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(54) METHOD FOR PREPARING CO-GRANULES, CO-GRANULES THUS OBTAINED AND USE THEREOF AS A COMPONENT IN DETERGENT COMPOSITIONS

VERFAHREN ZUR HERSTELLUNG VON COGRANULATEN, HIERAUS ERHALTENE COGRANULATE UND VERWENDUNG ALS KOMPONENTE IN WASCHMITTELZUSAMMENSETZUNGEN

PROCEDE POUR PREPARER DES CO-GRANULES, CO-GRANULES AINSI OBTENUS ET LEUR UTILISATION COMME CONSTITUANT DANS DES COMPOSITIONS DETERGENTES

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(56) References cited:

EP-A- 0 283 885	**EP-A- 0 574 685**
WO-A-95/20030	**DE-A- 3 624 336**

- **DATABASE WPI Section Ch, Week 7939 Derwent Publications Ltd., London, GB; Class D25, AN 79-70971B & JP,A,54 106 509 (LION FAT & OIL KK) , 21 August 1979**
- **Römpp Chemie Lexikon, 9th. ed., Georg Thieme Verlag edit., page 4719 (1992)**
- **Kirk-Othmer Encyclopedia of Chemical Technology, 3rd. ed., J. Wiley & Sons edit., vol. 20, page 855**
- **J.G. Vail Soluble Silicates, Einhold Pub. Corp. edit., vol. 1, pages 72 and 98 (1952)**

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Description

[0001] The present invention in the first place relates to a method for preparing co-granules as a component for and for incorporation in detergent compositions, which method comprises:

- preparing a solution or a slurry of at least
- an alkali metal citrate, and
- sodium disilicate,
- drying the mixture,
- compacting the dried product, and
- breaking up and sieving the compacted product.

[0002] The term "granule" is to be interpreted broadly and is intended to comprise various particulate forms such as granulate, coarse powder, tablets and noodles. Dishwashing compositions frequently consist of granules of one particular inorganic compound such as e.g. alkali silicate and these compositions often contain the other ingredients in the form of different particles e.g. of organic compounds etc. The granules, frequently silicate granules often dissolve only with difficulty. They lead to the formation of fines (dust).

[0003] A method for the preparation of granular alkali detergent compositions, comprising sodiummetasilicate, i.e. having an SiO_2/Na_2O molar ratio of 1, is described in EP-A-0 283 885, in which a mixture of the components is compacted, broken up and sieved. However, the ingredients are mixed together in dry form and subsequently compacted. In order to incorporate finely powdered components such as pentasodiumtriphosphate and zeolite NaA, at least two of the ingredients, including said finely powdered components are agglomerated and dried before being mixed with other dry components, like silicate, in the compaction step. In these granules, sodium salts of nitrilotriacetic acid or polymeric carboxic acids may be incorporated.

[0004] In silicate granules, segregation of different types of granular components (e.g. bleach system and enzymes or other usual ingredients) can take place. The problems are aggravated by the fact that silicate granules having a molar ratio SiO_2/Na_2O between 1.8 and 3.0 and a moisture content of below about 22% by weight dissolve only with considerable difficulty. Moreover, alkali silicate granules with a homogeneous distribution of moisture are difficult to obtain. Usually less moisture is present in the outer skin than in the inside, which is a consequence of drying and which reduces solubility during use.

[0005] Preparation of granules of builders e.g. phosphate replacing builders like di-, tri- or tetracarboxylic acid is difficult and therefor relatively expensive.

[0006] In this respect mention is made of EP-A-0 574 685 (Haarmann & Reimer Corp.) which relates to a method for the production of detergent builder formulations comprising granules of citric acid or an alkali metal salt thereof in combination with a detergent builder. Citric acid or a salt thereof is spray granulated form its partially purified fermentation broth in order to form free flowing granules. Detergent builders may be added to the fermentation broth of introduced during spray granulation in order to form granules which include such detergent builders.

[0007] Another method for preparing co-granules useful in detergent compositions is known inter alia from EP-A-0 421 664 (Rohm and Haas Company) disclosing a method for preparing a polymer containing granulate containing 20% by weight of polymer and at least 20% by weight of a water soluble inorganic compound. Such compounds are preferably sulphates, carbonates or silicates. Also other phosphate replacing builders may be present such as zeolites, carbonates, nitrilotriacetic acid, citric acid, tartaric acid, salts thereof, phosphonates etc. The examples disclose granules containing polymer and sodium sulphate or sodium carbonate.

[0008] The object of the present invention is to provide a method for preparing co-granules having a good solubility in water, giving less fines during handling, having a more even distribution of moisture, and preventing segregation of at least those ingredients included in the co-granules, which can be conveniently prepared.

[0009] According to the invention, this object is achieved by a method for preparing co-granules as a component for and for incorporation in detergent compositions, at least comprising an alkali metal citrate and sodium disilicate, which method comprises preparing a solution or a slurry of the ingredients, drying the mixture, compacting the dried product and breaking up and sieving the compacted product.

[0010] In connection with the invention reference is also made to JP-A-54 106 509, disclosing the preparation of spray dried granulated detergent compositions comprising a surfactant, an alkali metal silica salt and a phosphate salt. In the process of preparation an acid type surfactant or an organic acid such as citric acid is added to control the molar ratio of $SiO_2:M_2O$.

[0011] Usually a slurry is prepared in water and the mixture is dried by means of suitable drying techniques, like a turbine dryer e.g. a Turbogranulation dryer ex. Vomm-Turbo Technology, VOMM IMPIANTI E PROCESSI S.r.l., Milan, Italy.

In EP-A-0 526 978 it is disclosed that silicates can be simultaneously dried and granulated in this dryer. However, this dryer is less suited for the combined drying and granulation to produce co-granules containing substantial quantities of organic ingredients in conjunction with silicate. Due to the high attrition between the rotating blades and the film formed on the wall during the granulation phase, local overheating can cause partial decomposition of the organic ingredients, leading to (local-) coloring.

[0012] Drying can also conveniently be achieved by spray drying the slurry by a conventional technique using a spray tower in which the slurry is atomized and dried in a hot air stream. The conditions in the spray tower, when drying silicate or mixtures, containing silicate can be controlled in such a manner, that the bulk density, the particle size and shape can be optimised.

[0013] In order to achieve maximum solubility it is preferred to produce a powder product consisting of either small particles (below 100 microns) or hollow spheres with a particle size up to approximately 400 microns. After drying the resulting powder can be granulated, optionally after milling in a granulation process, e.g. using a Lõdige plow share mixer. For granulation usually a small amount of moisture is added. The powders obtained in a turbine dryer generally have a wider particle size distribution as part of the product is gathering at the wall creating larger particles. Furthermore it will be very difficult to produce hollow spherical particles in a turbine dryer.. Hollow particles have better accessibility and consequently a better solubility.

[0014] Furthermore powder particles obtained in a turbine dryer are less homogeneously dried as a result of their larger particles being more effectively dried at the outside and as a result of the difference in residence time between particles remaining in the gas stream and those sticking on the (heated) wall of the dryer.

[0015] Consequently fluidized bed drying results in a more even distribution of moisture and in better accessible particles.

[0016] It is also possible to spray the slurry onto fine particles while drying to form gradually growing granules. This can be performed in e.g. an AGT-unit for continuous drying and granulation ex Glatt-GmbH/Process Technology, Binzen, Lörrach, Germany.

[0017] Another possibility is to spray the slurry in a rotary drum granulator onto fines building up coarser particles followed by, or in conjunction with drying. The spray-on techniques lead to granules with a homogenous distribution of moisture and consequently a better solubility.

[0018] Such granules however comprise a relatively poor attrition resistance and provide a considerable dust problem during handling thereof. Further disadvantages of such processes are that it is extremely difficult to avoid caking of the product leading to large lumps. these processes also lead to more massive particles with less homogeneous distribution of the residual moisture, leading to worse dissolution.

[0019] If however, according to the invention the dried powder or the dried granulated product is subjected to a compacting treatment, an excellent product can be obtained, which shows no dust problem as a consequence of the high attrition resistance with a more homogeneous distribution of moisture, minimising the risk of segregation in the detergent compositions and in which the use of separate builders can be avoided. The product obtained shows no dust problems as a consequence of the high attrition resistance and also has a relatively high bulk density.
Preferably compaction is performed at a temperature between 0 and 90°C and more preferably between 20 and 50°C. The pressure depends on the method of compaction, i.e. the device used and the material which is to be compacted.

[0020] Preferably the moisture content of the dried product before compaction is adjusted to at least 5-25% (w/w), which further improves the bulk density and attrition resistance of the end product.

[0021] Compacting per se is known in the art. In this respect reference is made to US-A-3 875 282 (Stauffer), US-A-3 931 036 (Philadelphia Quartz) and US-A-2 463 680 (Wyandotte).

[0022] Compacting can be performed by a number of methods, however for the present method it is preferred that compaction is performed by passing the dry mixture between rollers forming a film. Such a film will expediently have a thickness of 1-10 mm. Compaction can also expediently be performed by making tablets.

[0023] Compaction can be carried out between two rollers in a continuous process as offered by the firm Alexanderwerke AG in Remscheid, Germany or in a tabletting operation.

[0024] The effectiveness of the compaction process depends on the pressure exerted on the powder layer/film and the temperature. In an Alexanderwerke unit, the pressure is exerted hydraulically on one of the rollers. The powder is pressed through the rollers and the dosing rate determines the thickness of the film, which is normally a few millimetres only. The minimum pressure needed to granulate the powders in a standard Alexanderwerke unit having rollers with a diameter of 48 cm and a length of 26 cm is about 130 bar. The maximum pressure the equipment tolerates is slightly above 200 bar. The temperature is controlled by internal cooling of the rollers. The temperature range that can be used is between 0 and 80% and preferably 20-50°C.

[0025] To provide granules with the desired particle size it is preferred to break up the compacted product and to sieve.

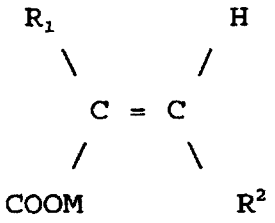
[0026] Advantageously the fines resulting from said sieve operation are returned to the dried product before compaction and the resulting oversize particles are returned to the breaking step. Although it is also possible to return the fines to the starting slurry. The oversize particles can advantageously be returned to the breaking operation.

[0027] Part of the alkali metal salt of citric acid, e.g. 30% can be replaced by a lower hydroxymonocarboxylic acid e.g. lactic acid.

[0028] Partial salts of the carboxylic acid in which one or more of the hydrogen ions of the carboxylic groups are replaced by metal ions are particularly useful. Especially sodium and potassium salts can be used with good results for the purpose of this invention. Potassium salts are sometimes preferred because of their higher solubility. The use of sodium citrate in the co-granules according to the present invention is preferred.

[0029] Sodium disilicate is used with special advantage.

[0030] In another preferred embodiment of the invention the co-granules further comprise at least one polymeric compound being either an acid and/or a salt of a polycarboxylic acid polymer or a polypeptide. Suitable polycarboxylic acid polymers comprise e.g. a water-soluble homopolymer or copolymer having a molecular weight of at least 500. It may be derived from a monocarboxylic acid or from a di-, tri- or polycarboxylic acid. The polymer will normally be used in the form of its water-soluble alkali metal salt form. One group of polymer materials found to be of value comprises homopolymers derived from a monomer of the formula:



wherein R_1 is hydrogen, hydroxyl, C^1-C^4 alkyl or alkoxy, acetoxy, or $-CH_2COOM$; R^2 is hydrogen, C^1-C^4 alkyl or -COOM and M is an alkalimetal. Examples of this group include the sodium and potassium salts of polyacrylic, polymethacrylic, polyitaconic, polymaleic and polyhydroxyacrylic acids and also the hydrolysis products of the corresponding polymerised acid anhydrides. Thus the polymer obtained by hydrolysis of maleic anhydride falls within this group. Suitable polypeptides which can be incorporated in the co-granules according to the present invention are e.g. polyaspertate and polyglutamate.

[0031] A second group of suitable polymeric materials comprises the copolymers of two or more carboxylic monomers of the above formula. Examples of this group include the sodium and potassium salts of copolymers of maleic anhydride with acrylic acid, methacrylic acid, crotonic acids, itaconic acid and its anhydride and/or aconitic acid. A third group of suitable polymeric materials comprises the copolymers of one carboxylic monomer of the above formula and two or more non-carboxylic acid monomers such as ethylene, propylene, styrene, alphamethylstyrene, acrylonitrile, acrylamide, vinylacetate, methylvinylketone, acrolein and esters of carboxylic acid monomers such as ethyl acrylate and methacrylate.

[0032] It is also advantageous if the co-granule further comprises at least one inorganic salt of the group consisting of alkali metal tripolyphosphate, alkali metal carbonate/bicarbonate/sesquicarbonate, alkali metal sulphate. (One of the advantages of incorporating such an inorganic salt is that it increases the solubility of the co-granule because these salts dissolve rapidly and thereby convert the co-granule to an open sponge-like structure so that the surface area of the granule is increased which leads to an increase of the solubility of the remaining solid material consisting especially of silicate).

[0033] Most of the salts also act as a builder reinforcing detergent activity. Non-phosphate inorganic salts as various carbonates especially alkali metal carbonate/bicarbonate/sesquicarbonate are preferred. In the co-granule the inorganic salts are usually present in the form of their lower stable hydrate(s).

[0034] In the method according to the invention the solution or slurry is preferably prepared by adding citric acid to a solution containing sodium disilicate, neutralising the carboxylic acid with alkali, optionally adding further ingredients as to obtain a solution or slurry with a water content of 30-60% (w/w), which solution or slurry is subsequently dried and compacted. The various ingredients of the solution or slurry can be used in the form of solid dry of hydrated forms, to which water is added.

[0035] An other aspect of the invention provides co-granules obtainable by the method according to the invention.

[0036] Preferably said co-granules have a bulk density of at least 700 g/dm^3, more preferably above 800g/dm^3, and most preferably a bulk density between 900 g/dm^3 and 1200 g/dm^3. High bulk densities are desirable at present, to be able to provide final detergents compositions with a relatively high specific weight.

[0037] The particle size of the co-granules according to the present invention is not critical however, it is preferred that the co-granules have an average particle size of 100 to 1500 micrometer, more preferably an average particle size of 400-900 micrometer and a Rosen Rammler N-value above 2.5. Particle size determination and the definition and determination of the Rosen Rammler N-value is described in detail in "Small Particle Statistics" by Herdan, C; second revised edition; Butterworth, London 1960, in particular page 86-101. Graph paper according to DIN 1171 (new) is often used to determine the N-value.

[0038] One of the preferred compositions of the co-granules according to the invention is:

5-90%	(w.w.)	sodium disilicate;
5-90%	(w.w.)	alkali metal salt of citric acid;
0-20%	(w.w.)	polymer;
0-40%	(w.w.)	alkali metal tripolyphosphate;
0-40%	(w.w.)	alkali metal (bi)carbonate, or sesquicarbonate;
0-10%	(w.w.)	organic phosphonate;
0-60%	(w.w.)	alkali metal sulphate;
5-25%	(w.w.)	moisture.

[0039] The organic phosphonates which can be present in the co-granules according to the present invention are e. g. the various organic polyphosponates, e.g. of the Dequest® range, which are especially added to phosphate-free machine dishwashing compositions. A drawback of these polymers is that some of them are not quite biodegradable and therefore environmentally less acceptable. Therefore some of the polyphosphonates, whilst being effective, are less acceptable as being P-containing products.

[0040] Additionally, minor ingredients may be incorporated in the composition. Said ingredients are here to be understood compounds like, the well-known enzyme stabilizers such as the polyalcohols, e.g. glycerol, and borax; anti-scaling agents; crystal-growth inhibitors, threshold agents; thickening agents; perfumes and dyestuffs and the like. Also a small amount of low- to non-foaming nonionic surfactant, which includes any alkoxylated nonionic surface-active agent wherein the alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof, is preferably used to improve the detergency and to suppress excessive foaming due to some protein soil. However, an excessive proportion of nonionic surfactant should be avoided. Normally, an amount of 0.1 to 5% by weight, preferably from 0.5 to 4% by weight, is quite sufficient.

[0041] Examples of suitable nonionic surfactants for use in the invention are the low- to non-foaming ethoxylated straight-chain alcohols of the Plurafac® RA series, supplied by the Eurane Company; of the Lutensol® LF series, supplied by the BASF Company and of the Triton® DF series, supplied by the Rohm & Haas Company.

[0042] The present invention in a third aspect provides a detergent composition comprising co-granules according to the invention. Preferably such a detergent composition comprises at least 40% of co-granules according to the invention and a bleach system and/or an enzyme system.

[0043] The bleach system and/or an enzyme system is then usually added in the form of separate particles which may have the same particle size distribution as the co-granules; also it is usually advantageous if the bulk density of these particles is comparable to that of the co-granules.

[0044] Preferably the detergent composition consists for at least 50% of co-granules according to the invention, and less than 30% of a bleach system and an enzyme system.

[0045] Enzymes are used for many purposes in various fields where biochemical reactions occur. In general, an enzyme can be described as a catalyst capable of permitting a biochemical reaction to quickly occur and can be classified according to the type of reaction they catalyze. Enzymes are characterized by a high specificity, that is to say, each enzyme can catalyze a single reaction of one substance or a very small number of closely related substances.

[0046] Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removability. Well-known and preferred examples of these enzymes are proteases, lipases and amylases. Lipases are classified as EC class 3, hydrolases, subclass EC 3.1., preferably carboxylic ester hydrolases EC 3.1.1. An example thereof are lipase 3.1.1.3 with the systematic name glycerol ester hydrolases. Amylases belong to the same general class as lipases, subclass EC 3.2, especially EC 3.2.1 glycose hydrolases such as 3.2.1.1 alpha-amylase with the systematic name alpha-1,4-glucan-4-glucanohydrolase; and also 3.2.1.2, beta-amylase with the systematic name alpha-1,4-glucan maltohydrolase. Proteases belong to the same class as lipases and amylases, subclass EC 3.4, particularly EC 3.4.4. peptide peptido-hydrolases such as EC 3.4.4.16 with the systematic name subtilopeptidase A.

[0047] Obviously the foregoing classes should not be used to limit the scope of the invention. Enzymes serving different functions can also be used in the practice of this invention, the selection depending upon the composition of biochemical soil, intended purpose of a particular composition, and the availability of an enzyme to degrade or alter the soil.

[0048] Lipases, sometimes called esterases, hydrolyse fatty soils. Lipases suitable for the use herein include those of animal, plant and microbiological origin. Suitable lipases are also found in many strain of bacteria and fungi. For example, lipases suitable for use herein can be derived from **Pseudomonas, Aspergillus, Pneumococcus, Staphylococcus,** Toxins, **Mycobacterium Tuberculosis, Mycotorula Lipolytica,** and Sclerotinia microorganisms, and can. be made using recombinant DNA manufacturing techniques.

[0049] Suitable animal lipases are found in the body fluids and organs of many species. A preferred class of animal lipase herein is the pancreatic lipase.

[0050] Lipase can be employed in the present cleaning compositions in an amount from about 0.005% to about 10%, preferably from 0.01 to 5% of the cleaning composition, on a pure enzyme basis.

[0051] The enzymes most commonly used in machine dishwashing compositions are amylolytic enzymes.

[0052] The amylolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in British patent specification No. 1,296,839, cultivated from the strains of **Bacillus lichenifonrmis** NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11 945, ATCC 8480 and ATCC 9945 A. Examples of such amylolytic enzymes are amylolytic enzymes produced and distributed under the trade name of SO-95® or Termamyl® by Novo Industri A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram.

[0053] The amylolytic activity can be determined by the method as described by P. Bernfeld in "Method of Enzymology", Vol. I (1955), page 149.

[0054] The compositions of the invention preferably also contain a proteolytic enzyme.

[0055] Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of **B. subtilis** and **B. licheniformis,** such as the commercially available subtilisins Maxatase® supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase®, supplied by Novo Industri A/S, Copenhagen, Denmark.

[0056] Particularly suitable is a protease obtained form a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available from Novo Industri A/S under registered trade names of Esperase® and Savinase®. The preparation of these and analogous enzymes is described in GB-A-1 243 784.

[0057] Another suitable protease useful herein is a fairly recent commercial product sold by Novo Industri A/S under the trade name Durazym®, as described in WO-A-89/06279. The enzymes are generally presented as granules, e.g. marumes, prills, T-granules etc., and may have enzyme activities of from about 500 to 1700 glycine units/milligram. The proteolytic activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology", Vol. 22 (1938), page 79 (one Anson Unit/g = 733 Glycine Units/milligram).

[0058] All these enzymes can each be present in a weight percentage amount of from 0.2 to 5% by weight, such that for amylolytic enzymes the final composition will have amylolytic activity of from 10^2 to 10^6 Maltose units/kg, and for proteolytic enzymes the final composition will have proteolytic enzyme activity of from 10^6 to 10^9 Glycine Units/kg.

[0059] The detergent composition may also comprise a bleach system encapsulated or not. The bleach system may be a chlorine-or bromine-releasing agent or a peroxygen compound. Among suitable reactive chlorine- or bromine-oxidizing materials are heterocyclic N-bromo- and N-chloro imides such as trichlorosio-cyanuric, tribromoisocyanuric, dibromoisocyanuric and dichloroisocyanuric acids, and salts thereof with watersolubilizing cations such as potassium and sodium. Hydantoin compounds such as 1,3-dichloro-5,5-dimethylhydantoin are also quite suitable.

[0060] Dry, particulate, water-soluble anhydrous inorganic salts are likewise suitable for use herein such as lithium, sodium or calcium hypochlorite and hypobromite. Chlorinated trisodium phosphate is another suitable material. Chloroisocyanurates are, however, the preferred bleaching agents. Potassium dichloroisocyanurate is sold by Monsanto Company as ACL-59®. Sodium dichloroisocyanurates are also available from Monsanto as ACL-60®, and in the dihydrate form, from the Olin Corporation as Clearon CDB-56®, available in powder form (particle diameter of less than 150 microns); medium particle size (about 50 to 400 microns); and coarse particle size (150-850 microns). Very large particles (850-1700 microns) are also found to suitable.

[0061] Organic peroxy acids or the precursors therefor may also be utilized in the bleach system. The peroxyacids usable in the present invention are solid and, preferably, substantially water-insoluble compounds.. By "substantially water-insoluble" is meant herein a water-solubility of less than about 1% by weight at ambient temperature. In general, peroxyacids containing at least about 7 carbon atoms are sufficiently insoluble in water for use herein.

[0062] Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxyacids such as:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-alpha-naphthoic acid;
(ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxylauric acid and peroxystearic acid;
(iii) phtlaloyl amido peroxy caproic acid (PAP).
Typical diperoxy acids useful therein include alkyl diperoxy acids and aryldiperoxy acids, such as:
(iv) 1, 12-diperoxydodecanedioic acid (DPDA);
(v) 1,9-diperoxyazelaic acid;
(vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vii) 2-decyldiperoxybutane-1,4-dioic acid.

[0063] Peroxyacid bleach precursors are well known in the art. As nonlimiting examples can be named N,N,N^1,N^1-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as described in US-A-4 751 015.

[0064] Inorganic peroxygen-generating compounds are also suitable for preparing the co-granules of the present invention. Examples of these materials are salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

[0065] If desirably, a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0 458 397, or the sulphonimines of US Patents 5,041,232 and 5,047,163 can be incorporated.

[0066] For chlorine bleaches the amount used in the co-granules of the invention may vary within the range of about 0,5% to about 3% as available chlorine (Av Cl). For peroxygen bleaching agents a suitable range will be from 0,5% to 3% av 0 (available oxygen) .

[0067] Finally the invention in a fourth aspect relates to the use of a co-granule according to the invention as a component in detergent compositions, more preferably in dishwashing compositions. More in particular the invention provides non-irritant detergent composition in which the amount of peroxygen bleach, protease and surfactant taken together is at most 20%, more in particular between 10 and 19.95% (w.w.) of the total composition.

[0068] In the following the invention will be illustrated by a number of examples. All parts and percentages mentioned are on a weight basis unless indicated otherwise.

EXAMPLES

1. Preparation of solutions/slurries for spray-drying

[0069] The following solutions were produced:

1a. Starting from anhydrous citric acid.

[0070]

Composition:		
	Dry basis (kg)	As Is (kg)
Citric acid. Oaq.	189.5	189.5
Water		189.5
NaOH (50%)	118.5	237
Sokalan CP 5 (40%)*	21.6	54
Sodium silicate (45%) **	150.8	335
Total	480.4	1005

*) Sokalan CP-5 is a copolymer (of acrylic acid and maleic acid) sold by BASF in Germany.

**) The sodium silicate used has a mol ratio SiO_2/Na_2O of 2.0

[0071] The citric acid was first mixed with water and under stirring and cooling it was neutralised by slowly adding caustic soda. The solution was kept at about 70°C while successively the polymer and the silicate liquor were added. The solution obtained was clear at 70°C.

1b. Starting from sodiumcitrate.2aq.

[0072]

Composition:		
	Dry basis	As Is
	(kg)	(kg)
Sodium citrate.2.aq	254.6	290.2
Water		325.8
Sokalan CP-5 (40%)*	21.6	54
Sodium silicate (45%)**	150.8	335
Total	427	1005

In this case the citrate was dissolved under stirring in water, which was preheated at 70°C. The polymer and the silicate solution were then added. The solution was again clear.

2. Spray-drying

[0073] Spray-drying was carried out in a co-current manner in a standard spray-tower. The gas was pre-heated to max. 230°C and the solution was introduced (sprayed) at about 70°C in order to save energy/maximize capacity.

[0074] The spraying conditions were as follows:

Gas temperature inlet	200 - 230°C
Gas temperature exit	120 - 140°C
Temperature solution	65 - 75°C

[0075] It was found, that at outlet'temperatures above 140°C the material leaving the tower was still slightly plastic. Therefore for the compositions used, this seemed to be the maximum practical temperature.

[0076] The powders obtained varied in properties as summarized below, which could be adjusted by varying the conditions within the ranges given.

Bulk density (g/cm^3)	200 - 680
Free moisture content (%, w.w.)*	7- 12
Particle size	90% below 250 micrometers.

*) Free moisture content is measured at 160°C in an IR (Infrared) METTLER Balans, as marketed by the German firm METTLER. The time of measurement at 160°C is 7 minutes.

3. Compaction

[0077] Compaction was carried out in a standard compaction-roller unit as marketed by the firm Alexanderwerke AG in Remscheid, Germany. Type: Walzenpresse Type WP 480 x 260 V.

[0078] The equipment consists of 2 rollers. The powder was pressed between the rollers by a screw. The powder flow could be controlled by the screw. The pressure of the rollers was controlled hydraulically as the upper roller was not in a fixed position. The maximum pressure was about 150 t, which is equivalent to a hydraulic pressure of about 200 bar and about 6 t per cm length of the roller.

[0079] The rollers rotated at a speed of 14 - 18 revolutions per min.

[0080] The rollers were kept at about 25°C by water cooling.

[0081] During the experiments, the hydraulic pressure was varied between 130 and 170 bar.

[0082] It was found, that 135 bar was about the minimum pressure acceptable for the product composition and the temperature chosen.
At higher temperatures, the pressures can be reduced.

[0083] The sheet formed was broken down and sieved, using sieves of 200 and 1200 micrometers. The finer particles were returned to the compactor and the larger particles were returned to the breaker..

Products obtained:

[0084]

Bulk density (g/cm^3)	870 - 900
Attrition test (fluid bed) (%,w.w.)*	3.6 - 5.2 *)
Dissolution time at 20°C **	0'50"-1'20"
Particles below 200 micrometers	0 - 0.2% (w.w.)
Particles above 1000 micrometers	10 - 25% (w.w.)
N Value (Rosen Rammler)	3.5 - 4.5

*) The attrition test was carried out in a fluid bed under standard conditions (air flow rate, time, amount of product used). The amount of finer particles formed (particle size below 200 micrometer) was measured and given as % by weight.

**) The dissolution time is the time needed for complete dissolution in water at 20°C and at a 5% (w.w.) concentration.

Comparative test

[0085] Above reported results are excellent as can be concluded from the fact, that standard granular sodium silicate with a mol. ratio SiO_2/Na_2O 2.0 produced according to the same process, i.e: Spray-drying a solution of the sodium-silicate (pre-heated at 70°C) under the same conditions as above and compacted under the same conditions had the following properties:

Bulk density (g/cm^3)	770 - 820
Attrition test (fluid bed) (% w.w.) *	10 - 30
Dissolution time at 20°C **	3'-5'

200 and 1200 micrometers. The finer particles were returned to the compactor and the larger particles were returned to the breaker.

Products obtained:

[0086]

Bulk density (g/cm^3)	870 - 900
Attrition test (fluid bed) (%,w.w.)*	3.6 - 5.2 *)
Dissolution time at 20°C **	0'50"-1'20"
Particles below 200 micrometers	0 - 0.2% (w.w.)
Particles above 1000 micrometers	10 - 25% (w.w.)
N Value (Rosen Rammler)	3.5 - 4.5

*) The attrition test was carried out in a fluid bed under standard conditions (air flow rate, time, amount of product used). The amount of finer particles formed (particle size below 200 micrometer) was measured and given as % by weight.

**) The dissolution time is the time needed for complete dissolution in water at 20°C and at a 5% (w.w.) concentration.

Comparative test

[0087] Above reported results are excellent as can be concluded from the fact, that standard granular sodium silicate with a mol. ratio SiO_2/Na_2O 2.0 produced according to the same process, i.e: Spray-drying a solution of the sodium-silicate (pre-heated at 70°C) under the same conditions as above and compacted under the same conditions had the following properties:

Bulk density (g/cm^3)	770 - 820
Attrition test (fluid bed) (% w.w.) *	10 - 30
Dissolution time at 20°C **	3'-5'

[0088] In case the same silicate solution was dried and granulated simultaneously in the Turbo-Dryer, following results were obtained:

Bulk density (g/cm^3)	850 - 950
Attrition test (fluid bed)(% w.w.) *	4 - 8
Dissolution time at 20°C **	7'-10'

Claims

1. Method for preparing co-granules as a component for and for incorporation in detergent compositions, which method comprises:

   - preparting a solution or a slurry of at least
   - an alkali metal citrate, and
   - sodium disilicate,
   - drying the mixture,
   - compacting the dried product, and
   - breaking up and sieving the compacted product.

2. Method according to claim 1, **characterised in that** compaction is performed at a temperature between 0 and 90° C

3. Method according to claim 1 or 2, **characterized in that** the moisture content of the dried product before compaction is adjusted to at least 5-25% (w/w).

4. Method according to one or more claims 1-3, **characterised in that** compaction is performed by passing the dried mixture between rollers.

5. Method according to one or more claims 1-4, **characterised in that** compaction is performed by making tablets.

6. Method according to one or more of claims 1-5, **characterised in that** the fines resulting form breaking up and sieving are returned to the dried product before compaction and the resulting oversized particles are returned to the breaking step.

7. Method according to one or more of the preceding claims, **characterised in that** the co-granules further comprise at least one polymeric compound, being either an acid and/or a salt of a polycarboxylic acid polymer or a polypeptide.

8. Method according to one or more of the preceding claims, **characterised in that** the co-granules further comprise at least one inorganic salt of alkali metal tripolyphosphate, alkali metal carbonate/bicarbonate/sesquicarbonate or alkali metal sulphate.

9. Method according to one or more of the preceding claims, **characterised in that** the slurry is prepared by adding citric acid to a solution containing the inorganic salt, neutralising the carboxylic acid with alkali, optionally adding further ingredients, as to obtain a solution or a slurry with a water content of 30-60% (w/w).

10. Co-granules obtainable by the method according to one or more of the claims 1-9.

11. Co-granules according to claim 10, **characterised by** having a bulk density of at least 700 g/dm^3, preferably above 800 g/dm^3.

12. Co-granules according to claim 11, **characterised in that** the bulk density of the co-granules is between 900 g/dm^3 and 1200 g/dm^3.

13. Co-granules according to one or more of claims 10-12, **characterised in that** the average particle size of the co-granules is 100 to 1500 µm.

14. Co-granules according to claim 13, **characterised in that** the average particle size of the co-granules is comprised between 400 and 900 µm and that the Rosen Rammler N-value thereof is above 2.5.

15. Detergent composition comprising co-granules according to one or more of claims 10-14.

16. Use of a co-granules according to one or more of claims 10-14 as a component in detergent compositions.

Patentansprüche

1. Verfahren zum Herstellen von Cogranulaten als eine Komponente für und für die Einmischung in Waschmittelzusammensetzungen, welches Verfahren aufweist:

   - Herstellen einer Lösung oder eines Schlamms aus zumindest einem Alkalimetallcitrat und Natriumdisilikat,
   - Trocknen der Mischung,
   - Verdichten des getrockneten Produkts, und
   - Zerkleinern und Sieben des verdichteten Produkts.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Verdichtung bei einer Temperatur zwischen 0 und 90 °C durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** der Feuchtigkeitsgehalt des getrockneten Produkts vor der Verdichtung auf zumindest 5 bis 25 Gew.-% eingestellt wird.

4. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** die Verdichtung durch Hindurchführen der getrockneten Mischung zwischen Rollen durchgeführt wird.

5. Verfahren nach einem oder mehreren der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die Verdichtung durch Bildung von Tabletten durchgeführt wird.

6. Verfahren nach einem oder mehreren der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die sich durch das Zerkleinern und Sieben ergebenden Partikel mit Untergrösse zu dem getrockneten Produkt vor der Verdichtung zurückgeführt werden und die sich ergebenden Partikel mit Übergröße zu dem Zerkleinerungsschritt zurückgeführt werden.

7. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Cogranulate weiterhin zumindest eine Polymerverbindung enthalten, die entweder eine Säure und/oder ein Salz eines Polykarbonsäurepolymers oder ein Polypeptid ist.

8. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Cogranulate weiterhin zumindest ein anorganisches Salz von Alkalimetall-Tripolyphosphat, Alkalimetall-Karbonat/Bikarbonat/Sesquikarbonat oder Alkalimetallsulfat aufweist.

9. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Schlamm hergestellt wird durch Hinzufügen von Zitronensäure zu einer das anorganische Salz enthaltenden Lösung, Neutralisieren der Karbonsäure mit Alkali, wahlweises Hinzufügen weiterer Bestandteile, um eine Lösung oder einen Schlamm mit einem Wassergehalt von 30 bis 60 Gew.-% zu erhalten.

10. Cogranulate, die durch das Verfahren nach einem oder mehreren der Ansprüche 1 bis 9 erhältlich sind.

11. Cogranulate nach Anspruch 10, **dadurch gekennzeichnet, dass** sie eine Schüttdichte von zumindest 700g/dm^3, vorzugsweise über 800 g/dm^3 haben.

12. Cogranulate nach Anspruch 11, **dadurch gekennzeichnet, dass** die Schüttdichte der Cogranulate zwischen 900 g/dm^3 und 1200 g/dm^3 liegt.

13. Cogranulate nach einem oder mehreren der Ansprüche 10 bis 12, **dadurch gekennzeichnet, dass** die mittlere Teilchengröße der cogranulate 100 bis 1500 µm beträgt.

14. Cogranulate nach Anspruch 13, **dadurch gekennzeichnet, dass** die mittlere Teilchengröße der Cogranulate zwischen 400 und 900 µm liegt und dass der Rosen-Rammler-N-Wert hiervon über 2,5 liegt.

15. Waschmittelzusammensetzung, welche Cogranulate nach einem oder mehreren der Ansprüche 10 bis 14 aufweist.

16. Verwendung von Cogranulaten nach einem oder mehreren der Ansprüche 10 bis 14, als eine Komponente in Waschmittelzusammensetzungen.

Revendications

1. Procédé de préparation de co-granulés comme composant de, et pour incorporation dans des compositions détergentes, ledit procédé comprenant :

- la préparation d'une solution ou d'une boue d'au moins un citrate de métal alcalin et un disilicate de sodium,
- le séchage du mélange,
- le compactage du produit séché, et
- la fragmentation et le tamisage du produit compacté.

2. Procédé selon la revendication 1, **caractérisé en ce que** le compactage est réalisé à une température comprise entre 0 et 90°C.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** la teneur en humidité du produit séché avant compactage est ajustée à au moins 5-25% (p/p).

4. Procédé selon l'une ou plusieurs des revendications 1-3, **caractérisé en ce que** le compactage est effectué en faisant passer le mélange séché entre des rouleaux.

5. Procédé selon l'une ou plusieurs des revendications 1-4, **caractérisé en ce que** le compactage est effectué en fabriquant des comprimés.

6. Procédé selon l'une ou plusieurs des revendications 1-5, **caractérisé en ce que** les fines résultant de la fragmentation et du tamisage sont renvoyées vers le produit séché avant compactage et les particules surdimensionnées résultantes sont renvoyées vers l'étape de fragmentation.

7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** les co-granulés comprennent en outre au moins un composé polymère, qui est soit un acide et/ou un sel d'un polymère acide polycarboxylique, soit un polypeptide.

8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** les co-granulés comprennent en outre au moins un sel inorganique d'un tripolyphosphate de métal alcalin, un carbonate/bicarbonate/sesquicarbonate de métal alcalin ou un sulfate de métal alcalin.

9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la boue est préparée par addition d'acide citrique à une solution contenant le sel inorganique, neutralisation de l'acide carboxylique par un alcali, le cas échéant addition d'autres ingrédients, de manière à obtenir une solution ou une boue avec une teneur en eau de 30-60% (p/p).

10. Co-granulés capables d'être obtenus par le procédé selon l'une quelconque des revendications 1-9.

11. Co-granulés selon la revendication 10, **caractérisés en ce qu'**ils ont une densité apparente d'au moins 700 g/dm^3, de préférence supérieure à 800 g/dm^3.

12. Co-granulés selon la revendication 11, **caractérisés en ce que** la densité apparente des co-granulés est entre 900 g/dm^3 et 1200 g/dm^3.

13. Co-granulés selon l'une quelconque des revendications 10-12, **caractérisés en ce que** la dimension moyenne des particules de co-granulés est entre 100 et 1500 µm.

14. Co-granulés selon la revendication 13, **caractérisés en ce que** la dimension moyenne des particules des co-granulés est comprise entre 400 et 900 µm et **en ce que** leur valeur N de Rosen Rammler est supérieure à 2,5.

15. Composition détergente comprenant des co-granulés selon l'une ou plusieurs des revendications 10-14.

16. L'utilisation de co-granulés selon l'une quelconque des revendications 10-14 comme composant dans des compositions détergentes.