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Particulate detergent additive product, preparation and use thereof in detergent compositions.

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FR-A- 2 443 502
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Description

This invention relates to detergent additive products in the form of particles or granules, methods of making thereof, and use thereof in detergent compositions. In particular, it relates to detergent additive containing particles having improved mechanical strength and attrition resistance together with excellent dispersibility and dissolution characteristics.

BACKGROUND AND PRIOR ART

It is widely recognized that the function of a number of detergent additive materials can be significantly impaired in detergent compositions by interaction between the additive material and other components of the composition. For example, enzyme, perfumes, fluorescers and bleach activators can deleteriously interact with peroxy bleaches; since organic bleach activators are generally hydrolysable compounds, they tend to hydrolyse or perhydrolyse owing to the action of moisture, alkaline substances and the percompound present in the detergent composition. Also peroxyacid bleach compounds and chlorine bleach compounds, such as the chloroisocyanurates, when incorporated in detergent compositions tend to attack oxidation-sensitive ingredients such as perfumes, fluorescers and dyes. Cationic compounds can be deleteriously affected by interaction with anionic ingredients, e.g. anionic surfactants.

Numerous attempts have been made to improve the storage-stability characteristics of detergent additive materials, such as bleach activators and the like, but such attempts have in general encountered only limited success. The most common way of approaching the problem has been to protect the additive material from its hostile environment by agglomerating, coating or encapsulating the material with a non-hygroscopic, preferably hydrophobic material. Conventionally, organic materials have found the greatest favour as coating/agglomerating agents because such materials readily form a substantially cohesive and continuous plastic matrix in which the additive material can be embedded. GB-A-1 204 123, GB-A-1,441,416 and GB-A-1,398,785 are representative of this general approach.

In general, these disclosures teach the incorporation of a fine particulate bleach activator (hereinafter also referred to as peroxyacid bleach precursor), optionally with additional stabilising compounds, into larger agglomerates, using organic solids having melting points in the range of 30°-60°C as the agglomerating agents.

Unfortunately, however, protection of sensitive ingredients within an organic plastic matrix as practised in the art can have detrimental effect on the dispersibility or dissolution characteristics of the ingredient in water, particularly at low temperatures.

U.S. Patent 4,009,113 discloses granular compositions comprising from about 40% to 80% of a bleach activator and an inert carrier material such as a long-chain fatty acid or ester wherein said precursor is substantially evenly distributed with said precursor compound to form a composite particle. The particle has an outer protective layer which can consist of, for example, polyvinyl alcohol. The particles according to this patent can be made in a one-step process using a machine termed a "Marumeriser"® made by Fuji Pandal KK, or in a two-step process wherein the precursor/carrier mixture is processed by extrusion to form extrudates, which are then broken down in a "Marumeriser" and formed into "spheres" and coating the spherical particles. It is stated that such compositions have both good storage stability and dispersibility in the wash water.

U.S. Patent 4,399,049 (= EP-A-0062523) discloses a detergent additive composition comprising from 75% to 95% (84-90%) of a particulate solid (e.g. bleach activator) having a particle size distribution such that at least about 50% thereof passes a 250 micrometer screen, and from 5% to 25% (10-16%) of ethoxylated non-ionic surfactant melting in the range of from 20°C to 60°C, wherein said composition is prepared via a radial extrusion process. It is stated that such compositions have improved storage stability together with excellent release and dispersibility characteristics in wash water.

EP-A-0106634 discloses activator-containing bodies comprising a bleach activator and an organic binder material having a melting point not below 40°C, wherein the bleach activator and binder material are evenly distributed throughout the body such that the body has the proper density, prepared via compaction pressing or a radial extrusion process. It is stated that such bodies have both superior storage stability and dispersibility in the wash water.

Still, in all of these prior art disclosures the primary objective has been the formation of a bleach additive granule containing a peroxy bleach activator whose chemical stability could be maintained in a hostile environment, e.g. during storage under conditions of elevated temperature and humidity in intimate contact with an alkaline peroxy bleach-containing detergent.

Indeed, since bleach activators, i.e. peroxyacid bleach precursors, are reactive compounds which function by the generation of peroxyacids in alkaline solutions containing a source of hydrogen peroxide, such as sodium perborate, a reaction which is often referred to as perhydrolysis, it is essential that detergent additive particles

comprising a bleach activator should disperse well and dissolve rapidly into the wash liquor to obtain maximum benefit from their use. Other detergent additive materials will also benefit from these properties.

However, it is also very desirable that the detergent additive material, particularly peroxyacid bleach precursors, enzymes, fluorescers, germicides and chlorinated or peroxyacid bleach compounds, be formed into granulated particles or granules, which have sufficient mechanical strength and attrition resistance to allow them to be stored and conveyed safely by bulk handling methods. The more aggressive the detergent additive material, the more important this criterion will be.

It was known how to meet the first criterion. It may also be known how to meet the second criterion, but this has hitherto been at the expense of the requirements set out for really good dispersibility and rapid dissolution of the particles.

DESCRIPTION OF THE INVENTION

The present invention seeks, as one of its objectives, to resolve these conflicting requirements by providing granulated particles containing a detergent additive, which will have the desirable properties of being non-friable, non-dusty and at the same time fast-dissolving.

Granulated particles, granules or particulate bodies in general, for being classified as non-friable, non-dusty and at the same time fast-dissolving, should desirably show an attrition value of less than 2%, preferably less than 1%; a dust yield of less than 1 mg/g, preferably less than 0.5 mg/g; and a dissolution rate of less than 150 seconds, preferably less than 100 seconds.

According to the invention there is provided a stable, non-friable, non-dusty and at the same time fast-dissolving particulate detergent additive product consisting of bodies of sizes ranging from 100 to 2000 μm , comprising a detergent additive material releasably enclosed within a water-soluble material, which is characterised in that each body comprises a core particle comprising

(a) from 25-95% by weight of a solid particulate storage-sensitive detergent additive material; and
(b) from 75-5% by weight of an organic binder material having a melting point of from 25° to 80°C; wherein (a) and (b) are substantially evenly distributed throughout the core particle, which core particle is provided with 1-10% by weight of an outer coating of an organic material having a melting point below that of the binder material of less than 60°C and solubility in water at 40°C greater than 20% by weight; said bodies having the shape of substantially rounded particles with average sphericity ≥ 0.85 and having a pore volume of not more than 0.25 cm^3/gram , and said product having a compression strength expressed in terms of compression modulus of greater than $0.5 \times 10^6 \text{ N/m}^2$.

Preferred bodies will have a core particle comprising from 50-90% by weight of the solid particulate detergent additive material and from 50-10% by weight of the organic binder material. It is further preferred that a pore volume of less than 0.2 cm^3/gram should be aimed at.

Definitions:

Sphericity is the ratio of the surface area of a sphere with the same volume as the particle to its actual surface area, and can be estimated by microscopy according to a method described by G. Herdan in "Small Particle Statistics", Butterworths, London, 2nd Edition, 1960.

Pore volume is measured by mercury porosimetry as described by T. Allen in "Particle Size Measurement", Chapman and Hall, London, 3rd Edition, 1980.

The compression modulus of the particles is measured as follows:

A sieve fraction of granules of size range from 710 to 1000 μm is placed in a cylindrical die of 16 mm diameter and 6 mm deep. The granules are compressed by lowering a piston into the die and simultaneously measuring the force. The force required to produce a strain of 30% (1.8 mm compression) is measured. This is then expressed as a stress and converted to a modulus by dividing by the strain (0.3).

Attrition value is measured by means of a spouted bed test, described in ISO/TC 47/WG 11, 1972, "Sodium perborate for industrial use, determination of rate of attrition", and using a 355-500 μm sieve fraction of the granules.

The apparatus consists of a 25 mm diameter glass tube, 400 mm long, mounted vertically. The lower end of the tube is fitted with a 3 mm thick stainless steel orifice plate with a 0.4 mm hole drilled centrally. The plate is sealed to the tube with flanges. The upper end of the tube is fitted with a removable dust filter. The orifice plate is fed with nitrogen from a compressed gas cylinder. The gas flow rate is adjusted by means of a pressure regulator to 7.0 ± 0.25 litres per minute measured at atmospheric pressure.

A 50 gram sample of granules is fluidized for 10 minutes. Afterwards, the contents of the tube and filter are removed and the percentage of particles passing a 150 μm sieve is determined.

Dust yield is measured using a fluid bed dust elutriation test and using a 1000-1400 μm sieve fraction of granules. The fluid bed used has an internal diameter of 34.5 mm and is 2000 mm tall. Air is supplied to the bed at superficial gas velocity of 0.8 m/sec. through a sintered glass distributor. The bed is filled with 60 grams of granules. Elutriation is carried out for 40 minutes. Elutriated dust is collected and weighed.

Dissolution rate is the time taken for 90% of the detergent additive material to have dissolved or dispersed in water of 23°C, buffered at pH 10, in a standard test wherein a weight of 250 mg granules is added to 500 ml of water in an agitated vessel, provided with a magnetic stirrer 40 mm in length and 9 mm diameter rotated at 730 rpm.

Binder materials

The materials that can be utilized as binders include nonionic surfactants, fatty acids, polyethylene glycols, anionic surfactants, and mixtures thereof having the characteristics as specified hereinbefore and hereinafter. In some cases, water-insoluble materials, such as silicone waxes, hydrocarbon waxes and triglycerides may also be utilized.

Examples of suitable nonionic surfactants are the condensation products of primary or secondary aliphatic alcohols having from 8-24 carbon atoms, in either straight chain or branched chain configuration, which may be saturated or unsaturated, with from 3 to 50 moles, preferably 3-25 moles of ethylene oxide per mole of alcohol. A specific example thereof is tallow alcohol/20 ethylene oxide which melts at about 40°C.

The preferred nonionic surfactants of this class are prepared from primary alcohols which are partly branched, such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol® and Neodol® are Trade Marks of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic® is a Trade Mark of ICI), or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial® by Liquichimica.

Other examples of nonionic surfactants that can be utilized as binder material are the condensation products of saturated or unsaturated, straight or branched chain carboxylic acids having from 8-24 carbon atoms with from 3 to 50 moles, preferably 3-25 moles of ethylene oxide per mole of carboxylic acid. Specific examples of nonionic surfactants of this class are those prepared from coconut fatty acid, palmitic, stearic and myristic acid.

Fatty acids utilizable herein are, for example, saturated or unsaturated fatty acids containing from 8-24 carbon atoms, such as lauric acid, myristic acid, palmitic acid, stearic acid, tallow acid or mixtures of tallow acid and coconut fatty acid, arachidic acid and behenic acid and mixtures thereof.

Suitable polyethylene glycols (PEG's), which are homopolymers of ethylene oxide having the general formula:



have an average molecular weight of from 400 to about 30,000, preferably from about 1000 to 20,000, and most preferably from 1500 to about 10,000. For example, these materials are obtainable from the Dow Chemical Company in molecular weights of 1500, 4000, 4500, 7500, 9500 and 20,000, which are wax-like products.

PEG 1500 has melting point of about 40°C, and solubility in water at 40°C of about 73%.

PEG 4000 has melting point of about 55°C, and solubility in water at 40°C of about 70%.

Suitable anionic surfactants are the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulphuric reaction products having in their molecular structure an alkyl group containing from 8 to 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_8 - C_{18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulphonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S. Patents 2,220,099 and 2,477,383. The preferred anionic surfactants are linear straight chain alkylbenzene sulphonates in which the average number of carbon atoms in the alkyl group is from 11 to 13, abbreviated as $\text{C}_{11-13}\text{LAS}$.

Other anionic surfactants herein are the water-soluble salts of the higher fatty acids, i.e. "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from 8 to 24 carbon atoms, and preferably from 12 to 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids.

Other anionic surfactants for use herein are the sodium alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sul-

phonates and sulphates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulphates containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulphates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains from 10 to 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulphonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulphonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulphonates containing from 12 to 20 carbon atoms; and beta-alkyloxy alkane sulphonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Mixtures of the above compounds, such as for example a mixture of a low-melting and a high-melting compound, are also quite suitable. Other suitable binder material mixtures are for example soap-fatty acid mixtures. It is also advantageous if polyethylene glycol is used to include some surfactant (nonionic and/or anionic) to improve wetting and dissolution.

Whereas the melting point of the binder material is an important requirement, there are no specific requirements with respect to the solubility and/or dispersibility in water of the binder material which can be applied to all detergent additives in general.

For example, highly insoluble detergent additive materials will desirably be compounded with highly soluble binder materials in order to achieve the desired dissolution rate, and highly soluble detergent additive materials may suffice with less water-soluble or even water-insoluble binder materials, such as long chain fatty acids and wax materials.

Generally, for peroxyacid bleach precursors a suitable binder material should desirably have a solubility in water of 40°C greater than 20% by weight.

Coating materials

The same classes of material usable as binder materials, i.e. nonionic surfactants, fatty acids, polyethylene glycol, soap, anionic surfactants and mixtures thereof, are suitable for use as the coating materials. It is, however, desirable that a coating material should be selected having a lower melting point than the binder material used, so that the coating can be applied without altering the granule. Preferably, a coating material is employed having a melting point of at least 5°C below that of the binder material used. Specific examples of a coating material are PEG 300 (m.p. -15 to 8°C), PEG 400 (m.p. 4 to 8°C) and PEG 600 (m.p. 22°C), which are very soluble materials of low viscosity.

The manufacturing process

The particulate detergent additive product of the invention can be prepared by a high shear energy mixing process. The process uses a high-speed mixer/granulator equipment having both a stirring action of high energy and a cutting action. Equipment for high shear energy processing may generally be subdivided according to whether the mixing shaft, to which are attached a mixing impeller or mixing impellers, is mounted either vertically or horizontally. When the shaft is vertical, a single mixing impeller which rotates in a horizontal plane is mounted within a close-fitting bowl-shaped vessel. The rotation of the impeller imparts high shear energy mixing to the powder. When the shaft is horizontal, one or more mixing impeller blades which rotate in a vertical plane are mounted within a close-fitting cylindrical vessel. Rotation of the impeller blades imparts high shear energy mixing to the powder. In addition, it is common practice to fit within the vessels small chopper blades which rotate at about 1000 rpm or more, and which serve to disintegrate oversize material produced during agglomeration. Both types of these high-speed mixer/granulators are commercially available and can be used to produce the detergent additive containing bodies of the invention as rounded, mechanically strong particles.

The Fukae (Trade Mark) FS-G mixer manufactured by Fukae Powtech Kogyo Co., Japan, has been found to give excellent results in batchwise operation. This apparatus is essentially in the form of a vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. Preferably, the stirrer and cutter may be operated independently of one another, and at separately variable speeds, by which the process can be controlled and adjusted to formulation changes.

Other mixers suitable for use in the process of the invention include the Diosna (Trade Mark) V series ex Dierks & Söhne, Germany; the Lödige (Trade Mark) FM series ("ploughshare" mixer) ex Morton Machine Co. Ltd, Scotland; and the Pharma Matrix (Trade Mark) ex T.K. Fielder Ltd, England. Other mixers believed to be suitable for use in the process of the invention are the Fuji (Trade Mark) VG-C series ex Fuji Sangyo Co., Japan; the Lödige MTG ex Morton Machine Co. Ltd, Scotland; and the Roto (Trade Mark) ex Zanchetta & Co. S.r.l.,

Italy. The Lödige mixer differs from the Fukae mixer mentioned above in that its stirrer has a horizontal axis; this configuration is suitable for continuous operation.

The use of a high shear energy mixing process is highly desirable to form the detergent additive containing bodies of the invention, which by a suitable selection of the binder and a suitable selection of the coating as described herein will be mechanically strong and highly attrition resistant and yet fast-dissolving.

Other known agglomeration processes by which a fine powder can be converted to a granular powder and which may be classified as:

- i) low shear energy mixing processes;
- ii) fluid bed processes, and processes involving the utilization of an air flow; and
- iii) compaction processes,

are not excluded, but they may be less suitable for achieving the desired results.

Low shear energy mixing processes include the use of pans, drums and low energy mechanical mixers. These generally produce irregularly shaped, weak, porous granules, not well suited to bulk handling because they readily attrite, though the porous nature of the particles can contribute to a good rate of dissolution.

Fluid bed processes and processes involving the utilisation of air flows generally produce porous, mechanically weak, but fast-dissolving granules. The mechanical weakness of the granules makes them unsuitable for the purpose of the invention.

Compaction processes include the various extrusion and tableting processes. They generally produce granules with defined shape characteristics, e.g. cylindrical particles (sometimes referred to as "noodles") and tablets. The strength of the granules depends on the pressure and other processing conditions and on the type and level of the binder used, and can vary over a very wide range. Granules produced by compaction methods and which have adequate strength for bulk handling are generally slow to dissolve. Because of their shape and internal tension, structure and consistency inherent in the process, they tend to crack and may still attrite.

Accordingly, in one preferred embodiment, the invention provides stable, non-friable, non-dusty and at the same time fast-dissolving detergent additive containing bodies as defined herein, obtainable by a high-shear energy mixing process using a high-speed mixer/granulator.

Two essential processing steps characterize the manufacture of the bodies, viz. 1) granulation to form the core particles and 2) coating of the core particles to form the finished bodies. Both processes can be effected sequentially in the same high-speed mixer/granulator or the core particles obtained from the H-S mixer/granulator can be discharged and coated in another suitable mixer, such as a fluidized bed mixer, a rotating inclined pan granulator, rotating drum mixer, tumbling mixer, V-mixer, ploughshare mixer and ribbon mixers.

The organic binder material may be charged to the mixer/granulator in solid or liquefied form. In both cases it is essential to maintain the temperature during granulation slightly above the melting point of the binder material, whereby the binder material is in a state capable of forming a matrix with the solid particulate detergent additive material.

Desirably, the core particles are cooled prior to coating. This can be done in a number of ways, e.g. within the H-S mixer/granulator, tray-cooling, rotating drum cooling and utilizing the cooling effect of pneumatic conveying. A preferred method of cooling is to utilize a fluid bed in which air at ambient temperature, or chilled below ambient temperature, is fed to the particle bed by means of a distributor plate. The fluid bed may be operated in batch or continuous mode.

It may also be desirable to screen the particulate mass to remove coarse material. This material may consist of oversize granules or material which has compacted within the apparatus and subsequently broken away. If desired, fine material may also be removed by screening or some other suitable means of size classification. These screening operations may be done before cooling, after cooling or after coating.

In another aspect the invention thus provides a process of preparing a particulate detergent additive product comprising the steps of treating 25 to 95 parts by weight of a solid particulate storage-sensitive detergent additive material in a high-speed mixer/granulator in the presence of 95 to 5 parts by weight of an organic binder material having a melting point of from 25° to 80°C, whereby granulation and spheronizing are effected, forming the core particles, followed by cooling and adding an organic material having a melting point below that of the binder material of less than 60°C and solubility in water at 40°C greater than 20% by weight, whereby coating of the core particles is effected, forming bodies having a substantially rounded form of average sphericity ≥ 0.85 and pore volume of not more than 0.25 m³/gram and a compression strength expressed in terms of compression modulus greater than 0.5 x 10⁶ N/m².

The detergent additive material

The detergent additives usable in the present invention may be selected from any group of solid particulate

storage-sensitive detergent additive materials.

Preferred detergent additives are enzymes, peroxyacid compounds, peroxygen and chlorine bleaches, fluorescenters and peroxyacid bleach precursors. A highly preferred detergent additive material, however, is an organic peroxyacid bleach precursor. Another highly preferred material is a peroxyacid compound.

For simplicity's sake, the invention will be further described with particular reference to peroxyacids and peroxyacid bleach precursors, it being understood that this does not imply a limitation.

Examples of the various classes of peroxyacid bleach precursors include:

(a) N-diacylated and N,N'-polyacylated amines, such as N,N,N',N'-tetraacetyl methylene diamine and N,N,N',N'-tetraacetyl ethylene diamine, N,N-diacetylaniline, N,N-diacetyl-p-toluidine;

1,3-diacylated hydantoins such as, for example, 1,3-diacetyl-5,5-dimethyl hydantoin and 1,3-dipropionyl hydantoin;

(b) N-alkyl-N-sulphonyl carbonamides, for example the compounds N-methyl-N-mesyl-acetamide, N-methyl-N-mesyl-benzamide, N-methyl-N-mesyl-p-nitrobenzamide and N-methyl-N-mesyl-p-methoxybenzamide;

(c) N-acylated cyclic hydrazides, acylated triazones or urazoles, for example monoacetylmalic acid hydrazide;

(d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-acetyl-N,N-succinyl hydroxylamine, O-p-methoxybenzoyl-N,N-succinyl hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl hydroxylamine and O,N,N-triacetyl hydroxylamine;

(e) N,N'-diacyl-sulphurylamides, for example N,N'-dimethyl-N,N'-diacetyl sulphurylamide and N,N'-diethyl-N,N'-dipropionyl sulphurylamide;

(f) Triacylcyanurates, for example triacetyl cyanurate and tribenzoyl cyanurate;

(g) Carboxylic acid anhydrides, such as benzoic anhydride, m-chloro-benzoic anhydride, phthalic anhydride and 4-chloro-phthalic anhydride;

(h) Sugar esters, for example glycoside pentaacetate;

(i) 1,3-diacyl-4,5-diacyloxy-imidazolidine, for example 1,3-diformyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-diacetoxy-imidazoline, 1,3-diacetyl-4,5-dipropionyloxy-imidazoline;

(j) Tetraacetylglycoluril and tetrapropionylglycoluril;

(k) Diacylated 2,5-diketopiperazine, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and 1,4-dipropionyl-3,6-dimethyl-2,5-diketopiperazine;

(l) Acylation products of propylenediurea or 2,2-dimethyl-propylenediurea (2,4,6,8-tetraazabicyclo-(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), especially the tetraacetyl- or the tetrapropionyl-propylenediurea or their dimethyl derivatives;

(m) Carbonic acid esters, for example the sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxycarbonyloxy)-benzene sulphonic acid;

(n) α -Acyloxy-(N,N')-polyacyl malonamides, such as α -acetoxy-(N,N')-diacetyl malonamide.

(o) Acyl phenol sulphonates and acyl alkyl phenol sulphonates, such as sodium-p-acetoxy benzene sulphonate, sodium-p-benzoyloxy benzene sulphonate, sodium-p-nonanoyloxy benzene sulphonate, and sodium-p-trimethyl hexanoyloxy benzene sulphonate.

These and other classes of peroxyacid bleach precursors are known and amply described in literature, such as in the GB-Patents 836,988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and U.S. Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors is that of the quaternary ammonium substituted peroxyacid precursors as disclosed in U.S. Patents 4,751,015 and 4,397,757, in EP-A-284292 and EP-A-331229. Examples of peroxyacid bleach precursors of this class are:

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride - (SPCC);

N-octyl,N,N-dimethyl-N10-carbophenoxy decyl ammonium chloride - (ODC);

3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and N,N,N-trimethyl ammonium toluoyloxy benzene sulphonate.

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; amides, including TAED; and the quaternary ammonium substituted peroxyacid precursors, particularly SPCC.

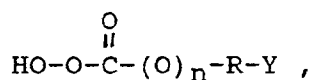
Specific preferred materials are solid and are incorporated in the instant bodies, particles or granules in finely divided form, i.e. with an average particle size of less than 250 μm , preferably less than 200 μm , particularly having main particle size between 50 and 150 μm .

Highly preferred activators include sodium-4-benzoyloxy benzene sulphonate; sodium-p-trimethylhexanoyloxy benzene sulphonate; sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-

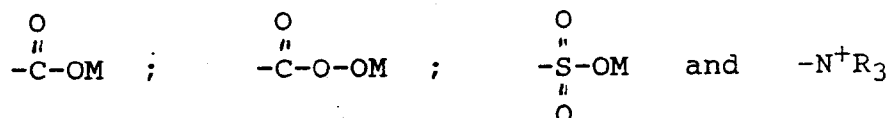
benzoyloxy benzoate; SPCC and trimethyl ammonium toluoyloxy benzene sulphonate, of which sodium-4-benzoyloxy benzene sulphonate and 2-(N,N,N-trimethylammonium)ethyl sodium-4-sulphophenyl carbonate chloride is particularly preferred.

Peroxyacid compounds include the organic peroxyacids and their salts and the inorganic peroxyacid salts, which are solid at room temperature and preferably have a melting point above 50°C.

Suitable organic peroxyacids can be represented by compounds of the general formula:

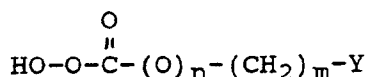


wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, n is 0 or 1, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic or cationic moiety in aqueous solution. Such groups can include, for example:

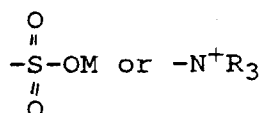
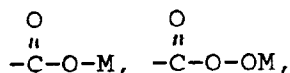


wherein M is H or a water-soluble, salt-forming cation.

The organic peroxyacids and salts thereof can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula:



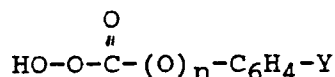
wherein Y can be H, -CH₃, -CH₂Cl,



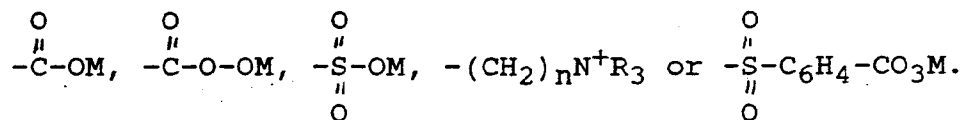
and m can be an integer from 1 to 20.

Specific examples of compounds of this type are diperoxyazelaic acid, peroxyauric acid and 1,12-diperoxydodecanedioic acid, and the magnesium salts thereof.

When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula:



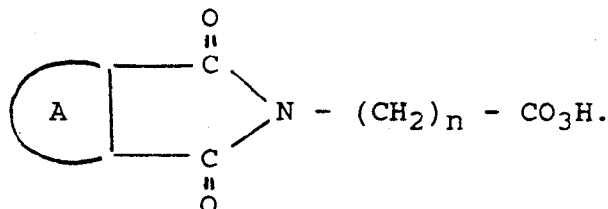
wherein Y is, for example, hydrogen, halogen, alkyl,



The percarboxy or percarbonic and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents, such as halogen or sulphonate groups.

Specific examples of such aromatic peroxyacids and salts thereof include peroxybenzoic acid, m-chloro-peroxybenzoic acid, p-nitro-peroxybenzoic acid, p-sulphonato-peroxybenzoic acid, diperoxyisophthalic acid, peroxy- α -naphthoic acid, and 4,4'-sulphonyl-diperoxybenzoic acid and magnesium salts thereof.

Another suitable class of peroxyacids is that of the imido-aromatic(poly)peroxycarboxylic acids as disclosed in EP-A-325289 having the general formula :



wherein A is an optionally substituted benzene ring and n is an integer from 1 to 12, preferably 5.

A specific compound representing the class is N,N-phthaloylamino-peroxy caproic acid.

A specific example of inorganic peroxyacid salts is potassium monopersulphate. A product comprising this compound is the triple salt, $\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$, available commercially under the trade-name Oxone[®] from E.I. DuPont de Nemours and Company.

Suitable enzymes include the amylolytic, lipolytic and proteolytic enzymes, usable for incorporation in detergent compositions.

Preferred proteolytic enzymes are normally solid, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be made of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. 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[®], as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase[®], as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase[®] and Savinase[®]. The preparation of these and analogous enzymes is described in British Patent Specification 1,243,785. Other commercial proteases are Kazusase[®] (obtainable from Showa-Denko of Japan), Optimase[®] (from Miles Kali-Chemie, Hannover, West Germany), and Superase[®] (obtainable from Pfizer of U.S.A.).

Fluorescent brightening agents are well-known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino) stilbene-2,2'-disulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate and sodium 2(stilbyl-4"-naphtho-1',2':4,5)-1,2,3-triazole-2"-sulphonate.

Other fluorescers to which the invention can be applied include the 1,3-diaryl pyrazolines and 7-alkylaminocoumarins.

Additionally, the particulate detergent additive bodies of the invention may also contain other components as desired to improve dissolution or other properties. These additional components, if present, are preferably incorporated in admixture with the detergent additive material in the core particle. Examples of such additional components are:

i) Water-soluble inorganic or organic salts which may be acid or neutral salts, such as sodium or potassium mono- or dihydrogen phosphates, sodium or potassium hydrogen sulphate, ammonium salts of strong acids, e.g. ammonium sulphate, sodium or potassium sulphate and chloride, and citrates.

ii) Acidic materials, such as citric acid; and water-soluble polymeric materials, such as low M.W. homo- and co-polymers of acrylic acid and their salts.

iii) Nonionic compounds, such as sugars, e.g. sucrose, fructose; and polyvinylpyrrolidone (PVP).

iv) Surfactants, if not already included under binders.

v) Water-insoluble materials, such as clays and foam depressants.

vi) Dispersants and water-swellaable materials, such as modified starches, modified celluloses, powdered cellulose, cellulose fibres, cross-linked PVP and starch-ethers, e.g. carboxymethylcellulose.

5 vii) Stabilisers, such as ethylene diamine tetra-(methylene phosphonic acid), diethylene triamine penta-(methylene phosphonic acid), ethylene diamine tetraacetic acid, and their salts.

Any of these optional components may be present in the core particle at a total level of up to about 60% by weight of the core particle, preferably not more than 25% by weight.

10 As explained above, the new detergent additive containing bodies (particles or granules) according to the invention are extremely suitable for incorporation in detergent powder compositions.

Accordingly, detergent compositions comprising the particulate detergent additive product as described herein are within the purview of the present invention.

When the detergent additive material is a bleach activator (a peroxyacid bleach precursor), the detergent composition requires as an essential component a peroxide bleaching compound capable of yielding hydrogen peroxide in aqueous solution.

15 Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxide compounds such as urea peroxide, and the inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates and persulphates. Mixtures of two or more such compounds may also be suitable. Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. So-

20 dium perborate monohydrate is preferred because it has excellent storage stability while also dissolving very quickly in aqueous bleaching solutions. This rapid dissolution will further contribute to the formation of higher levels of peroxycarboxylic acid, thereby enhancing surface bleaching performance.

Typically, the molar ratio of hydrogen peroxide (or a peroxide compound generating the equivalent amount of H_2O_2) to precursor may range from 0.5:1 to about 20:1, preferably 1:1 to 5:1, most preferably from 1:1 to

25 2:1.

A detergent formulation containing the bleach activator granules of the invention will usually also contain surface-active materials, detergency builders and other known ingredients of such formulations.

In such formulations the bleach activator granules may be incorporated in an amount wherein the peroxyacid bleach precursor is present at a level ranging from about 0.1% to 20% by weight, preferably from 0.5% to 10% by weight, particularly from 1% to 7.5% by weight, together with a peroxide bleaching compound, e.g. sodium perborate mono- or tetra-hydrate, the amount of which is usually within the range of from about 2% to 40%, preferably from about 4% to 30%, particularly from about 10% to 25% by weight.

30 The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may range up to 50% by weight, preferably being from about 1% to 40% by weight of the composition, most preferably 4% to 25%.

35 The detergent compositions of the invention will normally also contain a detergency builder. Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in U.S. patents 4,144,226 and 4,146,495.

45 Examples of precipitating builder materials include sodium orthophosphate, sodium carbonate and long-chain fatty acid soaps.

Examples of calcium ion-exchanging builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives.

50 In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyl malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder materials, or mixtures thereof.

55 These builder materials may be present at a level of, for example, from 5 to 80% by weight, preferably from 10 to 60% by weight.

Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives - if not already included in the instant granules - in the amounts in which such materials are normally employed in fabric-washing detergent compositions. Examples of these additives in-

clude lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids, lather depressants, such as alkyl phosphates and silicones, anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers, peroxide stabilizers, such as ethylene diamine tetraacetic acid and preferably phosphonates, e.g. ethylene diamine tetra-methylene phosphonic acid and diethylene triamine penta-methylene phosphonic acid or their salts, fabric-softening agents, inorganic salts, such as sodium sulphate, and, usually present in very small amounts, fluorescent agents, perfumes, enzymes, such as proteases, cellulases, lipases and amylases, germicides and colourants.

The following examples will more fully illustrate the embodiments of the invention. All parts, percentages and proportions referred to herein are by weight unless otherwise illustrated.

Examples I - X

The following bleach activator granules of compositions I - X were prepared in a Fukai (Trade Mark) high-speed mixer/granulator. All granules obtained had the shape of rounded particles of average sphericity around 0.9 and had pore volume of less than 0.15 cm³/gram. The attrition value, dust yield, compression modulus and dissolution rate of each granule composition were determined and the results, as tabulated below, show excellent physical properties of high mechanical strength combined with good dissolution rate.

C 7155 (R)

TABLE 1

Example	I	II	III	IV	V	VI	VII	VIII	IX	X
<u>Core Granule</u>										
Sodium-4-benzoyl oxybenzene sulphonate (SBOBS)	81	79	81	80	75	75	73	67	72	-
N,N,N',N'-tetraacetyl ethylene diamine (TAED)	-	-	-	-	-	-	-	-	-	84
Polyethylene glycol 4000	16	-	-	-	-	-	-	-	-	-
Polyethylene glycol 1500	-	16	-	12	15	15	15	14	-	13
Dobanol [®] 45/11EO	-	-	14	-	-	-	-	-	17	-
synperonic [®] A7*	-	-	-	4	-	-	-	-	-	-
Sodium sulphate	-	-	-	-	7.5	-	-	-	-	-
Sucrose	-	-	-	-	-	7.5	-	3	-	-
Cellulose fibres	-	-	-	-	-	-	7	10	7	-
<u>Coating</u>										
Polyethylene glycol 400	3	5	5	4	2.5	2.5	5	6	4	3
<u>Physical Properties</u>										
Attrition (%)	0.3	0.3	0.5	0.5	0.5	0.4	0.4	0.4	0.9	0.8
Dust Yield (mg/g)	0.2	0.05	0.1	0.1	0.07	0.07	0.2	0.2	0.4	0.1
Compression modulus (N/m ² x 10 ⁻⁶)	2.4	1.8	1.5	1.5	1.8	1.8	2.1	2.0	0.9	0.6
Dissolution time (sec.)	120	108	60	48	72	78	50	63	48	140

* primary alcohol/7 EO (ethylene oxide)

EXAMPLE XIManufacture of bleach activator granules of Examples I-X.

A Fukae® Model FS-GC-30 high-speed mixer/granulator was charged with 6 kg of the bleach precursor (SBOBS or TAED) with or without the optional ingredients sodium sulphate, sucrose or cellulose fibres, as required. The temperature was controlled at 55°C by means of the water jacket. The molten binder (PEG 4000 or PEG 1500 or Dobanol 45/11 EO or PEG 1500 + Synperonic A7) was run into the granulator over a period of 1 minute, during which time the mixing impeller was rotated at 100 rpm and the chopper blades were rotated at 3000 rpm. Mixing was then continued for a further 9 minutes.

Granulation was carried out over a period of 5 minutes, with the mixing impeller turning at 300 rpm and the chopper blades rotating at 3000 rpm. The temperature was then reduced to 20°C by means of the cooling jacket, and the speed of the mixing impeller reduced to 70 rpm and that of the chopper blades reduced to 1000 rpm. After cooling for 10 minutes, the coating liquid (PEG 400) was applied, and after a further 5 minutes the product was discharged. The product obtained contains a major proportion of granules of sizes between 350 and 1400 µm.

EXAMPLES XII - XIII

The following peroxyacid granules of compositions XII and XIII were prepared in a Lödige® high-speed mixer/granulator.

All granules obtained had the shape of rounded particles of average sphericity around 0.9 and had pore volume of less than 0.2 cm³/gram. The attrition value, compression modulus and dissolution rate of each granule composition were determined and the results, as tabulated below, show excellent physical properties of high mechanical strength combined with good dissolution rate.

Table 2

Example	XII	XIII
<u>Core granule</u>	<u>% by weight</u>	
6-(N,N-phthalimido)-peroxyhexanoic acid	32.0	32.7
Sodium sulphate	53.3	54.4
Lauric acid (Prefac® 2920)	10.7	10.9
<u>Coating</u>		
Synperonic® A7	4.0	-
Polyethylene glycol (PEG 400)	-	2.0
<u>Physical properties</u>		
Attrition (%)	0.4	0.4
Compression modulus (N/m ² x 10 ⁻⁶)	1.5	1.5
Dissolution time (sec.)	150	150

EXAMPLE XIVManufacture of bleach granules of Examples XII - XIII

The peroxyacid bleach granules were prepared with a Lödige model M4 ELOD high-speed mixer/granulator. The granulator was charged with 0.450 kg of the peroxyacid bleach and the appropriate weights of sodium sulphate and lauric acid. The temperature was controlled at 50°C by blowing warm air over the granulator. Granulation was carried out over a period of 2 minutes with the mixing impeller rotating at 300 rpm.

The granules produced were removed and cooled for 10 minutes in an Aeromatic (Trade Mark) laboratory fluid bed (Model STREA-1).

The granules were screened to remove particles over 1400 µm. Coatings were applied in a tumbling mixer at a temperature of 30°C.

Claims

1. A particulate detergent additive product consisting of detergent additive containing bodies of sizes ranging from 100 to 2000 µm, comprising a detergent additive material releasably enclosed within a water-soluble material, characterized in that each body comprises a core particle comprising:
 - (a) from 25-95% by weight of a solid particulate storage-sensitive detergent additive material; and
 - (b) from 75-5% by weight of an organic binder material having a melting point of from 25° to 80°C; where-in (a) and (b) are substantially evenly distributed throughout the core particle, which core particle is provided with 1-10% by weight of an outer coating of an organic material having a melting point below that of the binder material of less than 60°C and solubility in water at 40°C greater than 20% by weight, said bodies having a shape of substantially rounded particles with average sphericity ≥ 0.85 and having a pore volume of not more than 0.25 cm³/gram; said product having a compression strength expressed in terms of compression modulus of greater than 0.5x10⁶ N/m².
2. Detergent additive product according to claim 1, characterized in that the core particle comprises from 50-90% by weight of said solid particulate storage-sensitive detergent additive material and from 50-10% by weight of said organic binder material.
3. Detergent additive product according to claim 1 or 2, characterized in that the pore volume is less than 0.2 cm³/gram.
4. Detergent additive product according to claim 1, 2 or 3, characterized in that the binder material is selected from the group consisting of nonionic surfactants, fatty acids, polyethylene glycols and anionic surfactants, and, mixtures thereof.
5. Detergent additive product according to any of above claims 1-4, characterized in that the coating material is selected from the group consisting of nonionic surfactants, fatty acids, polyethylene glycols and anionic surfactants, and mixtures thereof, having a lower melting point than the binder material.
6. Detergent additive product according to any of the above claims 1-5, characterized in that the coating material has a melting point of at least 5°C below that of the binder material.
7. Detergent additive product according to any of the above claims 1-6, characterized in that the detergent additive is selected from the group consisting of enzymes, peroxyacid compounds, peroxygen and chlorine bleaches, fluorescers and peroxyacid bleach precursors.
8. Detergent additive product according to claim 7, characterized in that the detergent additive is a peroxyacid bleach precursor.
9. Detergent additive product according to claim 8, characterized in that the peroxyacid bleach precursor is sodium-4-benzoyloxybenzene sulphonate.
10. Detergent additive product according to claim 8 or 9, characterized in that the binder material has solubility in water at 40°C greater than 20% by weight.

11. A process for the preparation of a particulate detergent additive product according to any of the preceding claims comprising the steps of treating 25 to 95 parts by weight of a solid particulate storage-sensitive detergent additive material in a high-speed mixer/granulator in the presence of 75 to 5 parts by weight of an organic binder material having a melting point of from 25° to 80°C, whereby granulation and spheronizing are effected, forming the core particles, followed by cooling and adding an organic material having a melting point below that of the binder material of less than 60°C and solubility in water at 40°C greater than 20% by weight, whereby coating of the core particles is effected, forming bodies having a substantially rounded form of average sphericity ≥ 0.85 , a pore volume of not more than 0.25 cm³/gram and a compression strength expressed in terms of compression modulus greater than 0.5 x 10⁶ N/m².
12. A process according to claim 11, characterized in that the granulation is effected at a temperature slightly above the melting point of the binder material.
13. A process according to claim 11 or 12, characterized in that 50 to 90 parts by weight of said detergent additive material is treated in the presence of 50 to 10 parts by weight of said liquified organic binder material.
14. A process according to any of claims 11 to 13, characterized in that the binder material is selected from the group consisting of nonionic surfactants, fatty acids, polyethylene glycols and anionic surfactants, and, mixtures thereof.
15. A process according to any of the claims 11-14, characterized in that the coating material is selected from the group consisting of nonionic surfactants, fatty acids, polyethylene glycols and anionic surfactants, and mixtures thereof, having a lower melting point than the binder material.
16. A process according to any of the claims 11-15, characterized in that the coating material has a melting point of at least 5°C below that of the binder material.
17. A process according to any of the above claims 11-16, characterized in that the detergent additive material is selected from the group consisting of enzymes, peroxyacid compounds, peroxygen and chlorine bleaches, fluorescers and peroxyacid bleach precursors.
18. A process according to claim 17, characterized in that the detergent additive is a peroxyacid bleach precursor.
19. A process according to claim 18, characterized in that the peroxyacid bleach precursor is sodium-4-benzoyloxy benzene sulphonate.
20. A process according to claim 18 or 19, characterized in that the binder material has solubility in water at 40°C greater than 20% by weight.
21. A detergent powder composition incorporating a detergent additive product as claimed in any of the preceding claims 1-10.

Patentansprüche

1. Teilchenförmiges Waschmitteladditivprodukt bestehend aus einem Waschmitteladditiv mit Körpern einer Größe im Bereich von 100 bis 2000 µm, die ein Waschmitteladditivmaterial, freisetzbar eingeschlossen in einem wasserlöslichen Material umfassen, **dadurch gekennzeichnet**, daß jeder Körper ein Kernteilchen umfaßt, das
- (a) 25-95 Gew.-% eines festen teilchenförmigen lagerungsempfindlichen Waschmitteladditivmaterials und
- (b) 75-5 Gew.-% eines organischen Bindemittelmaterials mit einem Schmelzpunkt von 25 bis 80°C umfaßt, wobei (a) und (b) im wesentlichen gleichförmig im Kernteilchen verteilt sind, das Kernteilchen mit 1 bis 10 Gew.-% einer äußeren Beschichtung eines organischen Materials mit einem Schmelzpunkt unterhalb dem des Bindemittelmaterials von weniger als 60°C und einer Löslichkeit in Wasser bei 40°C von mehr als 20 Gew.-% versehen ist; die Körper eine Form von im wesentlichen runden Teilchen mit einer durchschnittlichen Kugelförmigkeit $\geq 0,85$ und einem Porenvolumen von nicht mehr als 0,25 cm³/g

aufweisen und das Produkt eine Druckfestigkeit, ausgedrückt durch den Kompressionsmodulus von mehr als $0,5 \times 10^6 \text{ N/m}^2$ besitzt.

- 5 2. Waschmitteladditivprodukt gemäß Anspruch 1, **dadurch gekennzeichnet**, daß das Kernteilchen 50-90 Gew.-% des festen teilchenförmigen lagerungsempfindlichen Waschmitteladditivmaterials und 50-10 Gew.-% des organischen Bindemittelmaterials umfaßt.
- 10 3. Waschmitteladditivprodukt gemäß Anspruch 1 oder 2, **dadurch gekennzeichnet**, daß das Porenvolumen weniger als $0,2 \text{ cm}^3/\text{g}$ beträgt.
- 15 4. Waschmitteladditivprodukt gemäß Anspruch 1, 2 oder 3, **dadurch gekennzeichnet**, daß das Bindemittelmaterial ausgewählt ist aus der Gruppe, bestehend aus nichtionischen Tensiden, Fettsäuren, Polyethylenglycolen und anionischen Tensiden und Gemischen davon.
- 20 5. Waschmitteladditivprodukt nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß das Beschichtungsmaterial ausgewählt ist aus der Gruppe, bestehend aus nichtionischen Tensiden, Fettsäuren, Polyethylenglycolen und anionischen Tensiden und Gemischen davon mit einem geringeren Schmelzpunkt als jener des Bindemittelmaterials.
- 25 6. Waschmitteladditivprodukt nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß das Beschichtungsmaterial einen Schmelzpunkt von mindestens 5°C unterhalb dem des Bindemittelmaterials aufweist.
- 30 7. Waschmitteladditivprodukt nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet**, daß das Waschmitteladditiv ausgewählt ist aus der Gruppe, bestehend aus Enzymen, Peroxysäureverbindungen, Persauerstoff- und Chlorbleichmitteln, Fluoreszenzmitteln und Peroxysäurebleichmittelvorstufen.
- 35 8. Waschmitteladditivprodukt gemäß Anspruch 7, **dadurch gekennzeichnet**, daß das Waschmitteladditiv eine Peroxysäurebleichmittelvorstufe ist.
- 40 9. Waschmitteladditivprodukt gemäß Anspruch 8, **dadurch gekennzeichnet**, daß die Peroxysäurebleichmittelvorstufe Natrium-4-benzoyloxybenzolsulfonat ist.
- 45 10. Waschmitteladditivprodukt gemäß Anspruch 8 oder 9, **dadurch gekennzeichnet**, daß das Bindemittelmaterial eine Löslichkeit in Wasser bei 40°C von mehr als 20 Gew.-% aufweist.
- 50 11. Verfahren zur Herstellung eines teilchenförmigen Waschmitteladditivprodukts nach einem der vorangehenden Ansprüche, umfassend die Schritte der Behandlung von 25 bis 95 Gewichtsteilen eines festen teilchenförmigen, lagerungsempfindlichen Waschmitteladditivmaterials in einem Hochgeschwindigkeitsmischer/Granulator in Gegenwart von 75 bis 5 Gewichtsteilen eines organischen Bindemittelmaterials mit einem Schmelzpunkt von 25 bis 80°C , wodurch Granulierung und Kugelbildung bewirkt wird, Formen der Kernteilchen, gefolgt von Kühlen und Zugabe eines organischen Materials mit einem Schmelzpunkt unterhalb dem des Bindemittelmaterials von weniger als 60°C , und einer Löslichkeit in Wasser bei 40°C von mehr als 20 Gew.-%, wodurch Beschichten der Kernteilchen bewirkt wird, Herstellen von Körpern mit einer im wesentlichen runden Form durchschnittlicher Kugelförmigkeit $\geq 0,85$, einem Porenvolumen von nicht mehr als $0,25 \text{ cm}^3/\text{g}$ und einer Druckfestigkeit, ausgedrückt als Kompressionsmodul, von mehr als $0,5 \times 10^6 \text{ N/m}^2$.
- 55 12. Verfahren nach Anspruch 11, **dadurch gekennzeichnet**, daß die Granulierung bei einer Temperatur bewirkt wird, die leicht oberhalb des Schmelzpunktes des Bindemittelmaterials liegt.
- 60 13. Verfahren nach Anspruch 11 oder 12, **dadurch gekennzeichnet**, daß 50-90 Gewichtsteile des Waschmitteladditivmaterials in Gegenwart von 50 bis 10 Gewichtsteilen des flüssigen organischen Bindemittelmaterials behandelt werden.
- 65 14. Verfahren nach einem der Ansprüche 11 bis 13, **dadurch gekennzeichnet**, daß das Bindemittelmaterial ausgewählt ist aus der Gruppe, bestehend aus nichtionischen Tensiden, Fettsäuren, Polyethylenglycolen und anionischen Tensiden und Gemischen davon.
- 70 15. Verfahren nach einem der Ansprüche 11 bis 14, **dadurch gekennzeichnet**, daß das Beschichtungsma-

terial ausgewählt ist aus der Gruppe, bestehend aus nichtionischen Tensiden, Fettsäuren, Polyethylenglycolen und anionischen Tensiden und Gemischen davon mit einem geringeren Schmelzpunkt als dem des Bindemittelmaterials.

5

16. Verfahren nach einem der Ansprüche 11 bis 15, **dadurch gekennzeichnet**, daß das Beschichtungsmaterial einen Schmelzpunkt von mindestens 5°C unterhalb dem des Bindemittelmaterials aufweist.

10

17. Verfahren nach einem der vorstehenden Ansprüche 11 bis 16, **dadurch gekennzeichnet**, daß das Waschmitteladditivmaterial ausgewählt ist aus der Gruppe, bestehend aus Enzymen, Peroxysäureverbindungen, Persauerstoff- und Chlorbleichmitteln, Fluoreszenzmitteln und Peroxysäurebleichmittelvorstufen.

18. Verfahren nach Anspruch 17, **dadurch gekennzeichnet**, daß das Waschmitteladditivmaterial eine Peroxysäurebleichmittelvorstufe ist.

15

19. Verfahren nach Anspruch 18, **dadurch gekennzeichnet**, daß die Peroxysäurebleichmittelvorstufe Natrium-4-benzoyloxybenzolsulfonat ist.

20. Verfahren nach Anspruch 18 oder 19, **dadurch gekennzeichnet**, daß das Bindemittelmaterialeine Löslichkeit in Wasser bei 40°C von mehr als 20 Gew.-% aufweist.

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21. Waschpulver mit einem Waschmitteladditivprodukt nach einem der vorangehenden Ansprüche 1-10.

Revendications

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1. Produit additif détergent sous forme de particules, se composant d'un additif détergent contenant des corps de tailles dans la gamme de 100 à 2 000 µm, comprenant un matériau additif détergent enfermé de façon libérable à l'intérieur d'un matériau hydrosoluble, caractérisé en ce que chaque corps comprend une particule centrale se composant:

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(a) de 25 à 95% en poids d'un matériau additif détergent sensible au stockage sous forme de particules solides et

(b) de 75 à 5% en poids d'un matériau liant organique ayant un point de fusion de 25°C à 80°C;

dans lequel (a) et (b) sont pratiquement régulièrement distribués à travers la particule centrale, laquelle particule centrale est prévue avec un revêtement externe, à raison de 1 à 10% en poids, d'un matériau organique ayant un point de fusion inférieur à celui du matériau liant de moins de 60°C et une solubilité dans l'eau à 40°C supérieure à 20% en poids, lesdits corps ayant une forme de particules pratiquement rondes avec une sphéricité moyenne $\geq 0,85$ et ayant un volume de pores ne dépassant pas 0,25 cm³/gramme; ledit produit ayant une résistance mécanique à la compression, exprimée en termes de module de compression, supérieure à $0,5 \times 10^{-6}$ N/m².

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2. Produit additif détergent selon la revendication 1, caractérisé en ce que le noyau de particule comprend de 50 à 90% en poids dudit matériau additif détergent sous forme de particules solides sensibles au stockage et de 50 à 10% en poids dudit matériau liant organique.

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3. Produit additif détergent selon la revendication 1 ou 2, caractérisé en ce que le volume de pores est inférieur à 0,2 cm³/gramme.

4. Produit additif détergent selon la revendication 1, 2 ou 3, caractérisé en ce que le matériau liant est choisi dans le groupe formé par les tensio-actifs non ioniques, les acides gras, les polyéthylène-glycols et les tensio-actifs anioniques, et leurs mélanges.

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5. Produit additif détergent selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'on choisit le matériau de revêtement dans le groupe formé par les tensio-actifs non ioniques, les acides gras, les polyéthylène-glycols et les tensio-actifs anioniques, et leurs mélanges, ayant un point de fusion inférieur au matériau liant.

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6. Produit additif détergent selon l'une quelconque des revendications, caractérisé en ce que le matériau de revêtement a un point de fusion d'au moins 5°C au-dessous du matériau liant.

7. Produit additif détergent selon l'une quelconque des revendications 1 à 6, caractérisé en ce que l'on choisit

l'additif détergent dans le groupe formé par les enzymes, les peroxyacides, les agents de blanchiment peroxygéné et à base de chlore, les azurants et les précurseurs de blanchiment à base de peroxyacide.

- 5 **8.** Produit additif détergent selon la revendication 7, caractérisé en ce que l'additif détergent est un précurseur de blanchiment à base de peroxyde.
9. Produit additif détergent selon la revendication 8, caractérisé en ce que le précurseur de blanchiment à base de peroxyacide est le 4-benzoyloxybenzène sulfonate de sodium.
- 10 **10.** Produit additif détergent selon la revendication 8 ou 9, caractérisé en ce que le matériau liant a une solubilité dans l'eau à 40°C supérieure à 20% en poids.
11. Procédé pour la préparation d'un produit additif détergent sous forme de particules selon l'une quelconque des revendications précédentes, comprenant les étapes consistant à traiter 25 à 95 parties en poids d'un matériau additif détergent sensible au stockage sous forme de particules solides dans un mélangeur/granulateur à vitesse élevée en présence de 75 à 5 parties en poids d'un matériau liant organique ayant un point de fusion de 25°C à 80°C, grâce auquel on effectue la granulation et la mise en forme sphérique, à former les particules centrales, suivi par un refroidissement et l'addition d'un matériau organique ayant un point de fusion au-dessous de celui du matériau liant de moins de 60°C et une solubilité dans l'eau à 40°C supérieure à 20% en poids, par lequel on effectue le revêtement des particules centrales, à former des corps ayant une forme pratiquement ronde de sphéricité moyenne $\geq 0,85$, un volume de pores ne dépassant pas 0,25 cm³/gramme et une résistance à la compression, exprimée en termes de module de compression, supérieure à 0,5 x 10⁻⁶ N/m².
- 15 **12.** Procédé selon la revendication 11, caractérisé en ce que l'on effectue la granulation à une température légèrement au-dessus du point de fusion du matériau liant.
13. Procédé selon la revendication 11 ou 12, caractérisée en ce que 50 à 90 parties en poids dudit matériau additif détergent est traité en présence de 50 à 10 parties en poids dudit matériau liant organique liquéfié.
- 30 **14.** Procédé selon l'une quelconque des revendications 11 à 13, caractérisé en ce que le matériau liant est choisi dans le groupe formé par les tensio-actifs non ioniques, les acides gras, les polyéthylèneglycols et les tensio-actifs anioniques, et, leurs mélanges.
- 35 **15.** Procédé selon l'une quelconque des revendications 11 à 14, caractérisé en ce que le matériau de revêtement est choisi dans le groupe formé par les tensio-actifs non ioniques, les acides gras, les polyéthylèneglycols et les tensio-actifs anioniques, et leurs mélanges, ayant un point de fusion inférieur à celui du matériau liant.
- 40 **16.** Procédé selon l'une quelconque des revendications 11 à 15, caractérisé en ce que le matériau de revêtement a un point de fusion d'au moins 5°C au-dessous de celui du matériau liant.
- 45 **17.** Procédé selon l'une quelconque des revendications 11 à 16, caractérisé en ce que le matériau additif détergent est choisi dans le groupe formé par les enzymes les peroxyacides, les agents de blanchiment peroxygénés et à base de chlore, les azurants et les précurseurs de blanchiment à base de peroxyacide.
- 50 **18.** Procédé selon la revendication 17, caractérisé en ce que l'additif détergent est un précurseur de blanchiment à base de peroxyacide.
- 51 **19.** Procédé selon la revendication 18, caractérisé en ce que le précurseur de blanchiment à base de peroxyacide est le 4-benzoyloxy benzène sulfonate de sodium.
- 52 **20.** Procédé selon la revendication 18 ou 19, caractérisé en ce que le matériau liant a une solubilité dans l'eau à 40°C supérieure à 20% en poids.
- 55 **21.** Composition de poudre détergente incluant un produit additif détergent selon l'une quelconques des revendications précédentes 1 à 10.