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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0067862 A1****Speckmann et al.**(43) **Pub. Date: Apr. 8, 2004**(54) **PARTICLE-SHAPED ACETONITRILE DERIVATIVES AS BLEACH ACTIVATORS IN SOLID DETERGENTS**(76) Inventors: **Horst-Dieter Speckmann**, Langenfeld (DE); **Joerg Poethkow**, Neuss (DE); **Birgit Middelhaue**, Monheim (DE); **Martina Kihn-Botulinski**, Solingen (DE)

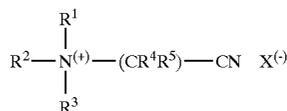
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Publication Classification(51) **Int. Cl.⁷ D06L 1/00**(52) **U.S. Cl. 510/311**(57) **ABSTRACT**

The invention aims to improve the oxidating and bleaching properties of inorganic peroxygen compounds during textile washing in a storage-resistant manner. In order to achieve this, particle-shaped compounds of formula (I) are essentially used, wherein R¹ represents H, CH₃, a C₂₋₂₄ alkyl or alkenyl radical, a substituted C₂₋₂₄ alkyl or alkenyl radical comprising at least one substituent from the group Cl, Br, OH, NH₂, CN, an alkyl or alkenyl radical comprising a C₂₋₂₄ alkyl group, or a substituted alkyl or alkenyl radical comprising a C₁₋₂₄ alkyl group and at least one further substituent on the aromatic ring; R² and R³ are independently chosen from CH₂-CN, CH₃, CH₂-H₃, CH₂-CH₂-CH₃, CH(CH₃)-CH₃, CH₂-OH, CH₂-CH₂-OH, -CH(OH)-CH₃, CH₂-CH₂-CH₂-OH, CH₂-CH(OH)-CH₃, CH(OH)-CH₂-CH₃, (CH₂CH₂-O)_nH, n being equal to 1, 2, 3, 4, 5 or 6; R⁴ and R⁵ independently have one of the designations cited above for R¹, R² or R³; and X represents a charge equalising anion. Textile detergent contains approximately 0.1 wt. % to 10 wt. % of one such bleaching agent.



**PARTICLE-SHAPED ACETONITRILE
DERIVATIVES AS BLEACH ACTIVATORS IN
SOLID DETERGENTS**

[0001] The present invention relates to the use of acetonitrile derivatives formulated in particle form as activators for, in particular inorganic, peroxygen compounds for the bleaching of colored textile soiling, and to detergents which comprise such activators.

[0002] Inorganic peroxygen compounds, in particular hydrogen peroxide and solid peroxygen compounds which dissolve in water to liberate hydrogen peroxide, such as sodium perborate and sodium carbonate perhydrate, have been used for a long time as oxidizing agents for disinfection and bleaching purposes. The oxidizing effect of the substances is, in dilute solutions, heavily temperature-dependent; thus, for example using H₂O₂ or perborate in alkaline bleach liquors, sufficiently rapid bleaching of soiled textiles is only achieved at temperatures above about 80° C. At lower temperatures, it is possible to improve the oxidizing effect of the inorganic peroxygen compounds by adding so-called bleach activators, for which numerous suggestions, mainly from the substance classes of N- or O-acyl compounds, for example polyacylated alkylenediamines, in particular tetraacetylenediamine, acylated glycolurils, in particular tetraacetylglycoluril, N-acylated hydantoin, hydrazides, triazoles, hydrotriazines, urazoles, diketopiperazines, sulfurylamides and cyanurates, and also carboxylic anhydrides, in particular phthalic anhydride, carboxylic esters, in particular sodium nonanoyloxybenzenesulfonate, sodium isononoylbenzenesulfonate and acylated sugar derivatives, such as pentaacetylglucose, have been disclosed in the literature. By adding these substances, it is possible to increase the bleaching effect of aqueous peroxide liquors such that even at temperatures around 60° C., the effects achieved are essentially the same as those achieved with the peroxide liquor on its own at 95° C.

[0003] In the search for energy-saving washing and bleaching processes, in recent years application temperatures significantly below 60° C., in particular below 45° C. down to the temperature of cold water have gained in importance.

[0004] At these low temperatures, the effect of the hitherto known activator compounds generally decreases noticeably. There has therefore been no lack of attempts to develop more effective activators for this temperature range although to date there has been no convincing success.

[0005] International patent application WO 98/23719 discloses that compounds of the general formula A



[0006] in which R¹, R² and R³, independently of one another, is an alkyl, alkenyl or aryl group having 1 to 18 carbon atoms, where the groups R² and R³ may also be part of a heterocycle including the N atom and optionally further heteroatoms, and X is a charge-balancing anion, can be used as activators for, in particular inorganic, peroxygen compounds in aqueous dishwashing solutions. This results in an improvement of the oxidizing and bleaching effect of, in particular inorganic, peroxygen compounds at low temperatures below 80° C., in particular in the temperature range from about 15° C. to 55° C. The compounds according to the general formula (A) are not, however, normally storage-

stable, particularly in combination with further ingredients of detergents and cleaners, and in particular are exceptionally sensitive toward moisture. Some of the representatives of the compounds according to the general formula (A) which have a particularly good bleach-enhancing effect are liquid at room temperature; others are produced in the course of their preparation in liquid form, for example as an aqueous solution, and can only be converted into the pure solid therefrom with considerable losses. In both cases, their use in solid, for example particle-shaped, compositions presents difficulties.

[0007] A subclass of such particle-shaped compositions is detergents in tablet form. Compared to pulverulent or liquid products, tableted compositions have a number of advantages: they are easier to dose and handle and, due to their compact structure, have advantages as regards storage and transportation. There is therefore an exceptionally broad prior art relating to detergent and cleaner shaped bodies, which is also evident from an extensive patent literature. In this connection, developers of tablet-shaped products had the idea of releasing certain ingredients via differently composed areas of the shaped body only under defined conditions in the washing or cleaning operation in order, in so doing, to improve the cleaning success. In this connection, as well as the core/coating tablets and ring/core tablets known sufficiently from pharmacy, multilayer shaped bodies in particular have become accepted which are nowadays supplied for many areas of washing and cleaning or hygiene.

[0008] Multiphase cleaning tablets for the WC are described, for example, in European patent application EP 0 055 100. This specification discloses toilet cleaning blocks which comprise a shaped body of a cleaning composition which dissolves slowly in which a bleach tablet is embedded. This specification also discloses a very wide variety of forms of multiphase shaped bodies. The shaped bodies are prepared in accordance with the teaching of this specification either by inserting a compressed bleach tablet into a mold and pouring a cleaning composition around this tablet, or by pouring some of the cleaning composition into the mold, followed by the insertion of the compressed bleach tablet and possibly subsequently pouring over further cleaning composition.

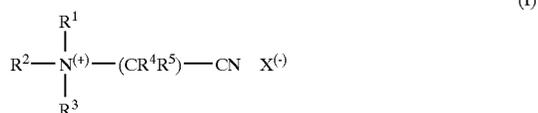
[0009] European patent application EP 0 481 547 also describes multiphase cleaning shaped bodies which are intended for use, according to this specification, for machine. dishwashing. These shaped bodies have the form of core/coating tablets and are prepared by stagewise compression of the constituents: firstly, a bleach composition is compressed to give a shaped body, which is placed into a die half-filled with a polymer composition, which is then filled up with further polymer composition and compressed to give a bleach shaped body provided with a polymer coating. The process is then repeated using an alkaline cleaning composition, resulting in a three-phase shaped body.

[0010] International patent application WO 98/23531 discloses heterocyclic N-alkylammonium nitrites of the type otherwise described above by formula (A) which has been formulated in granular form, where the carrier materials mentioned for the N-alkylammonium nitrites are, for example, silica, silicates and aluminum oxide.

[0011] It has now been found that certain acetonitrile derivatives formulated in particle form can be incorporated

in a storage-stable manner into solid, in particular tablet-shaped, textile detergents with elimination of the disadvantages mentioned above, where a further advantage which arises is an increased bleaching performance compared to compositions which comprise the acetonitrile derivative as a simple mixing or individual component.

[0012] The invention provides for the use of compounds of the general formula I, formulated to be particle-shaped using inorganic carrier materials which contain in particular silicate,



[0013] in which R¹ is —H, —CH₃, a C₂₋₂₄-alkyl or -alkenyl radical, a substituted C₂₋₂₄-alkyl or -alkenyl radical with at least one substituent from the group —Cl, —Br, —OH, —NH₂, —CN, an alkyl- or alkenyl radical with a C₁₋₂₄-alkyl group, or is a substituted alkyl- or alkenyl radical with a C₁₋₂₄-alkyl group and at least one further substituent on the aromatic ring, R² and R³, independently of one another, are chosen from —CH₂—CN, —CH₃, —CH₂—CH₃, —CH₂—CH₂—CH₃, —CH(CH₃)—CH₃, —CH₂—OH, —CH₂—CH₂—OH, —CH(OH)—CH₃, —CH₂—CH₂—CH₂—OH, —CH₂—CH(OH)—CH₃, —CH(OH)—CH₂—CH₃, —(CH₂CH₂—O)_nH where n=1, 2, 3, 4, 5 or 6, R⁴ and R⁵, independently of one another, have a meaning given above for R¹, R² or R³, and X is a charge-balancing anion, as activators for, in particular inorganic, peroxygen compounds in solid textile detergents which are used in essentially aqueous washing solutions.

[0014] The compounds according to formula I can be prepared by known processes or ones based on these, as published, for example, by Abraham in *Progr. Phys. Org. Chem.* 11 (1974), p. 1ff, or by Arnett in *J. Am. Chem. Soc.* 102 (1980), p. 5892ff.

[0015] Preference is given to the use of compounds according to formula I in which R¹, R² and R³ are identical. Of these, preference is given to those compounds in which said radicals are methyl groups. On the other hand, preference is also given to those compounds in which at least 1 or 2 of said radicals are methyl groups and the others have two or more carbon atoms.

[0016] The anions X⁻ include, in particular, the halides, such as chloride, fluoride, iodide and bromide, nitrate, hydroxide, phosphate, hydrogen phosphate, dihydrogen phosphate, pyrophosphate, metaphosphate, hexafluorophosphate, carbonate, hydrogen carbonate, sulfate, hydrogen sulfate, C₁₋₂₀-alkylsulfate, C₁₋₂₀-alkylsulfonate, optionally C₁₋₁₈-alkyl-substituted arylsulfonate, chlorate, perchlorate and/or the anions of C₁₋₂₄-carboxylic acids, such as formate, acetate, laurate, benzoate or citrate, alone or in any desired mixtures.

[0017] Preference is given to the use of compounds according to formula I in which X⁻ is chloride, sulfate, hydrogen sulfate, ethosulfate, lauryl sulfate, dodecylbenzenesulfonate, toluenesulfonate, cumenesulfonate, xylene-

sulfonate or methosulfate or mixtures thereof. Toluene-sulfonate and cumenesulfonate are understood here as meaning the anion of the ortho, meta or para isomers of methylbenzenesulfonic acid and isopropylbenzenesulfonic acid, respectively, and any desired mixtures thereof. Para-isopropylbenzenesulfonic acid is particularly preferred.

[0018] The compound according to general formula I is used in the detergents in particle-shaped form, i.e. applied to an inorganic carrier material. In this connection, application to the carrier material can be carried out by stirring the carrier material into a solution of the compound according to formula I, as is produced during the course of its preparation, and stripping off the solvent, which may or may not be aqueous, under reduced pressure, if desired at elevated temperature. However, it is also possible to spray the solution of the compound according to formula I onto the carrier material and, during this or possibly subsequently to it, subject it to a drying process. In this connection, it is preferred if the particles resulting from the formulating process have a diameter in the range from 0.4 mm to 1.2 mm.

[0019] Suitable carrier materials are all inorganic substances which do not interact with the compound according to formula I in an unreasonably negative manner, for example alkali metal carbonates, alkali metal sulfates, alkali metal hydrogen sulfates, alkali metal hydrogen carbonates, alkali metal phosphates, alkali metal dihydrogen phosphates, dialkali metal hydrogen phosphates and alkali metal silicates and mixtures thereof. Preference is given to using those carrier materials whose internal surface area is in the range from 10 m²/g to 500 m²/g, in particular 100 m²/g to 450 m²/g. The silicatic carrier materials which are particularly suitable for the purposes of the present invention include, for example, alkali metal silicates and also silicas, silica gels and clays, and mixtures thereof. However, the carrier material is preferably free from zeolites. In addition to the silicate component, silicate-containing carrier material optionally comprises further particle-shaped inert constituents which do not unreasonably impair the stability of the compounds according to formula I.

[0020] Silicas which have been produced by a thermal process (flame hydrolysis of SiCl₄) (so-called pyrogenic silicas) are equally suitable for use as are silicas produced by wet processes. Silica gels are colloidal silicas with elastic to solid consistency and a loose pore structure, resulting in a high liquid-uptake capacity. They can be prepared by the action of mineral acids on waterglass. Clays are naturally crystalline or amorphous silicates of aluminum, iron, magnesium, calcium, potassium and sodium, for example kaolin, talc, pyrophyllite, attapulgite, sepiolite, montmorillonite and bauxite. The use of aluminum silicate as carrier material or as a component of a carrier material mixture is also possible. The carrier material preferably has particle sizes in the range from 100 μm to 1.5 mm.

[0021] In the particle-shaped compounds of the formula I, preferably 10 to 50 parts by weight of the carrier material and 50 to 90 parts by weight of the compound according to formula I are present. The particles can also be completely or at least partially coated with inorganic and/or organic materials.

[0022] The acetonitrile derivative formulated to be particle-shaped using the, in particular, silicate-containing car-

rier material can additionally comprise an organic material with a melting point greater than 40° C., in particular nonionic surfactant, and/or be coated with such a material. This may have a positive influence on the disintegration properties of the corresponding particle in aqueous systems and/or on its storage stability.

[0023] An acetonitrile derivative according to formula I formulated in this way to be particle-shaped is preferably incorporated into detergents which are intended for use in washing solutions for textiles for bleaching colored soiling. In this connection, the term bleaching is understood as meaning both the bleaching of soiling present on the textile surface, in particular tea, and also the bleaching of soil detached from the textile present within the washing liquor.

[0024] In addition, the invention relates to solid detergents and, of these, preference is given to those for use in machine washing operations which comprise an abovementioned compound according to formula I in a corresponding particle-shaped form, and a process for the washing of laundry using a compound formulated in this way.

[0025] The use according to the invention as bleach activator consists essentially in creating, in the presence of a textile contaminated with colored soiling, conditions under which a peroxy oxidizing agent and the bleach-activating acetonitrile derivative can react with one another with the aim of obtaining secondary products which have a stronger oxidizing effect. Such conditions are present particularly when both reactants meet in aqueous solution. This can happen as a result of the separation addition of the peroxygen compound and the acetonitrile derivative to a solution which may or may not contain detergent. However, the process according to the invention is particularly advantageously carried out using a detergent according to the invention which comprises the bleach-activating acetonitrile derivative and optionally a peroxygen-containing oxidizing agent, preferably chosen from the group consisting of organic peracids, hydrogen peroxide, perborate and percarbonate, and mixtures thereof. The peroxygen compound can also be added separately to the solution, in a form without a diluent or preferably in the form of an aqueous solution or suspension, if a peroxide-free detergent is used.

[0026] Depending on the intended use, the conditions can be varied widely. For example, as well as purely aqueous solutions, mixtures of water and suitable organic solvents as reaction medium are also suitable. The amounts of peroxygen compounds used are generally chosen so that between 10 ppm and 10% active oxygen, preferably between 50 ppm and 5 000 ppm of active oxygen, are present in the solutions. The amount of bleach-activating acetonitrile derivative used also depends on the intended use. Depending on the desired degree of activation, 0.00001 mol to 0.25 mol, preferably 0.001 mol to 0.02 mol, of activator are used per mole of peroxygen compound, although these limits may also be exceeded or fallen below in special cases.

[0027] The invention further provides a solid detergent which comprises 0.1% by weight to 10% by weight, in particular 0.22% by weight to 6% by weight, of an acetonitrile derivative according to formula I in a form rendered particle-shaped as described above, in addition to customary ingredients compatible with the compound.

[0028] The solid compositions according to the invention, which may, for example, be in the form of pulverulent or

tablet-shaped solids, can in principle comprise all ingredients which are known and customary in such compositions apart from the bleach activator used according to the invention. The compositions according to the invention can, in particular, comprise builder substances, surface-active surfactants, peroxygen compounds, water-miscible organic solvents, enzymes, sequestering agents, electrolytes, pH regulators and further auxiliaries, such as color transfer inhibitors, foam regulators, additional bleach-enhancing active ingredients, and dyes and fragrances.

[0029] Suitable peroxygen compounds suitable for use in compositions according to the invention are, in particular, inorganic salts which release hydrogen peroxide under the washing conditions, which includes the alkali metal perborates, percarbonates, persulfates and/or persulfates, such as caroate, but also organic peracids or peracidic salts of organic acids, such as phthalimidopercaproic acid, perbenzoic acid or salts of diperdodecanedioic acid. Such solid peroxygen compounds can be used, for example, in the form of powders or granules, which may also be coated in a manner known in principle. Peroxygen compounds are present in amounts of preferably up to 50% by weight, in particular from 5% by weight to 30% by weight and particularly preferably from 8% to 25% by weight. The addition of small amounts of known bleach stabilizers, such as, for example, of phosphonates, borates or metaborates and metasilicates and magnesium salts, such as magnesium sulfate, may be appropriate.

[0030] The compositions according to the invention can comprise one surfactant or two or more surfactants, where anionic surfactants, nonionic surfactants and mixtures thereof, but also cationic, zwitterionic and amphoteric surfactants are particularly suitable.

[0031] Suitable nonionic surfactants are, in particular, alkyl glycosides and ethoxylation and/or propoxylation products of alkyl glycosides or linear or branched alcohols each having 12 to 18 carbon atoms in the alkyl moiety and 3 to 20, preferably 4 to 10, alkyl ether groups. It is also possible to use corresponding ethoxylation and/or propoxylation products of N-alkylamines, vicinal diols, fatty acid esters and fatty acid amides which correspond to said long-chain alcohol derivatives with regard to the alkyl moiety, and also of alkylphenols having 5 to 12 carbon atoms in the alkyl radical.

[0032] The nonionic surfactants used are preferably alkoxylation, advantageously ethoxylation, in particular primary alcohols having preferably 8 to 18 carbon atoms and on average 1 to 12 mol of ethylene oxide (EO) per mole of alcohol in which the alcohol radical may be linear or preferably methyl-branched in the 2-position, or can contain linear and methyl-branched radicals in the mixture, as are customarily present in oxo alcohol radicals. In particular, however, preference is given to alcohol ethoxylates with linear radicals from alcohols of native origin having 12 to 18 carbon atoms, e.g. from coconut alcohol, palm alcohol, tallow fatty alcohol or oleyl alcohol, and on average 2 to 8 EO per mole of alcohol. Preferred ethoxylated alcohols include, for example, C₁₂-C₁₄-alcohols having 3 EO or 4 EO, C₉-C₁₁-alcohols having 7 EO, C₁₃-C₁₅-alcohols having 3 EO, 5 EO, 7 EO or 8 EO, C₁₂-C₁₈-alcohols having 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C₁₂-C₁₄-alcohol with 3 EO and C₁₂-C₁₈-alcohol with 7 EO.

The degrees of ethoxylation given represent statistical average values which may be an integer or a fraction for a specific product. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, it is also possible to use fatty alcohols having more than 12 EO. Examples thereof are (tallow) fatty alcohols with 14 EO, 16 EO, 20 EO, 25 EO, 30 EO or 40 EO. Particularly in compositions for use in machine processes, it is possible to use extremely low-foam compounds. These include preferably C₁₂-C₁₄-alkylpolyethylene glycol polypropylene glycol ethers having in each case at to 8 mol of ethylene oxide and propylene oxide units in the molecule. However, it is also possible to use other known low-foam nonionic surfactants, such as, for example, C₁₂-C₁₈-alkylpolyethylene glycol polybutylene glycol ethers each having up to 8 mol of ethylene oxide and butylene oxide units in the molecule, and also terminally capped alkylpolyalkylene glycol mixed ethers. Particular preference is also given to the alkoxyated alcohols which contain hydroxyl groups, as are described in European patent application EP 0 300 305, so-called hydroxy mixed ethers. The nonionic surfactants also include alkyl glycosides of the general formula RO(G)_x are used, in which R is a primary straight-chain or methyl-branched, particularly methyl-branched in the 2-position, aliphatic radical having 8 to 22, preferably 12 to 18, carbon atoms, and G is a glyucose unit having 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization x, which gives the distribution of monoglycosides and oligoglycosides, is any desired number which, being a parameter to be determined analytically, may also assume fractional values, between 1 and 10; preferably x is 1.2 to 1.4. Likewise suitable are polyhydroxy fatty acid amides of the formula (II) in which R¹CO is an aliphatic acyl radical having 6 to 22 carbon atoms, R² is hydrogen, an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and 3 to 10 hydroxyl groups:



[0033] Preferably, the polyhydroxy fatty acid amides are derived from reducing sugars having 5 or 6 carbon atoms, in particular from glucose. The group of polyhydroxy fatty acid amides also includes compounds of the formula (III),



[0034] in which R³ is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R⁴ is a linear or branched or cyclic alkenyl radical or an arylene radical having 2 to 8 carbon atoms and R⁵ is a linear, branched or cyclic alkyl radical or an aryl radical or an oxyalkyl radical having 1 to 8 carbon atoms, where C₁-C₄-alkyl or phenyl radicals are preferred, and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two

hydroxyl groups, or alkoxyated, preferably ethoxyated or propoxyated, derivatives of this radical. [Z] is also here preferably obtained by reductive amination of a sugar such as glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds can then be converted into the desired polyhydroxy fatty acid amides for example in accordance with the teaching of the International patent application WO 95/07331 by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst. A further class of preferred nonionic surfactants, which are used either as the sole nonionic surfactant or in combination with other nonionic surfactants, in particular together with alkoxyated fatty alcohols and/or alkyl glycosides, are alkoxyated, preferably ethoxyated or ethoxyated and propoxyated fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, in particular fatty acid methyl esters, as are described, for example, in Japanese patent application JP 58/217598, or which are preferably prepared in accordance with the process described in International patent application WO 90/13533. Nonionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallow-alkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type may also be suitable. The amount of these nonionic surfactants is preferably not more than that of the ethoxyated fatty alcohols, in particular not more than half thereof. Suitable further surfactants are so-called gemini surfactants. This term is generally understood as meaning those compounds which have two hydrophilic groups per molecule. These groups are usually separated from one another by a so-called "spacer". This spacer is generally a carbon chain which should be long enough for the hydrophilic groups to have a sufficient distance such that they can act independently of one another. Such surfactants are generally characterized by an unusually low critical micelle concentration and the ability to drastically reduce the surface tension of water. In exceptional cases, the expression gemini surfactants is understood as meaning not only such "dimeric" surfactants, but also correspondingly "trimeric" surfactants. Suitable gemini surfactants are, for example, sulfated hydroxy mixed ethers according to German patent application DE 43 21 022 or dimer alcohol bis- and trimer alcohol tris-sulfates and -ether sulfates according to German patent application DE 195 03 061.

[0035] Terminally capped dimeric and trimeric mixed ethers according to German patent application DE 195 13 391 are characterized in particular by their bi- and multifunctionality. For example, said terminally capped surfactants have good wetting properties and are low-foam at the same time, meaning that they are suitable in particular for use in machine washing or cleaning processes. It is, however, also possible to use gemini-polyhydroxy fatty acid amides or poly-polyhydroxy fatty acid amides, as are described in International patent applications WO 95/19953, WO 95/19954 and WO 95/19955.

[0036] Suitable anionic surfactants are, in particular, soaps and those which contain sulfate or sulfonate groups. Suitable surfactants of the sulfonate type are preferably C₉-C₁₃-alkylbenzenesulfonates, olefinsulfonates, i.e. mixtures of alkene- and hydroxyalkanesulfonates and also disulfonates, as are obtained, for example, from C₁₂-C₁₈-monoolefins with terminal or internal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Also suitable are

alkanesulfonates which are obtained from C_{12} - C_{18} -alkanes, for example by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization. Also suitable are the esters of α -sulfo fatty acids (ester sulfonates), for example the α -sulfonated methyl esters of the hydrogenated coconut, palm, kernel or tallow fatty acids, which are prepared by α -sulfonation of the methyl esters of fatty acids of vegetable and/or animal origin having 8 to 20 carbon atoms in the fatty acid molecule and subsequent neutralization of the water-soluble monosalts, in consideration. These are preferably the α -sulfonated esters of hydrogenated coconut, palm, palm kernel or tallow fatty acids, it also being possible for sulfonation products of unsaturated fatty acids, for example oleic acid, to be present in small amounts, preferably in amounts not more than about 2 to 3% by weight. In particular, preference is given to α -sulfo fatty acid alkyl esters which have an alkyl chain with not more than 4 carbon atoms in the ester group, for example methyl esters, ethyl esters, propyl esters and butyl esters. With particular advantage, the methyl esters of the α -sulfo fatty acids (MES), but also their saponified disalts are used. Further suitable anionic surfactants are sulfated fatty acid glycerol esters, which represent mono-, di- and triesters and mixtures thereof, as are obtained during the production by esterification by a monoglycerol with 1 to 3 mol of fatty acid or during the transesterification of triglycerides with 0.3 to 2 mol of glycerol. Preferred alk(en)yl sulfates are the alkali metal and, in particular, the sodium salts of the sulfuric monoesters of C_{12} - C_{18} -fatty alcohols, for example from coco fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol or of C_{10} - C_{20} -oxoalcohols and those half-esters of secondary alcohols of this chain length. Also preferred are alk(en)yl sulfates of said chain length which contain a synthetic straight-chain alkyl radical produced on a petrochemical basis which have a degradation behavior analogous to that of the equivalent compounds based on fatty chemical raw materials. From a washing performance viewpoint, particular preference is in C_{12} - C_{16} -alkylsulfates and C_{12} - C_{15} -alkylsulfates and also C_{14} - C_{15} -alkylsulfates. 2,3-Alkylsulfates, which are prepared, for example, in accordance with the US American patent specifications U.S. Pat. No. 3,234,258 or U.S. Pat. No. 5,075,041 and can be obtained as commercial products of the Shell Oil Company under the name DAN®, are also suitable anionic surfactants. Also suitable are the sulfuric monoesters of the straight-chain or branched C_7 - C_{21} -alcohols ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl-branched C_9 - C_{11} -alcohols having on average 3.5 mol of ethylene oxide (EO) or C_{12} - C_{18} -fatty alcohols having 1 to 4 EO. The preferred anionic surfactants also include the salts of alkylsulfosuccinic acid, which are also referred to as sulfosuccinates or as sulfosuccinic esters, and the monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and in particular ethoxylated fatty alcohols. Preferred sulfosuccinates contain C_8 - C_{18} -fatty alcohol radicals or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol radical derived from ethoxylated fatty alcohols which, considered by themselves, represent nonionic surfactants. In this connection, particular preference is in turn given to sulfosuccinates whose fatty alcohol radicals are derived from ethoxylated fatty alcohols with narrowed homolog distribution. It is likewise also possible to use alk(en)ylsuccinic acid having preferably 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof. Further suitable

anionic surfactants are fatty acid derivatives of amino acids, for example of N-methyltaurine (taurides) and/or of N-methylglycine (sarcosides). In this connection, particular preference is given to the sarcosides or the sarcosinates and here primarily to sarcosinates of higher and optionally mono- or polyunsaturated fatty acids, such as oleyl sarcosinate. Further suitable anionic surfactants are, in particular, soaps. In particular, saturated fatty acids soaps are suitable, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and also soap mixtures derived in particular from natural fatty acids, for example coconut, palm kernel or tallow fatty acids. It is also possible to use the known alkenyl succinic acid salts together with these soaps or as a replacement for soaps.

[0037] The anionic surfactants, including the soaps, can be in the form of their sodium, potassium or ammonium salts, and also in the form of soluble salts of organic bases, such as mono-, di- or triethanolamine and/or -isopropanolamine. The anionic surfactants are preferably in the form of their sodium or potassium salts, in particular in the form of the sodium salts.

[0038] Surfactants are present in detergents according to the invention in quantitative fractions of preferably 5% by weight to 50% by weight, in particular from 8% by weight to 30% by weight.

[0039] A composition according to the invention preferably comprises at least one water-soluble and/or water-insoluble, organic and/or inorganic builder. The water-soluble organic builder substances include polycarboxylic acids, in particular citric acid and sugar acids, monomeric and polymeric aminopolycarboxylic acids, in particular methylglycinediacetic acid, nitrilotriacetic acid and ethylenediaminetetraacetic acid, and also polyaspartic acid, polyphosphonic acids, in particular aminotris-(methylenephosphonic acid), ethylenediaminetetrakis-(methylenephosphonic acid) and 1-hydroxyethane-1,1-diphosphonic acid, polymeric hydroxy compounds, such as dextrin, and polymeric (poly)carboxylic acids, in particular the polycarboxylates, accessible by oxidation of polysaccharides or dextrans, of European patent specification EP 0 625 992 or of International patent application WO 92/18542 or of European patent specification EP 0 232 202, polymeric acrylic acids, methacrylic acids, maleic acids and mixed polymers thereof, which may also contain small amounts of polymerizable substances without carboxylic acid functionality in copolymerized form. The relative molecular mass of the homopolymers of unsaturated carboxylic acids is generally between 3 000 and 200 000, that of the copolymers is between 2 000 and 200 000, preferably 30 000 to 120 000, in each case based on free acid. A particularly preferred acrylic acid-maleic acid copolymer has a relative molecular mass of from 30 000 to 100 000. Standard commercial products are, for example, Sokalan® CP 5, CP 10 and PA 30 from BASF. Suitable, although less preferred compounds of this class are copolymers of acrylic acid or methacrylic acid with vinyl ethers, such as vinyl methyl ethers, vinyl esters, ethylene, propylene and styrene, in which the proportion of the acid is at least 50% by weight. Water-soluble organic builder substances which may be used are also terpolymers which contain, as monomers, two unsaturated acids and/or salts thereof, and, as a third monomer, vinyl alcohol and/or an esterified vinyl alcohol or a carbohydrate. The first acidic monomer or salt thereof is derived from a monoethylenically

unsaturated C₃-C₈-carboxylic acid and preferably from a C₃-C₄-monocarboxylic acid, in particular from (meth)acrylic acid. The second acidic monomer or salt thereof can be a derivative of a C₄-C₈-dicarboxylic acid, where maleic acid is particularly preferred, and/or a derivative of an allylsulfonic acid which is substituted in the 2-position by an alkyl or aryl radical. Such polymers can be prepared, in particular, by processes described in German patent specification DE 42 21 381 and German patent application DE 43 00 772, and generally have a relative molecular mass between 1 000 and 200 000. Further preferred copolymers are those described in German patent applications DE 43 03 320 and DE 44 17 734 and have, as monomers, preferably acrolein and acrylic acid/acrylic acid salts or vinyl acetate. All said acids are generally used in the form of their water-soluble salts, in particular their alkali metal salts.

[0040] Such organic builder substances can if desired be present in amounts up to 40% by weight, in particular up to 25% by weight and preferably from 1% by weight to 8% by weight.

[0041] Suitable water-soluble inorganic builder materials are, in particular, alkali metal silicates, alkali metal carbonates and alkali metal phosphates, which may be in the form of their alkaline, neutral or acidic sodium or potassium salts. Examples thereof are trisodium phosphate, tetrasodium diphosphate, disodium dihydrogen diphosphate, pentasodium triphosphate, so-called sodium hexametaphosphate, oligomeric trisodium phosphate with degrees of oligomerization of from 5 to 1000, in particular 5 to 50, and the corresponding potassium salts or mixtures of sodium and potassium salts. The water-insoluble, water-dispersible inorganic builder materials used are, in particular, crystalline or amorphous alkali metal aluminosilicates, in amounts of up to 50% by weight, preferably not more than 40% by weight, and in liquid compositions in particular from 1% by weight to 5% by weight. Among these, the crystalline sodium aluminosilicates in detergent grade, in particular zeolite A, P and optionally X, alone or in mixtures, for example in the form of a cocrystallizate of the zeolites A and X (Vegobond® AX, a commercial product from Condea Augusta S.p.A.) are preferred. Amounts approaching the specified upper limit are preferably used in solid, particle-shaped compositions. Suitable aluminosilicates have, in particular, no particles with a particle size greater than 30 μm and preferably consist of at least 80% by weight of particles with a size below 10 μm. Their calcium-binding capacity, which can be determined in accordance with the details in German patent specification DE 24 12 837, is usually in the range from 100 to 200 mg of CaO per gram.

[0042] Suitable substitutes or partial substitutes for said aluminosilicate are crystalline alkali metal silicates which may be present on their own or in a mixture with amorphous silicates. The alkali metal silicates which can be used as builders in the compositions according to the invention preferably have a molar ratio of alkali metal oxide to SiO₂ of less than 0.95, in particular from 1:1.1 to 1:1.2 and can be in amorphous or crystalline form. Preferred alkali metal silicates are the sodium silicates, in particular the amorphous sodium silicates, with a molar ratio Na₂O:SiO₂ of 1:2 to 1:2.8. Those with an Na₂O:SiO₂ molar ratio of 1:1.9 to 1:2.8 can be prepared in accordance with the process in European patent application EP 0 425 427. The crystalline silicates used, which may be present on their own or in a mixture with

amorphous silicates, are preferably crystalline phyllosilicates of the general formula Na₂Si_xO_{2x+1}·yH₂O, in which x, the so-called modulus, is a number from 1.9 to 22, in particular 1.9 to 4, and y is a number from 0 to 33, and preferred values for x are 2, 3 or 4. Crystalline phyllosilicates which fall under this general formula are described, for example, in European patent application EP 0 164 514. Preferred crystalline phyllosilicates are those in which x in said general formula assumes the values 2 or 3. In particular, both β- and also δ-sodium disilicates (Na₂Si₂O₅·yH₂O) are preferred, where β-sodium disilicate can, for example, be obtained by the process which is described in International patent application WO 91/08171. δ-Sodium silicates with a modulus between 1.9 and 3.2 can be prepared according to Japanese patent applications JP 04/238 809 or JP 04/260 610. Virtually anhydrous crystalline alkali metal silicates, prepared from amorphous alkali metal silicates, of the abovementioned general formula in which x is a number from 1.9 to 2.1, which can be prepared as described in European patent applications EP 0 548 599, EP 0 502 325 and EP 0 452 428, can also be used in compositions according to the invention. In a further preferred embodiment of compositions according to the invention, use is made of a crystalline sodium phyllosilicate with a modulus of from 2 to 3, as can be prepared by the process of European patent application EP 0 436 835 from Sand and Soda. Crystalline sodium silicates with a modulus in the range from 1.9 to 3.5, as are obtainable by the processes of European patent specifications EP 0 164 552 and/or EP 0 294 753, are used in a further preferred embodiment of compositions according to the invention. Crystalline layered silicates of the formula given above are sold by Clariant GmbH under the trade name Na-SKS, e.g. Na-SKS-1 (Na₂Si₂₂O₄₅·xH₂O, kenyaite), Na-SKS-2 (Na₂Si₁₄O₂₉·xH₂O, magadiite), Na-SKS-3 (Na₂Si₈O₁₇·XH₂O) or Na-SKS-4 (Na₂Si₄O₉·xH₂O, makatite). Of these, Na-SKS-5 (α-Na₂Si₂O₅), Na-SKS-7 (β-Na₂Si₂O₅, natrosilite), Na-SKS-9 (NaHSi₂O₅·3H₂O), Na-SKS-10 (NaHSi₂O₅·3H₂O, kanemite), Na-SKS-11 (t-Na₂Si₂O₅) and Na-SKS-13 (NaHSi₂O₅), but in particular Na-SKS-6 (δ-Na₂Si₂O₅) are primarily suitable. An overview of crystalline phyllosilicates is given, for example, in the articles published in "Hoechst High Chem Magazine 14/1993" on pages 33-38 and in "Seifen-Öle-Fette-Wachse, Volume 116, No. 20/1990" on pages 805-808. In a preferred embodiment of compositions according to the invention, use is made of a granular compound of crystalline phyllosilicate and citrate, of crystalline phyllosilicate and the abovementioned (co)polymeric polycarboxylic acid, as is described, for example, in German patent application DE 198 19 187, or of alkali metal silicate and alkali metal carbonate, as is described, for example, in International patent application WO 95/22592, or is commercially available, for example, under the name Nabion® 15.

[0043] Builder substances can be present in the compositions according to the invention where appropriate in amounts up to 90% by weight. They are preferably present in amounts up to 75% by weight, in particular from 5% by weight to 50% by weight.

[0044] In addition to the bleach-activating acetonitrile derivatives according to formula I essential for the invention, it is possible to use known conventional bleach activators, i.e. compounds which, under perhydrolysis conditions, produce aliphatic peroxocarboxylic acids with

preferably 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or optionally substituted perbenzoic acid. Suitable substances are those which carry O- and/or N-acyl groups of said number of carbon atoms and/or optionally substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, in particular tetraacetylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycoluriles, in particular tetraacetylglycolurile (TAGU), N-acylamides, in particular N-nonanoylsuccinimide (NOSI), carboxylic anhydrides, in particular phthalic anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from the German patent applications DE 196 16 693 and DE 196 16 767, and also acetylated sorbitol and mannitol, and mixtures thereof (SORMAN) described in European patent application EP 0 525 239, acylated sugar derivatives, in particular pentaacetylglucose (PAG), pentaacetylfructose, tetraacetylxylose and octaacetylactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example N-benzoylcaprolactam, which are known from International patent applications WO 94/27970, WO 94/28102, WO 94/28103, WO 95/00626, WO 95/14759 and WO 95/17498. The hydrophilically substituted acylacetals known from German patent application DE 196 16 769 and the acyllactams described in German patent application DE 196 16 770 and International patent application WO 95/14075 are likewise preferably used. The combination of conventional bleach activators known from German patent application DE 44 43 177 can also be used. Such conventional bleach activators are present, if desired, in the customary quantitative range, preferably in amounts of from 0.1% by weight to 10% by weight, in particular 0.5% by weight to 7% by weight, based on the overall composition.

[0045] In addition to the conventional bleach activators listed above, or in place of them, it is also possible for the sulfonimines known from European patent specifications EP 0 446 982 and EP 0 453 003 and/or bleach-enhancing transition metal salts or transition metal complexes to be present as so-called bleach catalysts. Suitable transition metal compounds include, in particular, the manganese-, iron-, cobalt-, ruthenium- or molybdenum-salene complexes known from German patent application DE 195 29 905, and their N-analogous compounds known from German patent application DE 196 20 267, the manganese-, iron-, cobalt-, ruthenium- or molybdenum-carbonyl complexes known from the German patent application DE 195 36 082, the manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands described in German patent application DE 196 05 688, the cobalt-, iron-, copper- and ruthenium-ammine complexes known from German patent application DE 196 20 411, the manganese, copper and cobalt complexes described in German patent application DE 44 16 438, the cobalt complexes described in European patent application EP 0 272 030, the manganese complexes known from the European patent application EP 0 693 550, the manganese, iron, cobalt and copper complexes known from European patent specification EP 0 392 592, and/or the manganese complexes described in European patent specification EP 0 443 651 or the European patent applications EP 0 458 397, EP 0 458 398, EP 0 549 271, EP 0 549 272, EP

0 544 490 and EP 0 544 519. Combinations of bleach activators and transition metal bleach catalysts are known, for example, from German patent application DE 196 13 103 and International patent application WO 95/27775. Bleach-enhancing transition metal salts and/or complexes, in particular with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, are used if desired in customary amounts, preferably up to 1% by weight, in particular from 0.0025% by weight to 0.5% by weight and particularly preferably from 0.01% by weight to 0.1% by weight, in each case based on the total composition. Particularly preferred bleach catalyst complexes include cobalt-, iron-, copper- and ruthenium-ammine complexes, for example $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and/or $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$. In a further preferred configuration, the compositions contain, in addition to the bleach activator according to the formula I formulated to be particle-shaped, a bleach-enhancing active ingredient combination which is obtainable according to European patent application EP 0 832 969 by intimately mixing a water-soluble salt of a dihydric transition metal, chosen from cobalt, iron, copper and ruthenium, and mixtures thereof, a water-soluble ammonium salt and optionally an oxidizing agent based on peroxide, and also inert carrier materials, in amounts of from preferably 0.25% by weight to 25% by weight, in particular 1% by weight to 10% by weight; a preferred use of the particle-shaped bleach activator according to formula I takes place in the presence of such an active ingredient combination.

[0046] Additionally, the compositions according to the invention can comprise enzymes, such as proteases, amylases, pullulanases, mannanases, xylanases, cutanases, lipases, hemicellulases and cellulases, for example proteases such as BLAP®, Optimase®, Opticlean®, Maxacal®, Maxapem®, Esperase®, Savinase®, Purafect® OXP and/or Durazym®, amylases, such as Termamyl®, Amylase-LT®, Maxamyl®, Duramyl® and/or Purafect® OxAm, lipases, such as Lipolase®, Lipomax®, Lumafast® and/or Lipozym®, cellulases, such as Celluzyme®, Ecostone® and/or Carezyme®. The optionally used enzymes can, as described, for example, in International patent applications WO 92/11347 or WO 94/23005, be adsorbed to carrier substances and/or embedded in coating substances in order to protect them against premature deactivation. They are present in the compositions according to the invention preferably in amounts up to 2% by weight, in particular from 0.1% by weight to 1.5% by weight, particular preference being given to using enzymes stabilized against oxidative degradation, as known, for example, from the International patent applications WO 94/02597, WO 94/02618, WO 94/18314, WO 94/23053 or WO 95/07350.

[0047] The color transfer inhibitors suitable for use in textile detergents according to the invention include, in particular, polyvinylpyrrolidones, polyvinylimidazoles, polymeric N-oxides, such as poly(vinylpyridine N-oxide) and copolymers of vinylpyrrolidone with vinylimidazole.

[0048] Antiredeposition agents have the task of keeping the soiling detached from the fiber in suspended form in the liquor. Suitable for this purpose are water-soluble colloids, usually organic in nature, for example starch, glue, gelatin, salts of ether carboxylic acids or ether sulfonic acids of starch or of cellulose, or salts of acidic sulfuric esters of cellulose or of starch. Water-soluble polyamides containing acidic groups are also suitable for this purpose. Furthermore,

starch derivatives other than those mentioned above may be used, for example aldehyde starches. Preference is given to using cellulose ethers, such as carboxymethylcellulose (Na salt), methylcellulose, hydroxyalkylcellulose and mixed ethers, such as methylhydroxyethylcellulose, methylhydroxypropylcellulose, methylcarboxymethylcellulose and mixtures thereof, for example in amounts of from 0.1 to 5% by weight, based on the compositions.

[0049] In order to enhance the cleaning performance, the detergents according to the invention can, in particular, comprise soil release polymers, which are generally composed of carboxylic acid units and optionally polymeric diol units and contain, for example, ethylene terephthalate and polyoxyethylene terephthalate groups. Other monomer units, for example propylene glycol, polypropylene glycol, alkylene- or alkenylenedicarboxylic acids, isophthalic acid, carboxy- or sulfo-substituted phthalic acid isomers may be present in the soil release polymer. It is also possible to use terminally capped derivatives, i.e. polymers which have neither free hydroxyl groups nor free carboxyl groups, but, for example, carry C_{1-4} -alkyl groups or have been terminally esterified with monobasic carboxylic acids, for example benzoic acid or sulfolobenzoic acid. Also suitable are the polyesters known from European patent application EP 0 241 985 which, in addition to oxyethylene groups and terephthalic acid units, contain 1,2-propylene, 1,2-butylene and/or 3-methoxy-1,2-propylene groups, and glycerol units and are terminally capped with C_{1-4} -alkyl groups, the soil release polymers of ethylene terephthalate and polyethylene oxide terephthalate with a molar mass of from 900 to 9 000 used in the compositions of European patent application EP 0 253 567, where the polyethylene glycol units have molecular weights of from 300 to 3 000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 0.6 to 0.95, the polyesters with polypropylene terephthalate and polyoxyethylene terephthalate units and terminally capped at least proportionately by C_{1-4} -alkyl or acyl radicals known from European patent application EP 0 272 033, the sulfoethyl-terminally capped terephthalate-containing soil release polyesters mentioned in European patent application EP 0 274 907, the soil release polyesters with terephthalate, alkylene glycol and poly- C_{2-4} -glycol units prepared by sulfonation of unsaturated end-groups of European patent application EP 0 357 280, the cationic soil release polyesters with amine, ammonium and/or amine oxide groups known from European patent application EP 0 398 133 and the cationic soil release polyesters with ethoxylated, quaternized morpholine units of European patent application EP 0 398 137. Likewise suitable are polymers of ethylene terephthalate and polyethylene oxide terephthalate in which the polyethylene glycol units have molecular weights of from 750 to 5 000 and the molar ratio of ethylene terephthalate polyethylene oxide terephthalate is 50:50 to 90:10 and whose use in detergents is described in German patent specification DE 28 57 292, and also polymers with a molecular weight of from 15 000 to 50 000 comprising ethylene terephthalate and polyethylene oxide terephthalate, where the polyethylene glycol units have molecular weights of from 1000 to 10 000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 2:1 to 6:1, which, according to German patent application DE 33 24 258, can be used in detergents.

[0050] Textile detergents according to the invention can comprise derivatives of diaminostilbenedisulfonic acid or

their alkali metal salts as optical brighteners. Suitable are, for example, salts of 4,4'-bis(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)stilbene-2,2'-disulfonic acid or compounds of a similar structure which carry a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. In addition, brighteners of the substituted diphenylstyryl type may be present, for example the alkali metal salts of 4,4'-bis(2-sulfostyryl)diphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)diphenyl, or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)diphenyl. Mixtures of the abovementioned optical brighteners can also be used.

[0051] If the compositions foam excessively during use, preferably up to 5% by weight, in particular about 0.1% by weight to 3% by weight, of a foam-regulating compound, preferably from the group of silicone oils, mixtures of silicone oil and hydrophobized silica, paraffins, paraffin-alcohol combinations, hydrophobized silica, bis-fatty acid amides, and other further known commercially available antifoams can also be added to them. Further optional ingredients in the compositions according to the invention are, for example, perfume oils.

[0052] To establish a desired pH which does not result by mixing the other components by itself, the compositions according to the invention can comprise system- and environment-compatible acids, in particular citric acid, acetic acid, tartaric acid, maleic acid, lactic acid, glycolic acid, succinic acid, glutaric acid and/or adipic acid, but also mineral acids, in particular sulfuric acid or alkali metal hydrogen sulfates, or bases, in particular ammonium or alkali metal hydroxides. Such pH regulators are present in the compositions according to the invention preferably in amounts not exceeding 10% by weight, in particular in amounts from 0.5% by weight to 6% by weight.

[0053] In order to facilitate disintegration of compositions according to the invention, particularly when they are in the form of highly compacted shaped bodies, it is possible to incorporate disintegration auxiliaries, so-called tablet disintegrants, into them in order to shorten the disintegration times. Tablet disintegrants or disintegration accelerators are understood as meaning, according to Römpp (9th edition, Vol. 6, p. 4440) and Voigt "*Lehrbuch der pharmazeutischen Technologie*" (6th edition, 1987, pp. 182-184), auxiliaries which provide for the rapid disintegration of tablets in water or gastric juice and for the release of pharmaceuticals in resorbable form. These substances, which are also referred to as disintegrants because of their action, increase their volume as water enters, where firstly the intrinsic volume is increased (swelling), and secondly a pressure may be generated due to the liberation of gases, which causes the tablet to disintegrate into smaller particles. Well-known disintegration auxiliaries are, for example, carbonate/citric acid systems, it also being possible to use other organic acids. Swelling disintegration auxiliaries are, for example, synthetic polymers, such as polyvinylpyrrolidone (PVP) or natural polymers or modified natural substances such as cellulose and starch and their derivatives, alginates or casein derivatives. In preferred process variants, the premixes to be compressed to give tablets comprise 0.5 to 10% by weight, preferably 1 to 5% by weight and in particular 2 to 4% by weight, of a disintegration auxiliary, in each case based on the premix. The preferred disintegrants used for the purposes of the present invention are disintegrants based on cellulose,

such that preferred cleaner shaped bodies comprise such a cellulose-based disintegrant in amounts of from 0.5 to 10% by weight, preferably 1 to 5% by weight and in particular 2 to 4% by weight. Pure cellulose has the formal net composition $(C_6H_{10}O_5)_n$ and, considered formally, represents a β -1,4-polyacetal of cellobiose, which in turn is constructed of two molecules of glucose. Suitable celluloses consist here of about 500 to 5 000 glucose units and consequently have average molar masses of from 50 000 to 500 000. Cellulose-based disintegrants which can be used for the purposes of the present invention are also cellulose derivatives which are obtained from cellulose by polymer-analogous reactions. Such chemically modified celluloses include, for example, products from esterifications or etherifications in which hydroxyl hydrogen atoms have been substituted. However, celluloses in which the hydroxyl groups have been replaced by functional groups which are not bonded via an oxygen atom can also be used as cellulose derivatives. The group of cellulose derivatives includes, for example, alkali metal celluloses, carboxymethylcellulose (CMC), cellulose esters and cellulose ethers, and also aminocelluloses. Said cellulose derivatives are preferably not used on their own as disintegrants, but used in a mixture with cellulose. The content of cellulose derivatives in these mixtures is preferably below 50% by weight, particularly preferably below 20% by weight, based on the cellulose-based disintegrant. As cellulose-based disintegrant, particular preference is given to using pure cellulose which is free from cellulose derivatives. As a further cellulose-based disintegrant or as a constituent of this component, it is possible to use microcrystalline cellulose. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which only attack and completely dissolve the amorphous sections (about 30% of the overall cellulose mass) of the celluloses, but which leave the crystalline sections (about 70%) undamaged. Subsequent disaggregation of the microfibrillar celluloses produced by the hydrolysis produces the microcrystalline celluloses, which have primary particle sizes of about 5 μ m and can be compacted, for example, to give granules with an average particle size of 200 μ m.

[0054] The compositions according to the invention are preferably in the form of pulverulent, granular or tablet-shaped preparations which can be produced in a manner known per se, for example by mixing, granulation, roll compaction and/or spray-drying of the thermally stable components and admixing the more sensitive components, which include, in particular, enzymes, bleaches and the bleach activator.

[0055] The compositions according to the invention can be prepared in the form of non-dusting, storage-stable flowable powders and/or granules with high bulk densities in the range from 800 to 1000 g/l by, in a first process partial stage, mixing the builder components with at least some of the liquid mixing component with an increase in the bulk density of this premix, and subsequently—if desired after interim drying, combining the further constituents of the composition, including the particle-shaped bleach catalyst according to formula I, with the premix obtained in this way.

[0056] In a preferred configuration of compositions according to the invention, they are in the form of compressed bodies, in particular tablets, which are produced by compressing a premix which may comprise all of the above ingredients suitable for the composition according to the

invention. The premix can be composed as described above from a very wide variety of substances. Irrespective of the composition of the premixes to be compressed, physical parameters of the premixes can be chosen such that advantageous shaped body properties result. For example, in preferred variants, the particle-shaped premixes to be compressed have bulk weights above 600 g/l, preferably above 700 g/l and in particular above 800 g/l.

[0057] The particle size in the premixes to be compressed can also be adjusted to achieve advantageous shaped body properties. In preferred processes, the compressed particle-shaped premix has a particle size distribution in which less than 10% by weight, preferably less than 7.5% by weight and in particular less than 5% by weight, of the particles are larger than 1600 μ m or smaller than 200 μ m. In this connection, narrower particle size distributions are further preferred. Particularly advantageous variants here are characterized in that the particle-shaped premix to be compressed has a particle size distribution in which more 30% by weight, preferably more than 40% by weight and in particular more than 50% by weight, of the particles have a particle size between 600 and 1000 μ m.

[0058] To prepare tablet-shaped bodies, the premix is compacted in a so-called die between two punches to form a solid compact. This operation, which is referred to below for short as tableting, is divided into four sections: metering, compaction (elastic deformation), plastic deformation and ejection.

[0059] Firstly, the premix is introduced into the die, the fill level and thus the weight and the shape of the resulting shaped body being determined by the position of the lower punch and by the shape of the compression tool. Even in the case of high shaped body throughputs, constant metering is preferably achieved via a volumetric metering of the premix. In the subsequent course of tableting, the upper punch contacts the premix and is lowered further in the direction of the lower punch. In the course of this compaction, the particles of the premix are pressed closer to one another, with a continual reduction in the void volume within the filling between the punches. When the upper punch reaches a certain position (and thus when a certain pressure is acting on the premix), plastic deformation begins in which the particles coalesce and formation of the shaped body results. Depending on the physical properties of the premix, a portion of the premix particles is also crushed, and at even higher pressures, sintering of the premix results. With an increasing compression rate, i.e. high throughputs, the phase of elastic deformation becomes shorter and shorter, with the result that the shaped bodies which form can have voids which are greater or lesser in size. In the last step of tableting, the finished shaped body is ejected from the die by the lower punch and conveyed away by means of downstream transport devices. At this point in time, it is merely the weight of the shaped body which has been ultimately defined since the compacts may still change their shape and size as a result of physical processes (elastic relaxation, crystallographic effects, cooling, etc.).

[0060] Tableting is carried out in standard commercial tableting presses, which may in principle be equipped with single or double punches. In the latter case, not only is the upper punch used to build up the pressure, the lower punch as well moves toward the upper punch during the compres-

sion operation, while the upper punch presses downward. For small production volumes, preference is given to using excentric tableting presses in which the punch or punches is/are attached to an excentric disc, which in turn is mounted on an axle having a defined speed of rotation. The movement of these compression punches is comparable with the operation of a customary four-stroke engine. Compression can take place with one upper and one lower punch, or else a plurality of punches may be attached to an excentric disc, the number of die bores being increased correspondingly. The throughputs of excentric presses vary, depending on the model, from several hundred up to a maximum of 3000 tablets per hour.

[0061] For greater throughputs, the presses chosen are normally rotary tableting presses in which a relatively large number of dies is arranged in a circle on a so-called die table. The number of dies varies between 6 and 55, depending on the model, larger dies also being available commercially. Each die on the die table is allocated an upper and lower punch, it being possible again for the compressive pressure to be built up actively by the upper punch or lower punch only, or else by both punches. The die table and the punches move around a common vertical axis, and during rotation the punches, by means of a rail-like cam track, are brought into the positions for filling, compaction, plastic deformation and ejection. At those sites where considerable raising or lowering of the punches is necessary (filling, compaction, ejection), these cam tracks are assisted by additional low-pressure sections, low tension rails and discharge tracks. The die is filled by way of a rigid supply means, the so-called filling shoe, which is connected to a storage vessel for the premix. The compressive force on the premix can be adjusted individually for the upper and lower punch by way of compression paths, the pressure being built up by the rolling movement of the punch shaft heads past displaceable pressure rolls. In order to increase the throughput, rotary presses may also be provided with two filling shoes, where only one semicircle need be traveled to produce one tablet. For the production of two-layer and multilayer shaped bodies, a plurality of filling shoes is arranged in series, and the gently pressed first layer is not ejected before further filling. By means of suitable process control, it is possible in this way to also produce coated tablets and inlay tablets which have an onion-like construction, where in the case of the inlay tablets, the top face of the core or of the core layers is not covered and thus remains visible. Rotary tableting presses can also be equipped with single or multiple tools so that, for example, an outer circle with 50 bores and an inner circle with 35 bores can be used simultaneously for the compression. The throughputs of modern rotary tableting presses are more than one million shaped bodies per hour.

[0062] Suitable tableting machines are, for example, obtainable from the companies Apparatebau Holzwarth GbR, Asperg, Wilhelm Fette GmbH, Schwarzenbek, Hofer GmbH, Weil, KILIAN, Cologne, KOMAGE, Kell am See, KORSCH Pressen GmbH, Berlin, Mapag Maschinenbau AG, Bern (CH) and also Courtoy N.V., Halle (BE/LU). A particularly suitable apparatus is, for example, the hydraulic double-pressure press HPF 630 from LAEIS, D.

[0063] The shaped bodies can be prepared in a predetermined three-dimensional shape and predetermined size. Suitable three-dimensional shapes are virtually all configurations which can be sensibly handled, thus, for example

formation as bars, rods or ingots, cubes, blocks and corresponding three-dimensional elements having planar side faces, and also in particular cylindrical configurations with a circular or oval cross section. This last configuration covers here the supply form from the tablet to compact cylindrical sections with a height to diameter ratio of more than 1.

[0064] The three-dimensional shape of another embodiment of the shaped bodies is matched in its dimensions to the dosing compartment of standard commercial dishwashing machines, so that the shaped bodies can be dosed directly into the detergent compartment without dosing help, from where they are released during the cleaning operation. However, a use of the cleaner shaped bodies by means of dosing aids is of course also possible without problems.

[0065] Following compression, the shaped bodies have high stability. The fracture strength of cylindrically shaped bodies can be ascertained by means of the diametral fracture stress measurement. This can be determined by

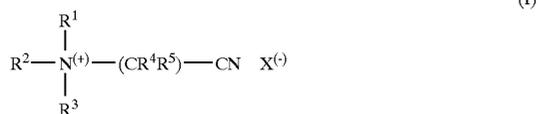
$$\sigma = \frac{2P}{\pi Dt}$$

[0066] Here, σ is the diametral fracture stress (DFS) in Pa, P is the force in N which leads to the pressure exerted on the shaped body, which pressure causes fracture of the shaped body, D is the diameter of the shaped body in meters and t is the height of the shaped body.

[0067] During the production of compressed shaped bodies, there is no restriction that only a particle-shaped premix is compressed to give a shaped body. Rather, the process can be extended to produce multilayer shaped bodies in a manner known per se by preparing two or more premixes which are compressed onto one another. Here, the premix initially introduced is gently precompressed in order to give a smooth top face which runs parallel to the base of the shaped body, and after introducing the second premix, is subjected to final compression to give the finished shaped body. In the case of three-layer or multilayer shaped bodies, a further precompression takes place after each addition of premix, before, following the addition of the final premix, the shaped body is subjected to final compression.

[0068] In view of the increasing technical complexity, a maximum of two-layer shaped bodies are preferred in practice. In this way, the division of certain ingredients between the individual layers can bring advantages. For example, it is possible to produce a two-layered shaped body by pressing two different particle-shaped premixes onto one another, of which one comprises one or more bleaches and the other the particle-shaped bleach activator according to formula I, meaning that the resulting composition has the bleach in the form of the, in particular inorganic, peroxygen compound in one layer, and the particle-shaped bleach activator according to formula I in the second layer. However, by using the bleach activator in a form formulated to be particle-shaped according to the invention, it is also possible without problems to incorporate the bleach and the bleach activator into the same layer, and to incorporate further sensitive constituents, in particular enzymes, into a separate second layer of the shaped body.

1. The use of compounds of the general formula I, formulated to be particle-shaped using inorganic carrier materials which contain silicate,



in which R¹ is —H, —CH₃, a C₂₋₂₄-alkyl or -alkenyl radical, a substituted C₂₋₂₄-alkyl or -alkenyl radical with at least one substituent from the group —Cl, —Br, —OH, —NH₂, —CN, an alkyl- or alkenylaryl radical with a C₁₋₂₄-alkyl group, or is a substituted alkyl- or alkenylaryl radical with a C₁₋₂₄-alkyl group and at least one further substituent on the aromatic ring, R² and R³, independently of one another, are chosen from —CH₂—CN, —CH₃, —CH₂—CH₃, —CH₂—CH₂—CH₃, —CH(CH₃)—CH₃, —CH₂—OH, —CH₂—CH₂—OH, —CH(OH)—CH₃, —CH₂—CH₂—CH₂—OH, —CH₂—CH(OH)—CH₃, —CH(OH)—CH₂—CH₃, —(CH₂CH₂—O)_nH where n=1, 2, 3, 4, 5 or 6, R⁴ and R⁵, independently of one another, have a meaning given above for R¹, R² or R³, and X is a charge-balancing anion, as activators for, in particular inorganic, peroxygen compounds in solid textile detergents which are used in essentially aqueous washing solutions.

2. The use as claimed in claim 1, characterized in that the carrier material has an internal surface area in the range from 10 m²/g to 500 m²/g, in particular 100 m²/g to 450 m²/g.

3. The use as claimed in claim 1 or 2, characterized in that the carrier material contains silicate from the group consisting of alkali metal silicates, silicas, silica gels and clays, and mixtures thereof.

4. The use as claimed in any of claims 1 to 3, characterized in that in the particle-shaped formulation form, 10 to 50 parts by weight of the carrier material and 50 to 90 parts by weight of the compound according to formula I are present.

5. The use as claimed in any of claims 1 to 4, characterized in that, in the compound according to formula I, R¹, R² and R³ are identical.

6. The use as claimed in claim 5, characterized in that, in the compound according to formula I, R¹, R² and R³ are methyl groups.

7. The use as claimed in any of claims 1 to 6, characterized in that the charge-balancing anion X⁻ is chosen from the halides, such as chloride, fluoride, iodide and bromide, nitrate, hydroxide, phosphate, hydrogen phosphate, dihydrogen phosphate, pyrophosphate, metaphosphate, hexafluorophosphate, carbonate, hydrogen carbonate, sulfate, hydrogen sulfate, C₁₋₂₀-alkyl sulfate, C₁₋₂₀-alkylsulfonate, optionally C₁₋₁₈-alkyl-substituted arylsulfonate, chlorate, perchlorate and/or the anions of C₁₋₂₄-carboxylic acids, such as formate, acetate, laurate, benzoate or citrate, alone or in any desired mixtures.

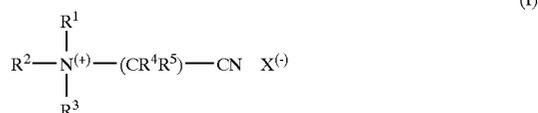
8. The use as claimed in any of claims 1 to 7, characterized in that the charge-balancing anion X⁻ is chloride, sulfate, hydrogen sulfate, ethosulfate, lauryl sulfate, dodecylbenzenesulfonate, toluenesulfonate, cumenesulfonate, xylenesulfonate or methosulfate or mixtures thereof.

9. The use according to one of claims 1 to 8, characterized in that the peroxygen compound to be activated is chosen

from the group consisting of organic peracids, hydrogen peroxide, perborate and percarbonate, and mixtures thereof.

10. The use as claimed in any of claims 1 to 9, characterized in that at the same time a bleach-enhancing active ingredient combination which is obtainable by intimately mixing a water-soluble salt of a divalent transition metal chosen from cobalt, iron, copper and ruthenium and mixtures thereof, a water-soluble ammonium salt and optionally an oxidizing agent based on peroxygen, and also inert carrier material is present.

11. A solid detergent characterized in that it comprises 0.1% by weight to 10% by weight, in particular 0.2% by weight to 6% by weight, of a compound of the general formula I, formulated to be particle-shaped using inorganic carrier materials which contain, in particular, silicate



in which R¹ is —H, —CH₃, a C₂₋₂₄-alkyl or -alkenyl radical, a substituted C₂₋₂₄-alkyl or -alkenyl radical with at least one substituent from the group —Cl, —Br, —OH, —NH₂, —CN, an alkyl- or alkenylaryl radical with a C₁₋₂₄-alkyl group, or is a substituted alkyl- or alkenylaryl radical with a C₁₋₂₄-alkyl group and at least one further substituent on the aromatic ring, R² and R³, independently of one another, are chosen from —CH₂—CN, —CH₃, —CH₂—CH₃, —CH₂—CH₂—CH₃, —CH(CH₃)—CH₃, —CH₂—OH, —CH₂—CH₂—OH, —CH(OH)—CH₃, —CH₂—CH₂—CH₂—OH, —CH₂—CH(OH)—CH₃, —CH(OH)—CH₂—CH₃, —(CH₂CH₂—O)_nH where n=1, 2, 3, 4, 5 or 6, R⁴ and R⁵, independently of one another, have a meaning given above for R¹, R² or R³, and X is a charge-balancing anion, in addition to customary ingredients compatible with the compound according to formula I.

12. The composition as claimed in claim 11, characterized in that it comprises a peroxygen compound from the group consisting of organic peracids, hydrogen peroxide, perborate and percarbonate, and mixtures thereof.

13. The composition as claimed in claim 11 or 12, characterized in that, in addition to the compounds according to formula I, 0.5% by weight to 7% by weight of compounds which release peroxocarboxylic acids under perhydrolysis conditions are present.

14. The composition as claimed in any of claims 11 to 13, characterized in that, in addition to the compounds according to formula I, it comprises a bleach-enhancing active ingredient combination which is obtainable by intimately mixing a water-soluble salt of a divalent transition metal chosen from cobalt, iron, copper and ruthenium, and mixtures thereof, a water-soluble ammonium salt and optionally an oxidizing agent based on peroxygen, and an inert carrier material.

15. The composition as claimed in any of claims 11 to 13, characterized in that, in addition to the compound according to formula I, bleach-catalyzing transition metal salts or complexes are present, in particular in amounts of from 0.0025% by weight to 0.5% by weight.

16. The composition as claimed in any of claims 11 to 15, characterized in that it is in the form of tablet-shaped bodies.

17. The composition as claimed in claim 16, characterized in that the tablet-shaped body has two layers.

18. The composition as claimed in claim 17, characterized in that, in one layer, it has the bleaching agent in the form of the, in particular inorganic, peroxygen compound and, in the second layer, the bleach activator according to formula I formulated to be particle-shaped using inorganic carrier materials which contain, in particular, silicate.

19. The composition as claimed in claim 17, characterized in that it has the bleaching agent in the form of the, in particular inorganic, peroxygen compound and the bleach activator according to formula I formulated to be particle-shaped using inorganic carrier materials which contain, in particular, silicate in the same layer, and further sensitive constituents, in particular enzymes, in a second layer.

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