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# (54) Method for preparing a granular detergent material

Verfahren zur Herstellung eines Reinigungsproduktes in Granulatform

Procédé de préparation d'un produit détergent granulaire

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**EP-A- 0 108 429**
**CA-A- 1 056 687**
**DE-A- 2 340 882**
**US-A- 1 813 701**
**US-A- 3 329 616**
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**US-A- 4 207 197**

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## Description

The present invention relates to a method for preparing a granular detergent material. More in particular, it relates to a method for preparing said granules from a dusty soap powder.

Soap is a common ingredient of detergent powder compositions. It may be included as a detergent active, a builder or a foam suppressor. It may be added to a slurry which is subsequently spray-dried, or dry-mixed with other particulate ingredients, including composite particles which are themselves the product of a spray-drying process.

When supplied as a raw material for incorporating in such compositions, soap is often in the form of a fine dusty powder. As well as being messy in the handling, such powders have a tendency to cause respiratory tract irritation in those working with them.

Other detergent components, such as mentioned above, are also often provided in the form of fine powders. In the case of alkaline detergent components, such as soda ash, the dangers of handling these substances are even more pronounced.

As to soap, it is known to incorporate extruded soap "noodles" in detergent compositions, which have a "particle" size much greater than found in the aforementioned dusty powders. However, this is often done purely for visual appeal, e.g. when such noodles are deliberately coloured, and this is not a very cost-effective means of supplying the soap, especially when formulating dry mixed powders.

US-A-3,761,549 and US-A-3,588,950 describe a process of making non-dusty granulates by means of gas fluidisation in a rotating drum. Granules which, it is said, can be made in this way include those with a core of potassium soap coated with sodium soap, a core of a strong caustic detergent coated with a mild caustic detergent or a core of potassium soap with a coating of metasilicate. As described, the core is formed by interactions during the fluidisation process and the coating is applied by spraying-on the coating as a liquid.

According to US-A-2,730,507, non-dusting soap granulates are formed by mixing soap dust with fatty acid and an alkaline material which saponifies the acid. Thus, the resultant particles consist of two kinds of soaps.

Various other processes for making detergent granulates, are known in the art.

DE-A-2,340,882 provides a process for preparing a detergent composition, in which a spray-dried granule is wetted and subsequently coated with a builder salt.

CA-A-1,056,687 refers to a process for agglomerating detergent material by coating a mixtures of constituents (including sodium tripolyphosphate) with an alkaline detergent salt in the presence of water.

US-A-4,207,197 relates to a process for preparing an agglomerated granular detergent composition, wherein one or more inorganic particulate components are mixed with an agglomerating agent.

EP-A-075,250 discloses a process for preparing a metasilicate containing granule coated with tripolyphosphate.

US-A-3,329,616 relates to a process for preparing a detergent composition, wherein particles consisting of a builder salt are coated with a surfactant in the presence of water as a binder.

We have now found that non-dusting granules of a soap powder may be made in a simplified process, optionally in mixture with a wide variety of other materials.

In particular, we have now found that the soap powder can be worked into a substantially non-dusty form from a pre-mix comprising:

a) from 1-10% by weight of the binder;
b) up to 40% by weight of a dusty soap powder;
c) the balance being the granulising particles.

This pre-mix is used to prepare a granular detergent material having a core of granulising particles coated with a soap powder and a binder, comprising up to 40% by weight of the soap powder and from 1 to 10% by weight of the binder.

The dusty soap powder and the granulising particles are admixed intimately and the resultant product is then admixed with the binder to form said pre-mix. Mixing of the pre-mix then continues until the granular detergent material is formed.

Consequently, the present invention provides a method for preparing a granular detergent material having a core of a granulising particle coated with a mixture of a dusty soap powder and a binder, which detergent material contains up to 40 % by weight of said dusty soap powder and from 1 to 10 % by weight of said binder, said method consisting of the steps of:

(a) intimately admixing, for about 0.5 - 5 minutes, of granulising particles and the dusty soap powder followed by admixing therewith of the binder, and
(b) continued mixing of the thus obtained pre-mix composition for at least 3 minutes.

The physical structure of the granular detergent material obtained by the method according to the invention can

vary. However, it is believed that the granulising particles are coated with the soap powder and the binder.

This granular detergent material is considerably less dusty than, for instance, known fine soap powders, yet the process defined above for its production is more cost-effective than extrusion techniques.

In the context of the specification, "granulating" as an adjective is used to refer to components which are capable of being processed to form compositions comprising granules. On the other hand, "granulising" is used to refer to particles which are capable of acting on other substances, during processing, to transform those substances into granules.

The granules obtained are, by themselves, suitable for incorporation in complete detergent powder compositions which also comprise one or more synthetic detergent actives selected from anionic, nonionic, cationic, zwitterionic or amphoteric surfactants. These complete compositions preferably also contain other ingredients usual in such powders, for example detergency builders (i.e. substances which sequester and/or precipitate calcium ions contributing to water hardness), soil-suspending and anti-redeposition agents, corrosion inhibitors, buffers, bleaches (including low-temperature systems comprising a bleach precursor and an activator therefor), enzymes, enzyme stabilisers, lather boosters or foam depressors, dyes, pigments, fluorescers and perfumes etc.

Soap-containing complete detergent powder compositions for which soap-containing granules according to the present invention are well suited to formulating include those generically and specifically described in patent specification EP-A-117,568.

As well as the soap powder, the base mixture also contains the granulising particles. Thus, it is preferred and desirable that these should have a beneficial effect in the complete composition. Therefore, it is preferred that the granulising particles should be of one or more substances which are usual ingredients in detergent powders such as recited in the preceding paragraph.

One preferred class of granulising particles comprises neutral and alkaline salts of alkali metal cations and organic or inorganic anions, into which class fall many of the aforementioned "usual ingredients" (which will be mentioned in more detail hereinbelow). For example, especially preferred salts are the alkali metal metasilicates (preferably hydrated), for example sodium metasilicate 5 aq. which is a corrosion inhibitor/alkaline buffer. Examples of other suitable salts are alkali metal orthophosphates, pyrophosphates and tripolyphosphates, such as potassium pyrophosphate 3 aq. and anhydrous sodium tripolyphosphate.

Alternatively, it is possible to use granulising particles which will have no particular benefit when incorporated in a complete detergent composition; so in that case, one would either have to accept their presence in the composition and accept the ensuing increase in costs.

For all granulising particles, whether salts or otherwise, as a general rule it is preferred that they should not be too pervious to water, which is why the salts should be hydrated. The granulising particles should also be capable of surviving without fragmentation in the mixing apparatus used (vide infra).

In general, the soap powder may be of any kind, provided it is compatible with the binder, the granulising particles and the mixing apparatus. On the latter point, it is believed to be important that it should not soften too much or melt with the heat of mixing, although some softening may aid the granulation process. Generally it will be added to the mixer in the form of the known fine dusty powders, in order to convert it to a more acceptable form. However, in some circumstances it may be possible to add them as larger particles or even lumps, depending on the type of mixer, the kind of soap powder and the working temperature. Amongst soaps which are capable of producing extremely good quality granules by this invention are tallow and hardened fish/rape soaps. In the case of softer soaps, better results may be obtained if the mixture is cooled during processing.

The binder is capable of bonding the fine detergent component particles to form and maintain granules thereof and to enable them to coat the granulising particles. Thus, it should be compatible with the soap powder and with the granulising particles. It should also possess a "setting property", either alone or by interaction with the soap powder. The binder comprises an aqueous solution of a polyacrylate polymer and/or neutral waterglass, or water. Generally, these substances will be used at aqueous concentrations at which the liquid is viscous and 'sticky'. Thus, for example, waterglasses may be in solutions from about 25% to about 50% by weight, typically around 34% by weight. It is also possible to utilise gums. The binder may also contain other ingredients such as dyes, optical brighteners.

Amongst the ingredients mentioned above in respect of complete detergent powder compositions are the synthetic anionic, nonionic, cationic, zwitterionic and amphoteric surfactants. These will be well known to those skilled in the art and, for example, may be selected from the classes, sub-classes and individual agents described in "Surface Active Agents", Vol. I by Schwartz & Perry (Interscience 1949) and "Surface Active Agents", Vol. II by Schwartz, Perry and Berch (Interscience 1958).

The preferred but optional other ingredients of the complete composition are the "usual ingredients". Most important of these are the detergency builders. Those which are crystalline, and in some cases amorphous, inorganic or non-polymeric organic salts may either be added to the complete detergent powder composition and/or constitute the granulising particles. This class includes water-soluble alkali metal phosphates, triphosphates, polyphosphates, silicates, borates, and also carbonates. Specific examples of such salts are sodium and potassium triphosphates, pyrophos-

phates, orthophosphates, hexametaphosphates, tetraborates, neutral silicates and carbonates.

Also in this class are the crystalline and amorphous zeolites and aluminosilicates. One such aluminosilicate is an amorphous water-insoluble hydrated compound of the formula $Na_x(AlO_2.SiO_2)_y$, wherein x is a number from 1.0 to 1.2 and y is 1, said amorphous material being further characterised by an $Mg^{++}$ exchange capacity of from 50 mg eq. $CaCO_3$/g to about 150 mg eq. $CaCO_3$/g and a particle diameter of from about 0.01 micron to about 5 microns. This ion exchange builder is more fully described in GB-A-1 470 250.

A second such water-insoluble synthetic aluminosilicate ion exchage material is crystalline and has the formula $Na_z[(AlO_2)_y(SiO_2)]$ x $H_2O$, wherein z and y are integers of at least 6; the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264, said aluminosilicate ion exchange material having a particle size diameter from about 0.1 micron to about 100 microns; a calcium ion exchange capacity on an anhydrous basis of at least about 200 milligrams equivalent of $CaCO_3$ hardness per gram; and a calcium ion exchange rate on an anhydrous basis of at least about 2 gralns/gallon/minute/gram. These synthetic aluminosilicates are more fully described in GB-A-1 429 143.

Examples of suitable organic builder salts in this class are:

(1) water-soluble amino polycarboxylates, e.g. sodium and potassium ethylene diamine tetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)-nitrilodiacetates;

(2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates (see US-A-2 379 942);

(3) water-soluble polyphosphonates, including specifically sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylene diphosphonic acid; sodium, potassium and lithium salts of ethylene di-phosphonic acid; and sodium, potassium and lithium salts of ethane-1,1,2-triphosphonic acid.

Other examples include the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethane diphosphonic acid, carboxyl diphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid, propane-1,1,2,3,-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid. Further examples are alkylmalonates, alkylsuccinates, alkylsulphocarboxylates and carboxymethyloxymalonates. These include the salts of the free acids or of esters thereof. Other polycarboxylate builders which can be used satisfactorily, include water-soluble salts of mellitic acid, citric acid, and carboxymethyloxy succinic acid and salts of polymers of itaconic acid and maleic acid.

Builders which would normally be added only to the complete composition (unless formulated into a substantially non-water pervious forms) are the polymer builders.

Amongst these polymer builders are the water-soluble salts of polycarboxylate polymers and copolymers as described in U.S. Patent specification No. 3 308 067.

Other usual ingredients which may be used as the granulising particles (as well as or alternatively being added in the complete composition are the oxygen bleaches such as alkali metal peroxygen compounds (perborates, percarbonates, etc.) as well as activators therefor. A large number of such activators is known, but one preferred agent in the context of this invention, especially as the granulising particles, is N,N,N',N'-tetraacetyl ethylenediamine, otherwise known as TAED.

The foregoing list of usual ingredients for use as the granulising particles or in the complete composition is not exhaustive and in the light of the teaching herein, a wide range of alternatives will now be appreciated by the skilled worker in this art.

The method for preparing the granular detergent material, according to the invention as described above, may be applied, using any mixing apparatus according to the scale intended but the Lödige (Trade Mark) batch-type of mixers, for example the FKM-range, are especially preferred.

In the Lödige batch-type of mixer, it has been found that the dusty soap powder and the granulising particles should to be admixed for about half to about 5 minutes (typically about 3); the binder is then added in an amount which by simple trial and error will be found to yield the best formed particles with minimum lumps present. A good guide is to add the binder slowly until the mix just takes on a slightly wet appearance. Below this concentration there is an increasing tendency for the granules to form imperfectly. Above this level, there is a progressive tendency for the mixture to stick to the knives of the mixer and eventually form lumps which contaminate the final product. After addition of the binder, mixing is continued for at least 3 minutes, most preferably for 5 or even 10 minutes, the best results being obtained after about 15 minutes or more.

The binder is added in an amount of about 1 to about 10% by weight, but we have found that in most situations the optimum is in the range from about 5 to about 7%. Generally speaking, the more dusty soap powder is present, the more binder is needed. It is possible to granulate up to 40% by weight of soap powder in the total composition by this method, but normally this will be from about 25 to about 38%. In most situations, the balance of the pre-mix will consist only of the granulising particles, but optionally small amounts of other components may also be present.

Granulising particles may be chosen from amongst a very wide range of particle sizes. Here, average particle size means the diameter value in which 50% of the particles are larger and 50% are smaller. Of course, the particles will not be as small as the fine dusty detergent component referred to previously. In general, the average particle size will be from about 75 μm to about 4,000 μm, preferably from about 250 μm to about 2,500 μm.

The invention will now be explained better by way of the following non-limiting Examples.

Examples 1-3

The following compositions were prepared by mixing of soap and granulising particles for three minutes in a Lödige M 20 (a batch-type of mixer), followed by addition of the binder and continued mixing for a further 15 minutes. In all cases the resulting product was a granular mixture. The products had the consistency shown. All amounts are percentages by weight.

| | Example | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Soap (1) | 37 | 27 | 26 |
| Granulising particles (2) | 57 | 60 | 67 |
| Binder (3) | 6 | 5 | 7 |
| Consistency | good | quite good (dusty tendency) | quite good (sticky tendency) |

(1) The soap had the following composition:

Fatty acid 95.7 weight %, water 4.4 weight %.

Fatty acid composition:

| | % wt | | % wt |
|---|---|---|---|
| C12 | 0.3 | C18 | 16.4 |
| C14 | 2.8 | C18 (i) | 40.3 |
| C16 | 24.8 | C18 (ii) | 4.3 |
| C16 (i) | 3.5 | C18 (iii) | 0.2 |
| C17 | 1.2 | C20 | 1.2 |
| C17 (i) | 0.7 | | |

(i), (ii), (iii) refer to the number of double bonds in the acid chain (degree of unsaturation).

(2) Sodium metasilicate 5 aq.

(3) Sodium waterglass (34% by weight in water)

| Particle Size Distribution (%) | | | |
|---|---|---|---|
| <180 μm | 21.1 | >500 μm | 16.6 |
| >180 μm | 13.3 | >710 μm | 11.2 |
| >250 μm | 28.4 | >1000 μm | 9.5 |

Examples 4-6

To compare different granulising particles, the following were prepared. In all cases the resulting product was good non-dusty, non-sticky granules. Amounts are in percentages by weight.

| | Example | | |
|---|---|---|---|
| | 4 | 5 | 6 |
| Soap (1) | 31 | 31 | 31 |
| Granulising particles (2) | 60(a) | 60(b) | 60(c) |
| Binder (3) | 9 | 9 | 9 |

(1), (3) as Examples 1-3

(2) (a) Anhydrous sodium tripolyphosphate
(b) Potassium pyrophosphate 3 aq.
(c) as Examples 1-3

Example 7 ( comparative )

Examples 1-3 were repeated, using as the dusty detergent component a mixture of :

| | |
|---|---|
| Alkyl benzene sulphonate | 18.0 |
| Burkeite adjunct | 20.0 |
| Soap | 4.0 |
| Sodium carboxymethyl cellulose | 0.5 |
| Savinase (enzyme) | 0.65 |
| Perfume | 0.35 |
| Na-metasilicate 5 aq. | 6.0 |

the granulising particles :

| | |
|---|---|
| STP | 48.5 |

binder :

| | |
|---|---|
| Na-waterglass solution, 34% | 2.0 |

A free-flowing mixture of granular particles was obtained having excellent powder properties.

**Claims**

1. A method for preparing a granular detergent material having a core of a granulising particle coated with a mixture of a dusty soap powder and a binder comprising an aqueous solution of either neutral water glass and/or a poly-acrylate polymer, or water, which detergent material contains up to 40% by weight of said dusty soap powder and from 1 to 10% by weight of said binder, said method consisting of the steps of:

   (a) intimately admixing, for about 0.5. - 5 minutes, of granulising particles and the dusty soap powder followed by admixing therewith of the binder, and
   (b) continued mixing of the thus obtained premix composition for at least 3 minutes.

2. A method as claimed in claim 1, wherein the continued mixing of the premix composition is carried out for at least 5 minutes.

3. A method as claimed in claim 1 and claim 2, wherein the granulising particle comprises crystals of a salt of an alkali metal cation and an organic or inorganic anion.

4. A method as claimed in claim 3, wherein said crystals are selected from alkali metal metasilicates and alkali metal orthophosphates, pyrophosphates and tripolyphosphates and mixtures thereof.

5. A method as claimed in any one of claims 1 to 4, wherein the granulising particles have an average size in the range of from 75 μm to 4,000 μm.

**Patentansprüche**

1. Verfahren zur Herstellung eines Reinigungsmittels in Granulatform mit einem Kern aus einem granulierenden Teilchen, beschichtet mit einem Gemisch aus einem staubförmigen Seifenpulver und einem Bindemittel, das eine wässerige Lösung von entweder neutralem Wasserglas und/oder einem Polyacrylatpolymer oder Wasser umfaßt, wobei der Waschmittelstoff bis zu 40 Gew.-% des staubförmigen Seifenpulvers und 1 bis 10 Gew.-% des Bindemittels enthält, wobei das Verfahren aus den Schritten besteht:

   (a) inniges Anmischen für etwa 0,5 bis 5 Minuten von granulierenden Teilchen und dem staubförmigen Seifenpulver gefolgt von Anmischen des Bindemittels damit und
   (b) Fortführen des Mischens der so erhaltenen Vormischungszusammensetzung für mindestens 3 Minuten.

2. Verfahren nach Anspruch 1, wobei das fortführende Mischen der Vormischungszusammensetzung für mindestens 5 Minuten ausgeführt wird.

3. Verfahren nach Anspruch 1 und 2, wobei das granulierende Teilchen Kristalle eines Salzes von einem Alkalimetallkation und einem organischen oder anorganischen Anion umfaßt.

4. Verfahren nach Anspruch 3, wobei die Kristalle ausgewählt sind aus Alkalimetallmetasilicaten und Alkalimetallorthophosphaten, Pyrophosphaten und Tripolyphosphaten und Gemischen davon.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die granulierenden Teilchen eine durchschnittliche Teilchengröße im Bereich von 75 μm bis 4000 μm aufweisen.

**Revendications**

1. Procédé pour préparer une matière détergente granulaire ayant un noyau d'une particule de granulation revêtue d'un mélange d'une poudre de savon pulvérulente et d'un liant comprenant une solution aqueuse soit d'un verre soluble neutre et/ou d'un polymère polyacrylate, soit de l'eau, ladite matière détergente contient jusqu'à 40% en poids de ladite poudre de savon pulvérulente et de 1 à 10% en poids dudit liant, ledit procédé comprenant les étapes consistant:

   (a) à mélanger intimement, pendant environ 0,5 à 5 minutes, les particules de granulation et la poudre de savon pulvérulente suivi par un mélange du liant avec eux, et
   (b) à continuer à mélanger la composition de prémélange ainsi obtenue pendant au moins 3 minutes.

2. Procédé selon la revendication 1, dans lequel on effectue le mélange continu de la composition de prémélange pendant au moins 5 minutes.

3. Procédé selon la revendication 1 et la revendication 2, dans lequel la particule de granulation comprend des cristaux d'un sel d'un cation de métal alcalin et d'un anion organique ou minéral.

4. Procédé selon la revendication 3, dans lequel on choisit lesdits cristaux parmi les métasilicates de métal alcalin et les orthophosphates, les pyrophosphates et les tripolyphosphates de métal alcalin et leurs mélanges.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel les particules de granulation ont une granulométrie moyenne dans la gamme de 75 µm à 4 000 µm.