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Körnige Zusammensetzungen

Compositions granulaires

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Description

The present invention relates to the granulation of powders to improve their storage stability in particular of bleach activator powders to form granulates for detergent powders.

It is well known to incorporate into detergent compositions bleaching compounds such as perborates and other peroxy bleaches and to activate the bleaches in situ using activators for these bleach compounds. The activators must be prevented from coming into contact with the bleach in the presence of water so as to reduce or eliminate reaction of the activator with the bleach compound prior to dissolution of the entire detergent composition in water. This may be done by providing the bleach and bleach activator in separate compositions or by forming the activator into dry granules with binder, the granules being one component in the dry particulate detergent composition.

In DE-A-2048331 bleach activator granules are produced by mixing dry particles of the activator with inorganic salts containing water of hydration and then moistening the blend with water or a solution of granulating aid, which is selected from inorganic salts, organic binders and detergent compounds.

An improvement of the process in DE-A-2048331 is described in EP-A-0037026 where, instead of incorporating all of the organic binder in solution or dispersion in the water used to moisten the dry bleach activator, part or all of the binder is mixed as dry particles with the activator particles, before the moistening takes place. The organic binders which may be used are selected from starch and cellulose and starch derivatives.

In EP-A-0238341 dry particles of activator and organic binder are moistened with a solution of a sequestering agent, usually a polyphosphonic acid. The binder can be a synthetic polymer, polyacrylates, polymaleates and polyvinyl pyrrolidones being mentioned, but is usually a derivative of a natural polymer such as a cellulose ether, usually carboxymethyl cellulose (CMC).

In EP-A-0240057 bleach activator compositions containing a plain material are produced for instance by moistening a dry mix of the activator with an aqueous dispersion containing the clay and a water-soluble film forming polymer having a low content of carboxyl groups. The film forming polymer is usually a synthetic polymer formed from ethylenically unsaturated compounds. Specific examples used are copolymers of maleic anhydride and vinyl methyl ether and of maleic acid and acrylic acid. The film-forming polymers must be water soluble and are used in the process in solution and are the sole organic binders.

In EP-A-0241962 a non-phosphorous bleach activator granule is provided by moistening a dry mix of particulate activator with an aqueous solution of a low- to non-carboxylate film-forming polymer. The polymer may be a synthetic polymer formed from ethylenically unsaturated monomers or may be a natural polymer or derivative, such as carbohydrates and carbohydrate ethers. Polymers which are specifically exemplified are polyvinyl acetate and a vinyl dextrin polymer. The polymer is apparently water-soluble since it is used in aqueous solution.

In EP-A-0,292,314 components of detergent compositions including a chlorine-releasing bleaching additive, manganese gluconate (a catalyst for peroxygen bleaching), diperoxydodecanedioic acid (a peroxygen bleach) and potassium dichlorocyamuric acid are encapsulated. The process involves suspending the powders in a fluidised bed, then introducing a polymer latex into the fluidised bed, the bed being kept at a temperature of about or above the glass transition temperature of the polymer in the latex. The polymer is insoluble in water at pH 7 but is soluble or swellable in alkali. Polymers used are copolymers of (meth)acrylic acid with esters thereof, preferably having glass transition temperature in the range 30 to 80°C. The process used is termed the Wurster procedure as described in US-A-3253944 and is carried out in apparatus supplied by Aeromatic or Glatt.

Wurster (US-A-3253944) describes a process in which particles are sprayed with coating material which is introduced into high velocity fluidising airstream. The airstream is heated so that the coating is dried. The process is conducted batchwise, that is a batch of powder is introduced into the tower, fluidised and, when coating of the material is sufficient, the fluidising gas is turned off and the product removed.

A new procees according to the present invention in which particles of a detergent additive having an average particle size in the range 20 to 300 µm are agglomerated by moistening them while mixing with an aqueous liquid in the presence of a film-forming polymer which has a lower solubility in water at pH 7 than in aqueous solution at pH 10 is characterised in that the process is carried out in two separate stages, in the first stage of which the particles are mixed om a high shear mixer with the aqueous liquid in the presence of film-forming polymer and in the second of which the moist product of stage one is dried at raised temperature, and in that the agglomerated product has an average particle size in the range 300 to 1400 µm.

In this specification the solubility of the polymer is measured by the following technique.

Firstly dried samples of all the polymers are obtained. Where necessary the solvent or dispersing liquid in the product as supplied is removed under vacuum at 70°C. Portions (1g) of each dried polymer are then dispersed in a small amount of deionised water, or suitable organic solvent, in two 100ml beakers. The solvent is then completely removed by heating at up to 70°C under partial vacuum for several hours. As a result a uniform thickness of dry polymer film is obtained. The beakers are then tared.

Deionised water (50ml), at pH7, is added to one of each of the prepared polymer samples, and 50ml of dilute sodium hydroxide solution (pH10) is added to the remainder. The beakers are left to stand for 16 hours at room temperature. The liquid is then carefully removed. Each beaker is dried at reduced pressure at 70°C to remove all entrained solvent. Further heating 120°C is required with vacuum, in some cases, to remove retained solvent. Each beaker is then re-weighed and the loss of polymer assessed.

The solubility is given as the percentage of polymer removed with the solvent.

The solubility in water at pH7 should be less than about 50 preferably less than 20, more preferably less than 10 for the polymer to be of use in the present invention. The solubility can be less than 5 or even as low as about 2.

The solubility in alkaline solution at pH10 should be at least 5, preferably at least 10 and often at least 20, for instance around 50 or more. The solubility should be higher than in water at pH7.

In the new process the polymer is preferably added to the detergent additive particles in the form of an aqueous dispersion of polymer particles. The polymer particles preferably have a size of less than 25 µm, more preferably less than 10 µm, and even more preferably less than 5 µm, for instance around 1 µm or less. The polymer is preferably an emulsion polymer, ie a polymer which has been prepared as an emulsion and so the polymer dispersion is itself an emulsion.

The concentration of polymer in the dispersion is usually at least 10% by weight, preferably at least 20% by weight, more preferably more than 40% by weight and can be as much as 50% or more. The aqueous liquid in which the polymer particles are suspended is such as to prevent dissolution of the polymer into the liquid.

The polymer dispersion is preferably the product of an oil-in-water polymerisation of an emulsion of water-insoluble ethylenically unsaturated monomer or monomer blend. The product may be the direct product of such a polymerisation or may have further additives or may have had other components removed following the polymerisation process. Preferably it is the direct product and thus preferably contains any stabiliser or emulsifier used in the polymerisation. Such polymerisation methods are known per se.

When the granule produced by a process in which an aqueous dispersion of a water-insoluble polymer is used, the water of the aqueous dispersion is removed in the drying step, allowing the particles to fuse to form a film of polymer on the granule surface.

In the new processes it is often helpful to incorporate additionally a non-film-forming binder, for instance one of the conventional starch or cellulose derivatives used in the above mentioned prior art. The non-film-forming binder is preferably used in the form of dry particles and is thus usually premixed with the particulate activator. It could alternatively be dissolved in the aqueous granulating liquid by which the dry activator is moistened.

Any non-film-forming binder is generally present in an amount of less 10% by weight, more preferably less than 5% by weight and most preferably less than 2% by weight, based on the composition of the product granules. The amount of non-film-forming binder is thus preferably lower than that required to give adequate binding in the absence of the film-forming polymer.

The film-forming polymer is generally used in an amount of at least 0.1% by weight, preferably at least 1% by weight. Usually the amount of film-forming polymer does not need to be higher than 75% and is usually less than 50%, preferably less than 25% by weight, and is more preferably less than 10% by weight. The amounts are based on the weight of the product granules.

The particles are used in an amount such that the detergent additive is present in the product of the process in an amount of at least 20%, preferably in the range 50 to 99% by weight more preferably 70-90% by weight.

The particles of detergent additive which are granulated in the process may be any particles which are required to be agglomerated for instance to render them more easily handlable (being of larger particle size) or, usually, more storage stable by preventing chemical reaction with other active compounds in their environment.

The particles are materials used in detergents, such as catalysts, colourants or enzymes. The invention is of particular benefit in granulating bleach components for instance precursors for bleaches, for instance chlorine-releasing bleach additives, peroxygen-releasing bleach additives or, most suitably, bleach activators.

Particulate bleach activators include organic activators which are compounds which form carboxylic peracids on reaction with perhydroxyl ions in wash liquor. An organic activator is preferably tetra acetyl ethylene diamine but may be any of the known detergent bleach activators, such as those described in GB-A-2,048,930 or EP-A-0037026. Other preferred activators include polyacetyl mono-, di-, or polysaccharides such as penta acetyl glucose, sulphonates such as isononanoyl oxybenzene sulphonate, nonyl benzoates glycourils such as tetra acetyl glycouril, N-acyl amides, acylated diketopiperazines, and other N-acyl amines. Inorganic catalysts such as manganese salts may also be treated in the process.

By using the above mentioned processes the granules which are formed have a greatly improved strength compared to granules formed using the cellulose or starch derivatives used in the prior art. It is believed that the film-forming polymers form a non-brittle film around the granules which is resistant to breaking up. This improves their storage stability and handling properties.

The film-forming binder improves the physical form of the granules by providing them with a film coating, whereas in the prior art using the non-film-forming binder alone produces granules having small particles of binder on the surface which can form dust after storage and which tend to break up by attrition to form dust comprising activator particles and binder particles.

The application of the film-forming polymer from an aqueous dispersion allows the use of concentrated dispersions, which have low viscosities and are therefore easily handleable, which means that a relatively small amount of water is added in the process which means there is less water to evaporate in the drying step. The polymer becomes more evenly dispersed than if it is added as a solid. When the film-forming polymer is used in conjunction with a non-film-forming binder, the combination allows low amounts of each component to be used. The use of non-film-forming polymer in conjunction with the film-forming polymer allows a greater rate of throughput in the granulating step than the process using the film-forming polymer alone.

The use of a film-forming polymer which is soluble in alkaline solution but not in water, as well as allowing the process benefits described above from the application from aqueous dispersion, allows the production of granules which disperse and dissolve easily in the laundry wash liquor. The granules are chemically very stable on storage as water is not attracted to the granules so that premature contact and reaction of the activator and bleach in the presence of water cannot take place.

A granular bleach activator when used in a laundry detergent, results in a decrease in localised dye and fabric damage ("pinpoint spotting") thought to be due to high local concentrations of bleach, as compared to granules produced by binding with CMC alone.

The film-forming polymer is preferably formed from a water-insoluble blend of ethylenically unsaturated monomers. To provide suitable solubility characteristics the monomer preferably includes an acidic monomer, for instance a carboxylic acid or sulphonic acid monomer. Suitable monomers are maleic acid, acrylic acid and, most preferably, methacrylic acid. The acid monomers are generally copolymerised with a suitable amount of a comonomer such as alkyl esters or amides of those acids or alkyl amide derivatives of the corresponding amides of the carboxylic acids. Suitable comonomers are thus lower alkyl esters of acrylic and methacrylic acid, usually the C_{1-4} alkyl esters. The polymers preferably have molecular weights of up to 5,000,000, preferably up to 1,000,000. The molecular weight is preferably at least 500, more preferably at least 1,000 and most preferably 5,000 or more. The polymerisation is carried out in the conventional manner, preferably by the oil-in-water suspension or emulsion polymerisation described above.

By selection of suitable ratios of monomer components and producing a polymer of an appropriate molecular weight, the polymers can be provided with the preferred solubility characteristics. The inclusion of acid monomers provides the polymers with their alkali solubility since in the presence of alkali the acidic monomers will be ionised which will increase their solubility.

Suitable polymers are for instance those used for enteric film coatings, such as those used for pharmaceuticals and which are insoluble in gastric juices (which is acidic) but soluble in alkaline media such as intestinal juices. Such polymers are for instance available under the Eudragit trade mark, for instance the Eudragit L series and the Eudragit S series. Another suitable polymer is available under the Glascol trade mark from Allied Colloids Limited.

Where the particles granulated are of bleach activator the granules may contain sequestering agents, to improve the rate of disintegration and the stability of the bleach in the laundry liquid. Such sequestering agents are for instance any of the phosphonates used in EP-A-0238341. The sequestering agent may be added in the granulated liquid or may be used in particulate form as one of the dry ingredients. Furthermore the granule may contain an inorganic salt, such as sodium chloride, sodium sulphate, sodium nitrate, sodium citrate or sodium carbonate or magnesium sulphate. The inorganic salt may be added in the granulating liquid or as part of the dry ingredients, in particulate form.

The process may include the use of granulating binders additional to the film-forming and non-film-forming binders mentioned earlier. For instance it may sometimes be advantageous to include a small amount of a granulating liquid at the beginning or end of the granulating process, comprising an aqueous solution of a film-forming polymer such as a vinylmethylether/maleic acid copolymer, a polyacrylic acid homopolymer, usually in salt form, or polyvinyl pyrrolidone.

Other components of the final composition may be included in the granulating process if desired in any suitable amounts. Preferably however such additions provide less than 10% and generally less than 5% by weight of the granules. One component that can usefully be included in granules for detergent composition is optical brightening agent since its incorporation in the granules avoids the problems associated with incorporating it in the remainder of the detergent composition. For instance it may be damaged by the spray drying to which the remainder of the composition is generally subjected. Another component that can conveniently by co-granulated is an antisudsing (anti foaming) or foam stabilising agent. Other components that may be cogranulated are other components of detergent compositions such as surfactants, anti redeposition acids, builders, pigments or dyes, perfumes and enzymes.

The particles to be granulated should be provided in the form of small particles having an average particle size in the range 20 to 300 µm. Preferably substantially none of the particles has a size above 300 µm or, at the most, 500 µm. The particulate binder preferably has an average particle size below 200 µm, generally below 100 µm and is preferably free of particles above 200 µm in size.

During the mixing and contacting stage it is preferred that no external heating source heats the apparatus, the air surrounding the particles or the liquid components. The mixing applies a large amount of kinetic energy to the particles.

The mixing and contacting of the liquid component(s) is preferably carried out whilst the particles fall under the influence of gravity as well as being given kinetic energy by the mixer.

The mixing and contacting step itself can be carried out by apparatus and methods known per se, in which the dry ingredients are mixed and after or substantially simultaneously with mixing in a high shear mixer are contacted with the liquid component(s), for instance by spraying. The process may be carried out in, eg a Schugi Flexomix or a Lödige mixer.

Once the granules have passed through the first stage in which the liquid components are contacted with the particles they are subsequently dried in a separate stage and in a separate part of the apparatus. The drying is conveniently carried out in a fluidised bed which prevents further agglomeration of the granules. The bed is kept at a temperature at which drying is adequately fast but below which the active material(s) becomes unstable. A suitable temperature is in the range 30-100°C, for instance 40-80°C.

The process is usually carried out continuously which allows good control of the product quality to be achieved and is more efficient than a batch process of the type described in EP-A-0292314.

The granules preferably have an average particle size of 300 to 1400 µm. Preferably substantially none of them have a size above 2000 µm and preferably not above 1700 µm. Preferably none of the granules have a size below 50 µm and most preferably none have a size below about 125 µm.

The resultant granules can be incorporated in to compositions, for instance conventional detergent compositions including laundry detergent compositions, in solid (particulate) gel or liquid form. Where the active compound in the particle is bleach activator the detergent composition usually contains suitable bleach component that is activated by the activator. The preferred bleaches are peroxy compounds, especially perborates such as sodium perborate tetrahydrate but others that can be used include sodium perborate monohydrate or sodium percarbonate.

A detergent composition containing the granules may contain, in addition to surfactants, detergent builders and anti-redeposition aids, enzymes, anti-sudsing agents, foam stabilisers, optical brightening agents, pigments, dyes and perfumes, sequestrants, halide salts such as sodium bromide, manganese salts such as mananous sulphate and inert fillers such as sodium sulphate or silicate. A particular advantage of the invention is that it is not necessary to include phosphates, although they may be included if desired. Typical amounts are 1 to 5% based on the total detergent, or 10 to 50% based on the bleach.

The following examples illustrate the invention.

Product Test Methods

The following tests are used:

1. Storage stability of granules.

The granules are stored at 80% relative humidity and 37°C for 4 hours to simulate adverse storage conditions. The granules are then inspected and subjectively assessed for their physical properties to assess their loss of granule integrity due to moisture uptake. They are rated on a scale of 1 (almost no change) to 10 (almost total loss of structure).

2. Fabric Damage

It is intended that the test represents undissolved detergent adhering to clothing during prolonged soaking. Woven woollen cloth, treated by the Hercosett process and undyed, was obtained from the Society of Dyers and Colourists, Bradford, West Yorkshire.

The test detergent formulation is enclosed in a "pouch" of wool which is left to soak for 16 hours in water at room temperature. After rinsing and drying the pieces were examined by eye and ranked on a scale of 1 to 10, higher numbers being worse according to the number of raised yellow spots present. These are areas which have been irreversibly damaged by peroxygen species.

3. Compressability and particle size distribution change after compression.

A cylindrical mould is filled with the granular material, thus it initially contains a fixed volume of the material. The granular material has previously been stored for a period of four hours at a temperature of 37°C and at a relative humidity of 80%, in order to simulate severe storage conditions. A plunger is pressed down on the top of the material in the die at a standard pressure of 1.298×10^5 kgf/m^2 for a period of 5 minutes, to simulate a period of time at the bottom of a large storage bag. The volume change can be measured at this stage.

The particle size distribution of the granules is measured by sieve analysis after the storage step of a) and again after the compression test. The results are reported as the percentage change of particles within the stated size range or retained on the sieve of the stated size (as specified in the results).

Polymers

The following film-forming polymers are used to form granules:

A Glascol polymer - an emulsion believed to contain a polymer formed from monomers including about 20-25 mole % methacrylic acid with alkyl (meth)acrylates (Allied Colloids)

Viscalex VG2 - acrylic acid ester copolymer, emulsion (Allied Colloids - Viscalex is a trade mark).

Gantrez S-97 - methylvinyl ether - maleic acid copolymer solution, (GAF - Grantrez is a trade mark).

PVP K-30 - polyvinyl pyrrolidone, solid (GAF)

Each polymer was tested for its solubility at pH 7 and pH 10 by the method described above. The results are shown in Table 1.

TABLE 1:

SOLUBILITY AT pH 7 and pH 10		
	pH 7	pH 10
GLASCOL	2	50
VISCALEX VG2	6	20
GANTREZ S-97	100	100
GAF PVP K-30	100	100

Examples 1-4 (Comparative A-C)

In the following examples the dry components (TAED, Na_2SO_4 and binder (where appropriate)) are mixed in a laboratory granulator for about 3 minutes after which the liquid components (water and/or binder dispersion or solution, where appropriate) are sprayed on whilst mixing is continued for a further 2 minutes. The granular product is then discharged and dried for 15 minutes at 60°C using a fluid bed drier. The proportions of the components in the resultant product is shown in the following table:

TABLE 2:

EXAMPLE FORMULATIONS							
EXAMPLE	A	B	C	1	2	3	4
TAED	92	92	88	89	86	92	90
GLASCOL				4.9	9.6	7	
VISCALEX VG2							4.5
GANTREZ S-97			10				
PVP K-30		7					
CMC	7			0.3			0.3
Na_2SO_4				4.9			4
WATER	to 100%						

In example A (comparative) the CMC was added as dry powder. In examples B, C and 1-4 the CMC was added as a 4% aqueous solution.

The film-forming polymers are added as supplied, ie the emulsion polymers are added with the liquid and the solid polymers are added with the dry ingredients.

The products are then subjected to the above-described tests. The results are shown in Table 3.

TABLE 3:

RESULTS OF TESTS							
Test/Composition	A	B	C	1	2	3	4
1	10	7	5	2	2	4	2
2	8			3	3	3	9
3 less than 425µm	18	16	13	9			16
more than 600µm	-13	-9	-4	-1			-6

The results show that the compositions formed by the process of the invention including a film-forming polymer with the defined solubility characteristics as well as cmc are less susceptible to deterioration during storage, having reduced particle size change in the test 3b and better results on the subjective storage test, no. 1. The results are also improved compared to the comparative examples using the film-forming polymers that are soluble at pH7. The results also show that the fabric damage is far less for the composition containing the Glascol product which is far more soluble at pH10 than pH7 (examples 1-3) than for the conventional granule. The composition formed with the other emulsion polymer Viscalex also has desirable overall characteristics.

Example 5

Granules were produced in a similar manner as described above to give a product which consisted of 90.8% TAED, 3.6% cmc, 4.3% $NaSO_4$. The granules were subjected to the compressibility test, test 3, and compared with comparative example A as used above. The results are shown in Table 4.

TABLE 4

		COMPOSITION	
	Test	A	Example 5
3 size fraction	retained on 850µm	-29.4	0.0
	retained on 710µm	-33.4	2.9
	retained on 600µm	-26.4	3.6
	retained on 500µm	-13.0	2.1
	retained on 425µm	-4.1	1.1
	less than 425µm	0	0
	% change in volume	25	12.6

Results show that A tends to break down significantly and compress substantially. Example 5 tends to aggregate only very slightly - almost insignificantly - as well as resisting compression as compared to conventional formulation (A) using cmc alone.

Claims

1. A process in which particles of a detergent additive having an average particle size in the range 20-300µm are agglomerated by moistening them while mixing with an aqueous liquid in the presence of a film-forming polymer which has a lower solubility in water at pH 7 than in aqueous solution at pH 10 characterised in that the process is carried out in two separate stages, in the first stage of which the particles are mixed in a high shear mixer with the aqueous liquid in the presence of film-forming polymer and in the second of which the moist product of stage one is dried at raised temperature and in that the agglomerated product has an average particle size in the range 300 to 1400µm.

2. A process according to claim 1 in which the polymer is added to the particles in the form of an aqueous dispersion of polymer particles.

3. A process according to claim 2 in which the polymer particles have a size of less than 25 µm.

4. A process according to claim 3 in which the polymer particles have a size of less than 10 µm, preferably less than 5 µm, more preferably around 1 µm or less.

5. A process according to any of claims 2 to 4 in which the polymer dispersion is an emulsion, which is preferably the product of an oil-in-water polymerisation of an emulsion of water-insoluble ethylenically unsaturated monomer or monomer blend.

6. A process according to any preceding claim in which a non-film-forming binder is incorporated, which is preferably a starch or a cellulose derivative.

7. A process according to claim 6 in which the non-film-forming binder is added as dry binder particles, preferably premixed with the said particles.

8. A process according to any preceding claim in which the film forming polymer is used in an amount of at least 0.1% by weight, preferably at least 1% by weight, usually less than 25% and preferably less than 10% by weight based on the weight of the product granules.

9. A process according to any preceding claim in which the particles of detergent additive comprise a bleach component, preferably a bleach precursor or a bleach activator, most preferably tetraacetylethylenediamine.

10. A granular detergent composition containing the product of a process according to any preceding claim.

11. A composition according to claim 10 in which the particles comprise bleach activator and which further comprises a bleach component that is capable of being activated by the bleach activator in aqueous solution.

Patentansprüche

1. Verfahren, in welchem Teilchen eines Detergens-Additivs mit einer durchschnittlichen Teilchengröße im Bereich von 20 - 300 µm agglomeriert werden durch Befeuchtung, während man sie mit einer wäßrigen Flüssigkeit in Anwesenheit eines filmbildenden Polymers, das in Wasser bei pH 7 eine niedrigere Löslichkeit als in wäßriger Lösung bei pH 10 aufweist, mischt, dadurch gekennzeichnet, daß das Verfahren in zwei getrennten Stufen durchgeführt wird, wobei in der ersten Stufe die Teilchen mit der wäßrigen Flüssigkeit in Anwesenheit von filmbildendem Polymer in einem Hochscher-Mischer gemischt werden und in der zweiten Stufe das feuchte Produkt von Stufe 1 bei angehobener Temperatur getrocknet wird, und daß das agglomerierte Produkt eine durchschnittliche Teilchengröße im Bereich von 300 bis 1400 µm aufweist.

2. Verfahren nach Anspruch 1, in welchem das Polymer den Teilchen in Form einer wäßrigen Dispersion von Polymer-Teilchen zugesetzt wird.

3. Verfahren nach Anspruch 2, in welchem die Polymer-Teilchen eine Größe von weniger als 25 µm aufweisen.

4. Verfahren nach Anspruch 3, in welchem die Polymer-Teilchen eine Größe von weniger als 10 µm, vorzugsweise weniger als 5 µm, noch bevorzugter etwa 1 µm oder weniger, aufweisen.

5. Verfahren nach irgendeinem der Ansprüche 2 bis 4, in welchem die Polymer-Dispersion eine Emulsion ist, die vorzugsweise das Produkt einer Öl-in-Wasser-Polymerisation einer Emulsion von wasserunlöslichem ethylenisch ungesättigtem Monomer oder Monomer-Mischung ist.

6. Verfahren nach irgendeinem vorangehenden Anspruch, in welchem ein keinen Film bildendes Bindemittel, das vorzugsweise eine Stärke oder ein Cellulose-Derivat ist, einverleibt wird.

7. Verfahren nach Anspruch 6, in welchem das keinen Film bildende Bindemittel in Form trockener Bindemittel-Teilchen, vorzugsweise mit den Teilchen vorgemischt, zugesetzt wird.

8. Verfahren nach irgendeinem vorangehenden Anspruch, in welchem das filmbildende Polymer in einer Menge von

mindestens 0,1 Gewichts-%, vorzugsweise mindestens 1 Gewichts-%, üblicherweise weniger als 25 Gewichts-% und vorzugsweise weniger als 10 Gewichts-%, bezogen auf das Gewicht der Produkt-Körner, eingesetzt wird.

9. Verfahren nach irgendeinem vorangehenden Anspruch, in welchemdieDetergens-Additiv-TeilcheneineBleichmittel-Komponente, vorzugsweise eine Bleichmittel-Vorstufe oder einen Bleichmittel-Aktivator, am meisten bevorzugt Tetraacetylethylendiamin, umfassen.

10. Granuläre Detergens-Zusammensetzung, enthaltend das Produkt eines Verfahrens gemäß irgendeinem vorangehenden Anspruch.

11. Zusammensetzung nach Anspruch 10, in welcher die Teilchen Bleichmittel-Aktivator umfassen und die weiter eine Bleichmittel-Komponente umfaßt, die in wäßriger Lösung durch den Bleichmittel-Aktivator aktiviert werden kann.

Revendications

1. Procédé dans lequel les particules d'un additif détergent, ayant une taille particulaire comprise entre 20 et 300 µm, sont agglomérées par leur humectation cependant qu'elles sont mélangées avec un liquide aqueux en présence d'un polymère filmogène qui a dans l'eau à pH 7 une solubilité inférieure à celle observée dans une solution aqueuse à pH 10, procédé caractérisé en ce que le procédé est mis en oeuvre en deux étapes séparées ; dans la première étape du procédé, les particules sont mélangées dans un mélangeur à cisaillement élevé avec le liquide aqueux en présence du polymère filmogène et, dans la seconde étape, le produit humecté provenant de l'étage ou de l'étape 1 est séché à température élevée, et en ce que le produit aggloméré a une taille particulaire moyenne comprise entre 300 et 1 400 µm.

2. Procédé selon la revendication 1, dans lequel le polymère est ajouté aux particules en étant sous forme d'une dispersion aqueuse de particules du polymère.

3. Procédé selon la revendication 2, dans lequel les particules du polymère ont une taille inférieure à 25 µm.

4. Procédé selon la revendication 3, dans lequel les particules du polymère ont une taille inférieure à 10 µm, de préférence inférieure à 5 µm et encore mieux une taille voisine de 1 µm ou même inférieure.

5. Procédé selon l'une quelconque des revendications 2 à 4, dans lequel la dispersion du polymère est une émulsion, qui est de préférence le produit d'une polymérisation du type huile-dans-eau d'une émulsion d'un monomère ou d'un mélange de monomères à insaturation éthylénique, qui est insoluble dans l'eau.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel un liant non filmogène est incorporé, ce liant étant de préférence un amidon ou une fécule ou un dérivé de la cellulose.

7. Procédé selon la revendication 6, dans lequel le liant non filmogène est ajouté sous forme de particules sèches de liant, de préférence prémélangées avec lesdites particules.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère filmogène sert en une quantité d'au moins 0,1 % en poids, de préférence au moins 1 % en poids, habituellement moins de 25 % et de préférence moins de 10 % en poids, sur la base du poids des granules du produit.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel les particules de l'additif détergent comprennent un constituant à rôle de blanchiment, de préférence un précurseur d'agent de blanchiment ou un activateur de blanchiment, de façon extrêmement préférable de la tétraacétyléthylènediamine (TAED).

10. Composition de détergent granulaire contenant le produit d'un procédé selon l'une quelconque des revendications précédentes.

11. Composition selon la revendication 10, dans laquelle les particules comprennent de l'activateur de blanchiment et qui, en outre, comprend un constituant à rôle d'agent de blanchiment qui est capable d'être activé par l'activateur de blanchiment en solution aqueuse.