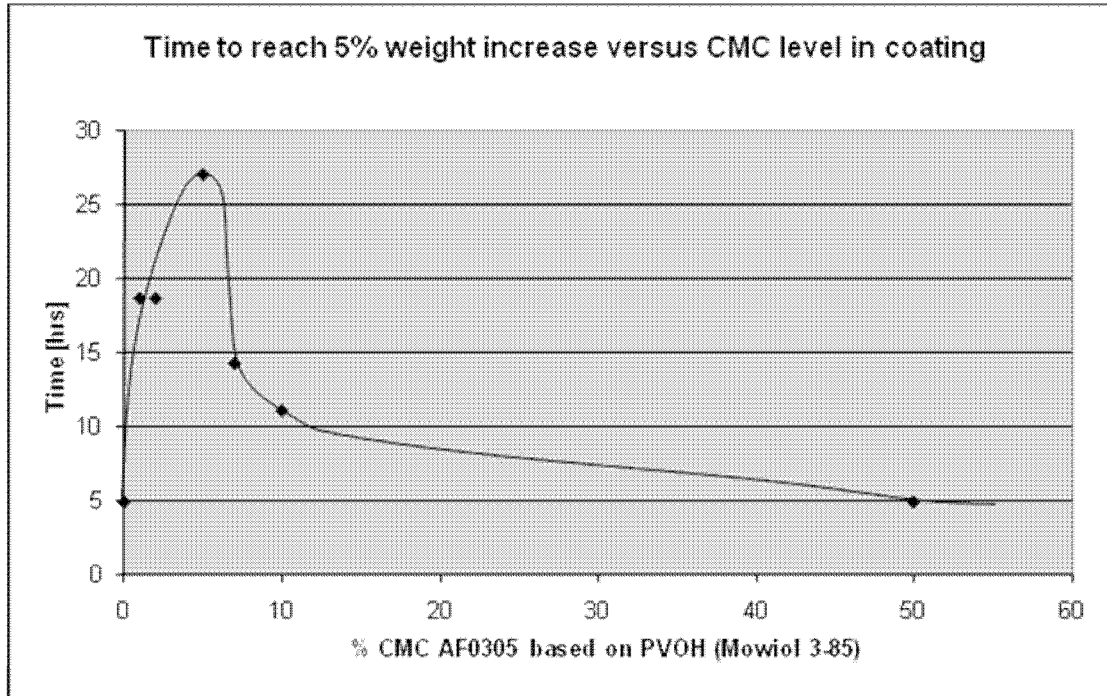


Figure 5 Graphical representation of results shown in Table 4.

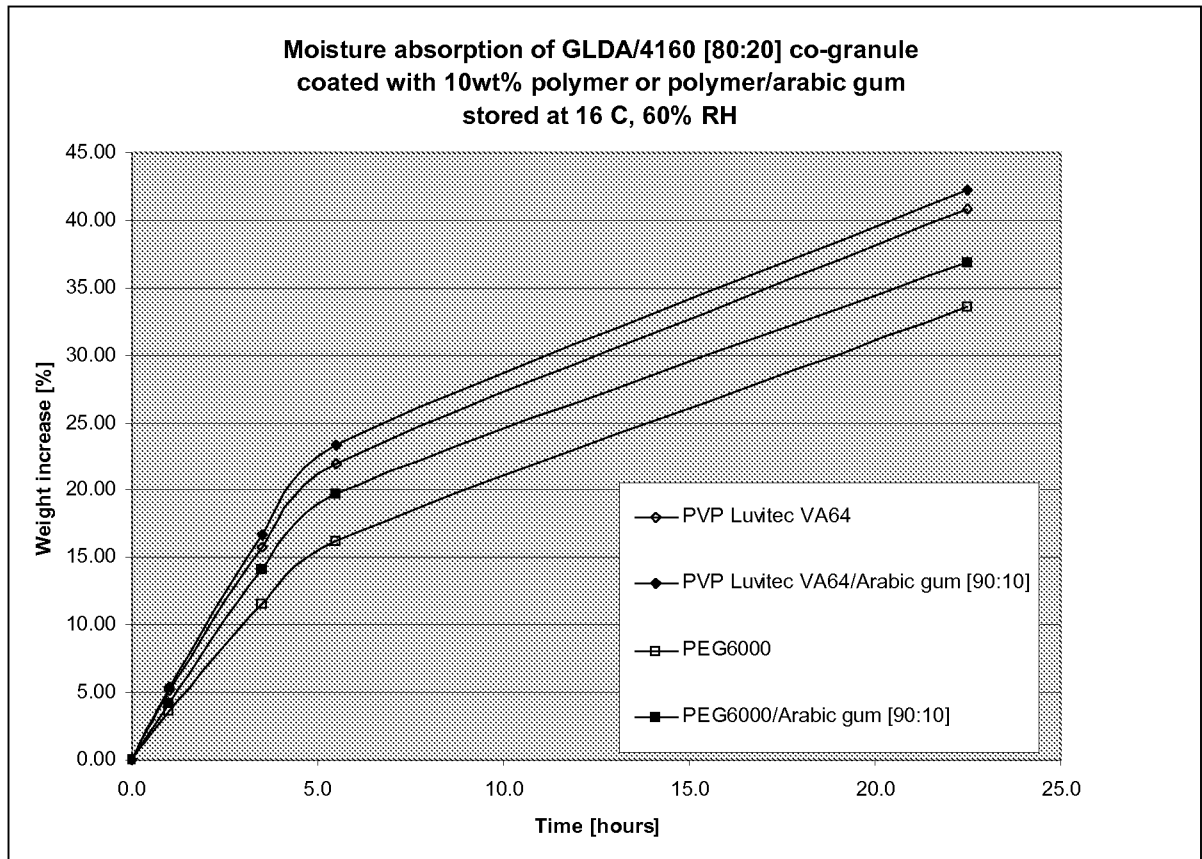


Figure 6 Graphical representation of moisture uptake of Table 5.

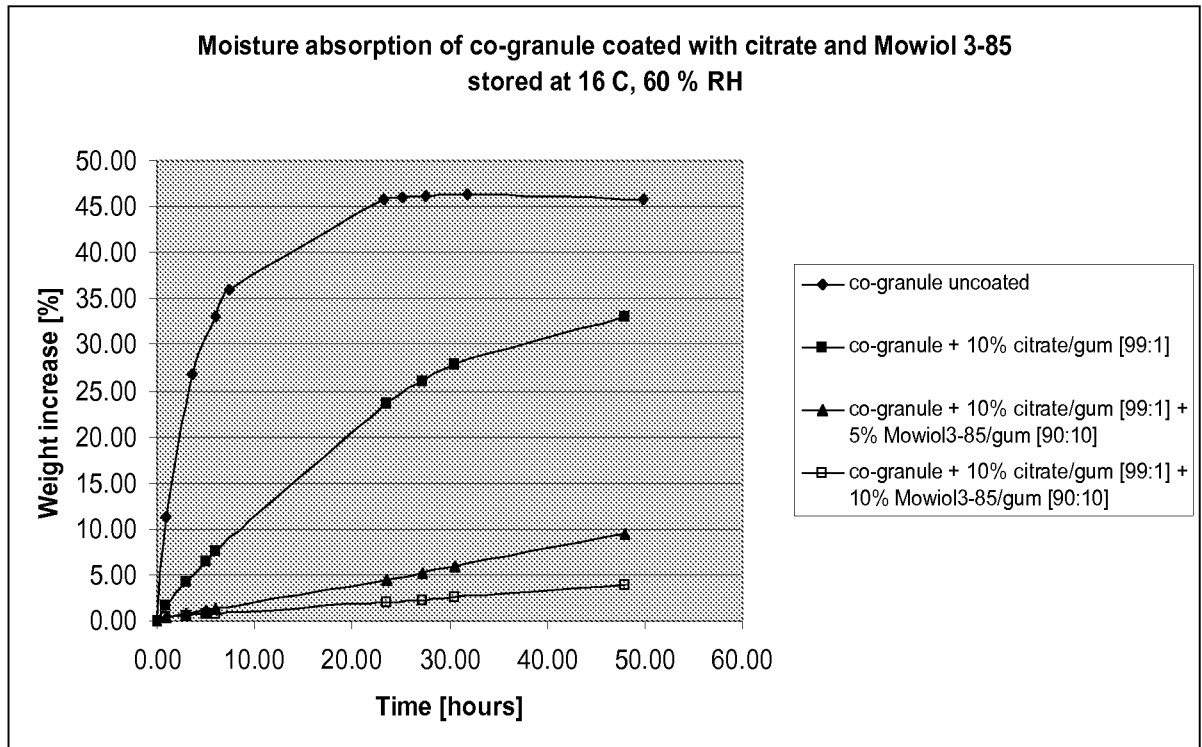


Figure 7 Graphical representation of moisture absorption results as shown in Table 6.

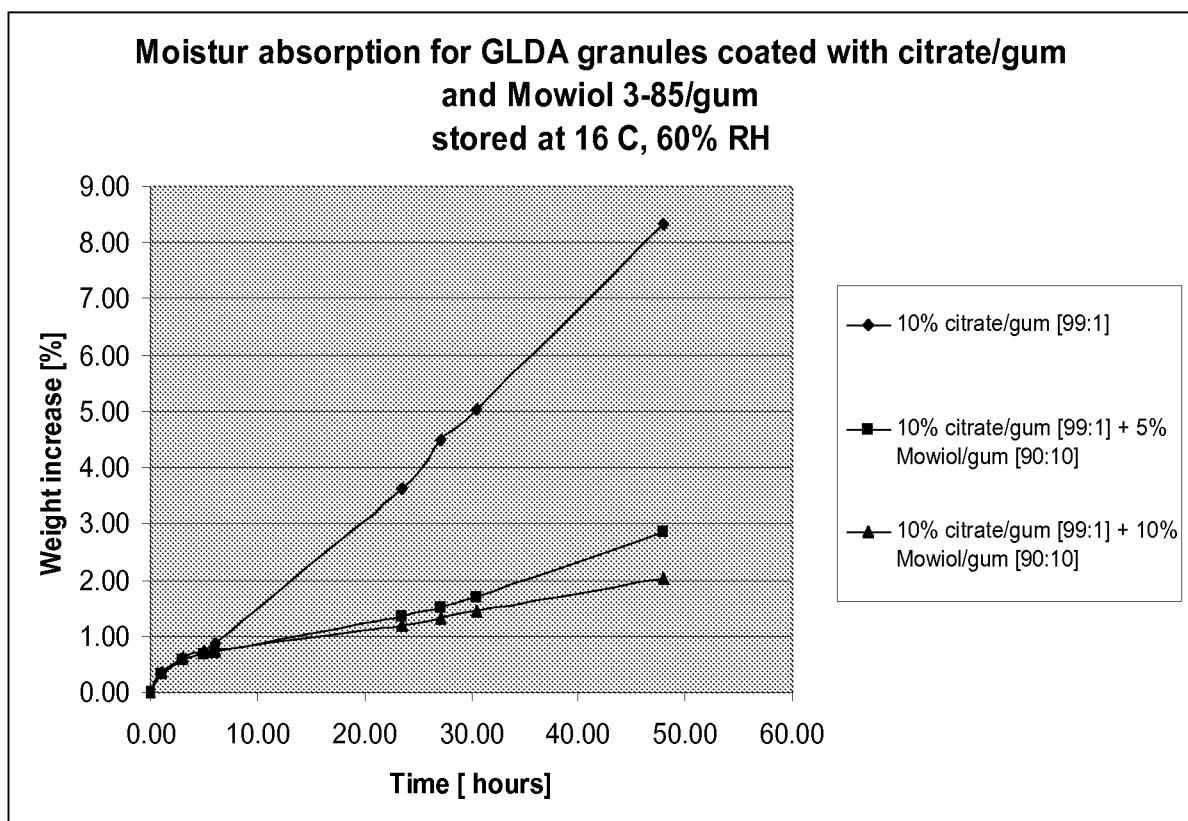


Figure 8. Graphical representation of Table 7.

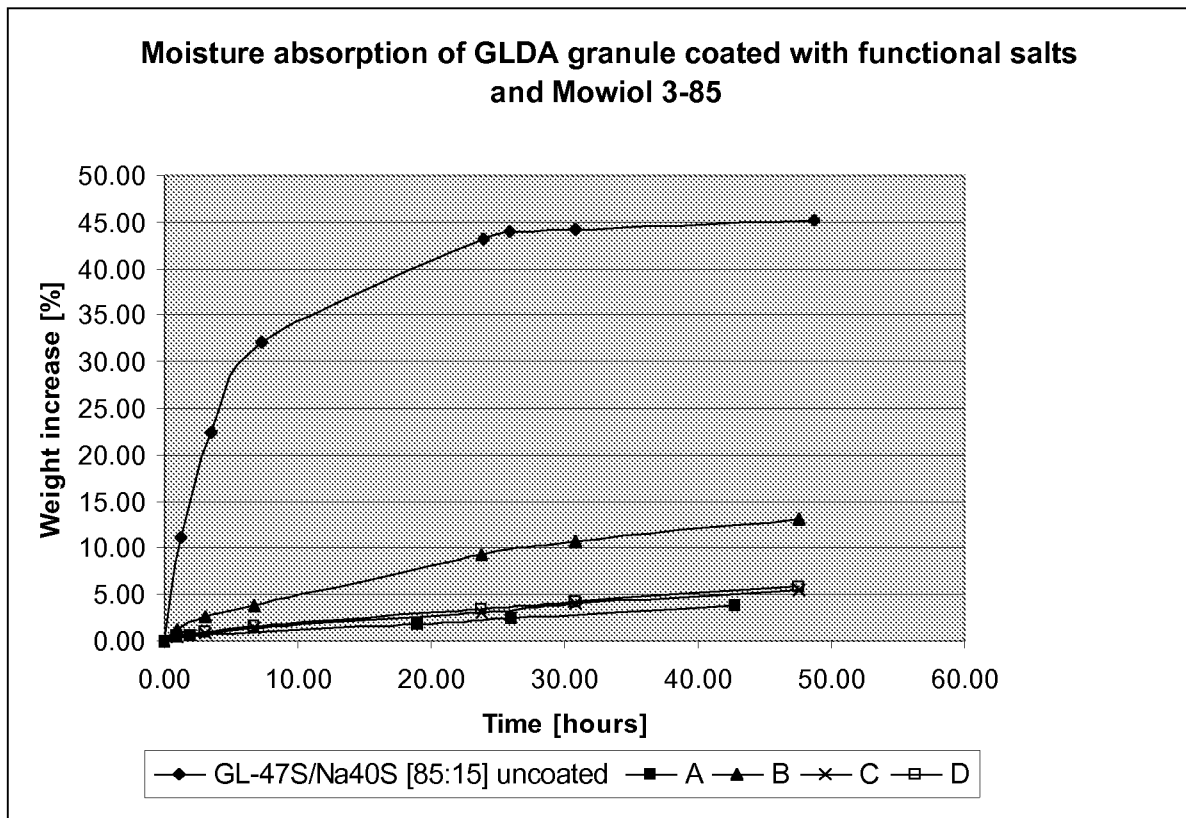


Figure 9 graphical representation of weight increase data as shown in Table 8  
(AG is an abbreviation for Arabic gum)

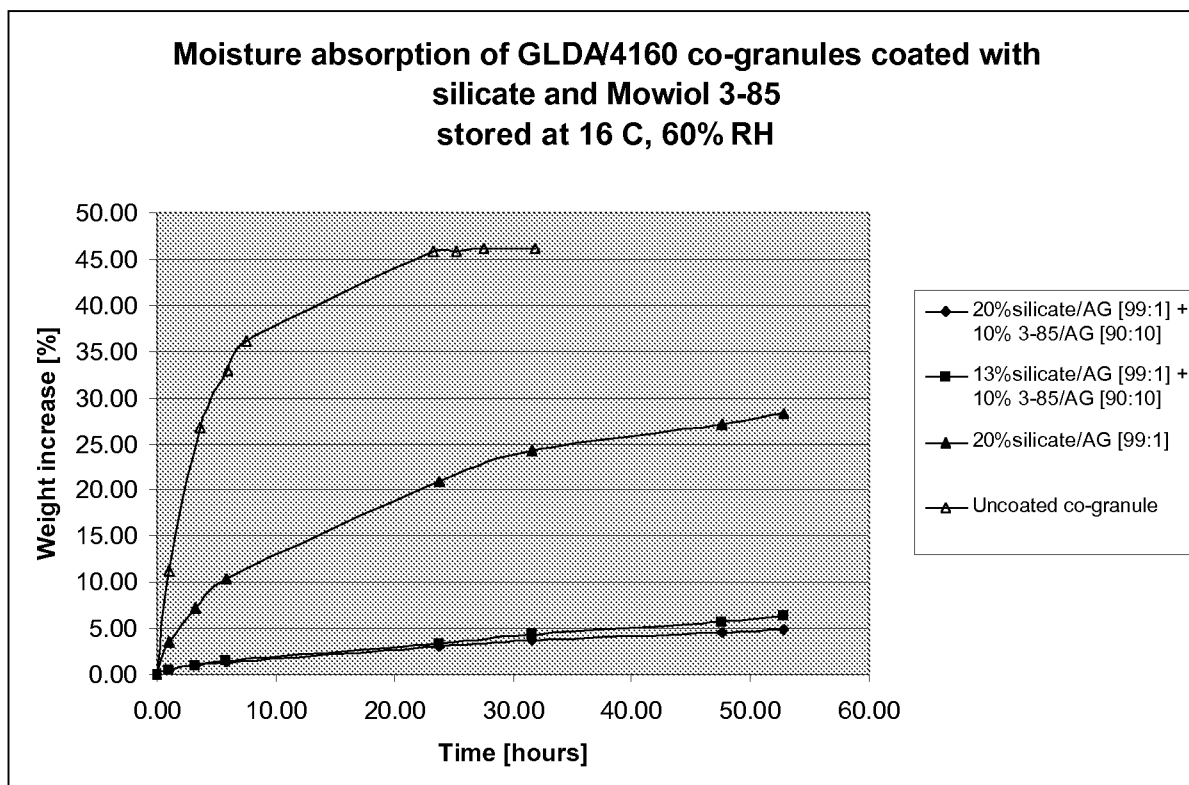


Figure 10 Graphical representation of moisture absorption as shown in Table 9

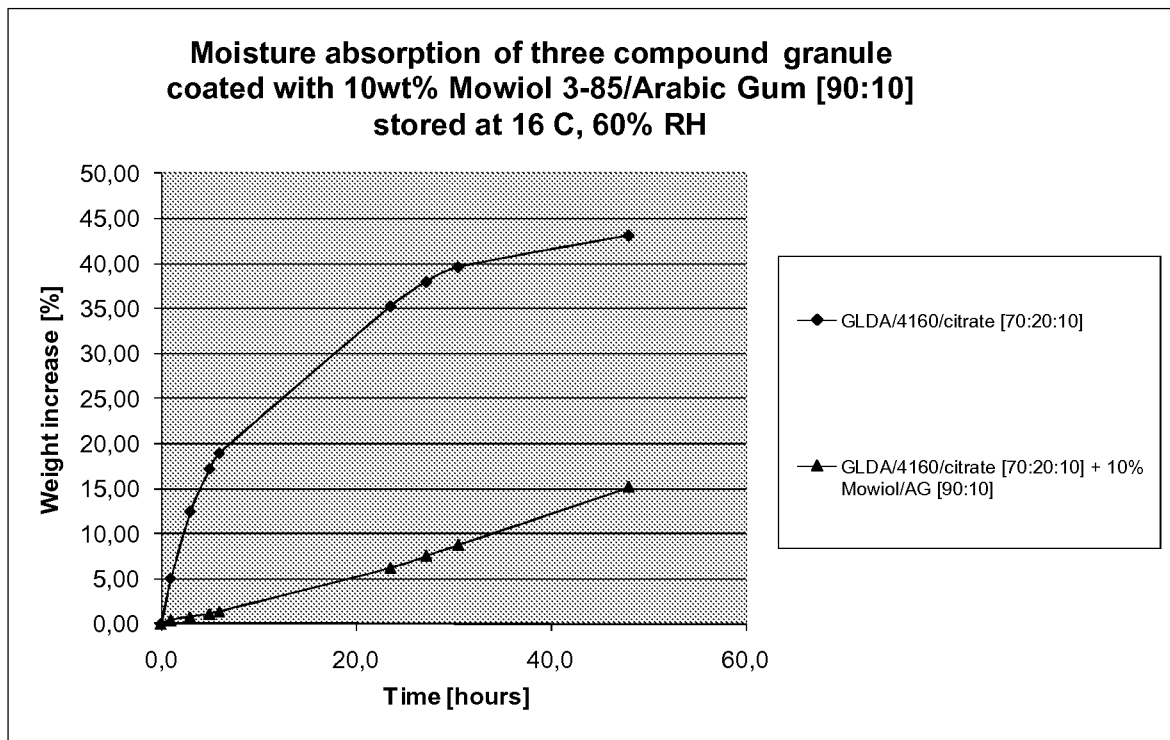


Figure 11 Graphical representation of results shown in Table 10 (AG = Arabic Gum).

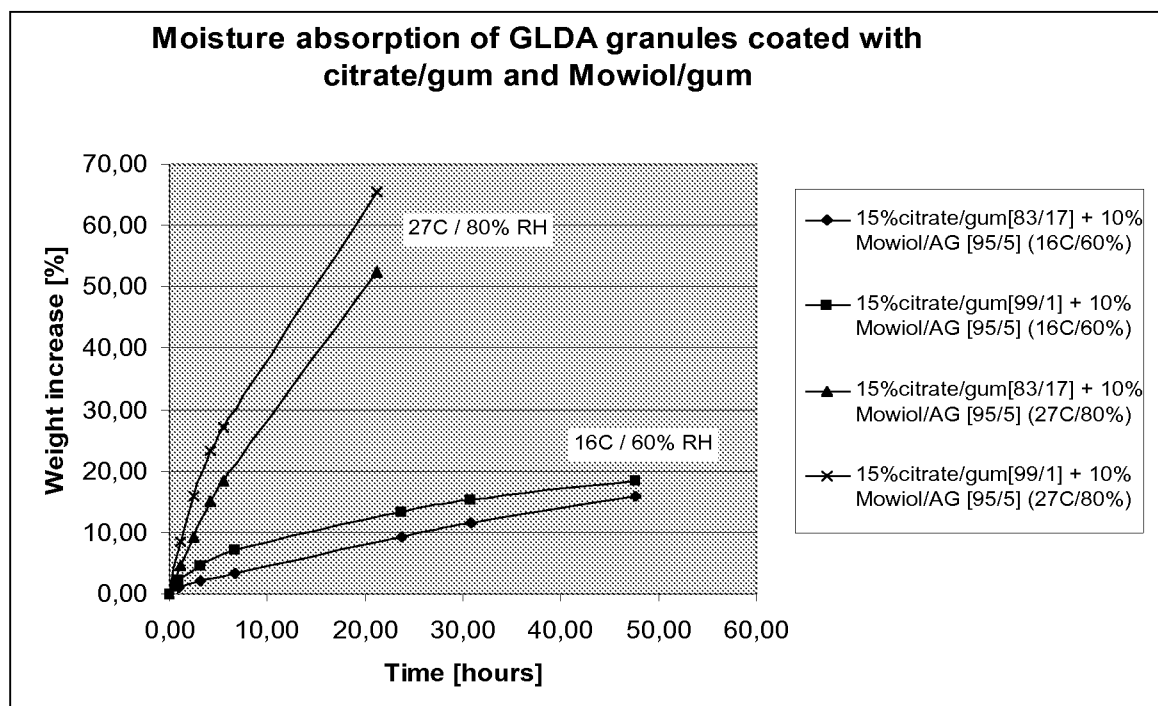
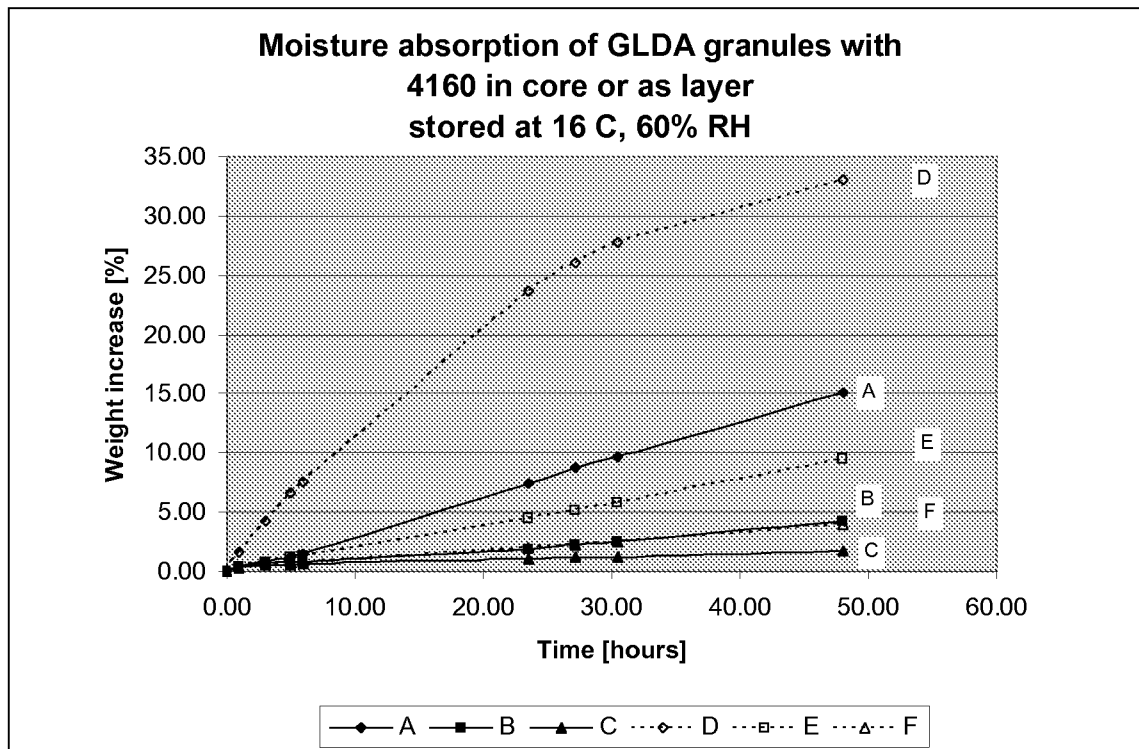


Figure 12 Graphical representation of moisture absorption data shown in Table 11.



# INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/060671

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|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|
| A. CLASSIFICATION OF SUBJECT MATTER                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                              |                                                    |
| INV. C11D3/33                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | C11D3/37                                                                                                                                     | C11D7/32                                           |
| C09K8/536                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | C11D3/22                                                                                                                                     | C08J3/12                                           |
| 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)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                              |                                                    |
| C11D B01J C09K C08J                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                              |                                                    |
| 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                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                              |                                                    |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                              |                                                    |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Citation of document, with indication, where appropriate, of the relevant passages                                                           | Relevant to claim No.                              |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | GB 2 374 082 A (PROCTER & GAMBLE [US] )<br>9 October 2002 (2002-10-09)<br>the paragraph ;<br>page 9 - page 10<br>the whole document<br>----- | 1-20                                               |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | US 2008/300159 A1 (SEEBECK TANJA [DE] ET AL)<br>4 December 2008 (2008-12-04)<br>the whole document<br>-----                                  | 1-20                                               |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                              |                                                    |
| * Special categories of cited documents :<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"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)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br>"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<br>"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<br>"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.<br>"&" document member of the same patent family |                                                                                                                                              |                                                    |
| Date of the actual completion of the international search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                              | Date of mailing of the international search report |
| 26 October 2011                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                              | 07/11/2011                                         |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                              | Authorized officer<br><br>Culmann, J               |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/060671

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) |             |    | Publication<br>date |
|-------------------------------------------|----|---------------------|----------------------------|-------------|----|---------------------|
| GB 2374082                                | A  | 09-10-2002          | CA                         | 2439424     | Al | 17-10-2002          |
|                                           |    |                     | CA                         | 2439523     | Al | 17-10-2002          |
|                                           |    |                     | CN                         | 1527875     | A  | 08-09-2004          |
|                                           |    |                     | CN                         | 1501973     | A  | 02-06-2004          |
|                                           |    |                     | EP                         | 1373463     | Al | 02-01-2004          |
|                                           |    |                     | EP                         | 1373464     | Al | 02-01-2004          |
|                                           |    |                     | JP                         | 2004536166  | A  | 02-12-2004          |
|                                           |    |                     | JP                         | 2004532312  | A  | 21-10-2004          |
|                                           |    |                     | WO                         | 02081616    | Al | 17-10-2002          |
|                                           |    |                     | WO                         | 02081617    | Al | 17-10-2002          |
|                                           |    |                     | US                         | 2003017959  | Al | 23-01-2003          |
|                                           |    |                     | US                         | 2003073604  | Al | 17-04-2003          |
|                                           |    |                     | -----                      |             |    |                     |
| US 2008300159                             | Al | 04-12-2008          | CA                         | 2633735     | Al | 12-07-2007          |
|                                           |    |                     | CN                         | 101351539   | A  | 21-01-2009          |
|                                           |    |                     | EP                         | 1803801     | Al | 04-07-2007          |
|                                           |    |                     | EP                         | 1971675     | Al | 24-09-2008          |
|                                           |    |                     | WO                         | 2007077143  | Al | 12-07-2007          |
|                                           |    |                     | JP                         | 2009522420  | A  | 11-06-2009          |
|                                           |    |                     | KR                         | 20080081960 | A  | 10-09-2008          |
| -----                                     |    |                     |                            |             |    |                     |