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(54) **LAUNDRY DETERGENT**

(57) A combination of polyethylene oxide) in which the medium polymerization degree of the ethylene oxide is in the range of from 22,000 to 228,000, fumed silica, and at least one calcium salt increases the detergency of laundry detergents.

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## Description

**[0001]** The present invention relates to surfactant-containing laundry detergents that comprise high molecular weight polyethylene oxide), fumed silica, and calcium salt. It also relates to the use of the combination of said ingredients to prevent accumulation of stains on fabrics by applying said combination in water to the fabrics, and to a process of laundering fabrics which makes use of said combination.

**[0002]** Laundry detergents generally contain, in addition to the ingredients such as surfactants and builder materials that are indispensable for the washing process, further constituents that can be grouped under the heading of "washing adjuvants" and encompass such different groups of active substances as foam regulators, greying inhibitors, bleaching agents, bleach activators, and color transfer inhibitors. Also included among such adjuvants are substances that impart soil-repelling properties to the laundry fibers and that, if present during the washing operation, assist the soil-releasing capability of the other laundry-detergent constituents. Soil-release-enabling substances of this kind are often referred to as "soil release" active substances or, because of their ability to make the treated surface (for example, of the fibers) less prone to stains adhering to it, as "soil repellents."

**[0003]** The soil-release-enabling action of, for example methyl cellulose is known. Because of their chemical similarity to polyester fibers, soil-release-enabling active substances that are particularly effective for textiles made of said material are copolyesters that contain dicarboxylic acid units, alkylene glycol units, and polyalkylene glycol units. Soil-release-enabling copolyesters of the aforesaid kind, and the use thereof in laundry detergents, have been known for some time.

**[0004]** Surprisingly it has now been found that a combination of certain substances, including a quite different kind of polymer, is also capable of delivering the useful effect of repelling soils.

**[0005]** One aspect of the present invention is a solid laundry detergent in powder form, preferably suitable for washing fabrics by hand, comprising surfactant and a combination of polyethylene oxide) in which the medium polymerization degree of the ethylene oxide is in the range of from 22,000 to 228,000, fumed silica, and at least one calcium salt.

**[0006]** The mean molecular weight (weight average, $M_w$) of said polyethylene oxide) preferably is in the range of from 1,000,000 g/mol to 10,000,000 g/mol.

**[0007]** Preferred anions in the calcium salts are acetate, benzoate, borate, bromide, butyrate, carbonate, chloride, citrate, formate, fumarate, gluconate, iodide, lactate, malate, maleate, malonate, nitrate, oxalate, phosphate, propionate, salicylate, silicate, succinate, sulfate, tartrate, and mixtures thereof. More preferred are carbonate, sulfate, and their mixtures.

**[0008]** Preferably the weight ratio of said polyethylene oxide) to fumed silica is in the range of from 25 : 1 to 40 : 1, and/or that the weight ratio of said polyethylene oxide) to calcium salt is in the range of from 55 : 1 to 40 : 1.

**[0009]** When applying said combination of polyethylene glycol, fumed silica, and calcium salt to fabrics in an aqueous system, the tendency of the so-treated fabrics to accumulate hard-to-be-removed stains is reduced, so that it is easier to clean a fabric so treated, having been worn after the treatment, in comparison to a fabric not treated with said combination. Accordingly, another aspect of the invention is the use of a combination defined above to prevent accumulation of stains on fabrics by applying said combination in water to the fabrics. Still another aspect of the invention is the use, by treating fabrics with a combination defined above in water, to facilitate the removal of stains, accumulated on fabrics after the treatment, when washed. This washing of fabrics after the accumulation of stains may be performed with any common detergent, but preferably is performed with a detergent according to the invention in order to prolong the positive effects of the present invention.

**[0010]** In addition, detergents comprising the combination defined above do also show an improved detergency in comparison to detergents not comprising it. Accordingly, another aspect of the present invention is the use of the combination defined above to increase detergency of detergents.

**[0011]** When using detergents comprising the combination defined above in a process of hand washing, not only the advantages mentioned above do occur, but additional benefits such as the delivery of a pleasant sensorial feeling and reduced skin irritation as well as a reduction of dryness or harshness on hands are observed. Therefor, another aspect of the invention is a process of hand washing laundry, by manually contacting laundry in need of washing with an aqueous laundry liquor comprising 2.2 g/l to 2.7 g/l of a detergent of the invention. Such process preferably is carried out by using water of a temperature in the range of from 20 °C to 35 °C, more preferred from 20 °C to 30 °C. Such process also preferably is carried out by applying manual force to the laundry immersed in the laundry liquor for a period of from 5 minutes to 20 minutes, more preferred from 5 minutes to 10 minutes. After applying the wash liquor containing the detergent according to the invention, the laundry may be treated as is usual for other washing processes, that is it may be rinsed with water once or several times, a fabric softener may be applied to it, and the laundered items may be dried.

**[0012]** A detergent according to the present invention, or that is to be used according to the present invention or is utilized in the method according to the present invention, contains by preference peroxygen-based bleaching agents, in particular in quantities in the range from 5 wt % to 70 wt %, as well as (if applicable) bleach activator, in particular in quantities in the range from 2 wt % to 10 wt %. The suitable bleaching agents are, by preference, the peroxygen compounds usually used in laundry detergents, such as percarboxylic acids, for example diperdodecanoic acid or

phthaloylaminoper-oxycaproic acid, hydrogen peroxide, alkali perborate that can be present as a tetra- or monohydrate, percarbonate, perpyrophosphate, and persilicate, which as a rule are present as alkali salts, in particular as sodium salts. Bleaching agents of this kind are present, in laundry detergents that contain a cellulose derivative used according to the present invention, by preference in quantities of up to 25 wt %, in particular up to 15 wt %, and particularly preferably from 5 wt % to 15 wt %, based in each case on the entire detergent, percarbonate being used in particular. The optionally present component of bleach activators encompasses the N- or O-acyl compounds usually utilized, for example multiply acylated alkylenediamines, in particular tetraacetylethylenediamine, acylated glycourils, in particular tetraacetyl glycouril, N-acylated hydantoins, hydrazides, triazoles, urazoles, diketopipera-zines, sulfuryl amides, and cyanurates, also carboxylic acid anhydrides, in particular phthalic acid anhydride, carboxylic acid esters, in particular sodium isononanoyl phenolsulfonate, and acylated sugar derivatives, in particular pentaacetyl glucose, as well as cationic nitrile derivatives such as trimethylammonium acetonitrile salts. In order to avoid interaction with the per-compounds during storage, the bleach activators can in known fashion have been coated with encasing substances or granulated; tetraacetylethylenediamine granulated with the aid of carboxymethyl cellulose and having average particle sizes from 0.01 mm to 0.8 mm, granulated 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine, and/or trialkylammonium acetonitriles are particularly preferred. Such bleach activators are contained in laundry detergents by preference in quantities of up to 8 wt %, in particular from 2 wt % to 6 wt %, based in each case on the entire detergent.

**[0013]** In a preferred embodiment, a detergent according to the present invention, used according to the present invention, or utilized in the method according to the present invention contains nonionic surfactant, selected from fatty alkylpolyglycosides, fatty alkylpolyalkoxylates, in particular-ethoxylates and/or -propoxylates, fatty acid polyhydroxyamides and/or ethoxylation and/or propoxylation products of fatty alkyl amines, vicinal diols, fatty acid alkyl esters, and/or fatty acid amides, as well as mixtures thereof, in particular in a quantity in the range from 2 wt % to 25 wt %.

**[0014]** A further embodiment of such detergents encompasses the presence of synthetic anionic surfactant of the sulfate and/or sulfonate type, in particular fatty alkyl sulfate, fatty alkyl ether sulfate, sulfo-fatty acid ester, and/or sulfo-fatty acid di-salts, in particular in a quantity in the range from 2 wt % to 25 wt %. The anionic surfactant is preferably selected from the alkyl or alkenyl sulfates and/or the alkyl or alkenyl ether sulfates in which the alkyl or alkenyl group possesses 8 to 22, in particular 12 to 18 carbon atoms. These usually are not individual substances, but rather cuts or mixtures. Preferred among them are those whose proportion of compounds having longer-chain groups in the range from 16 to 18 carbon atoms is above 20 wt %.

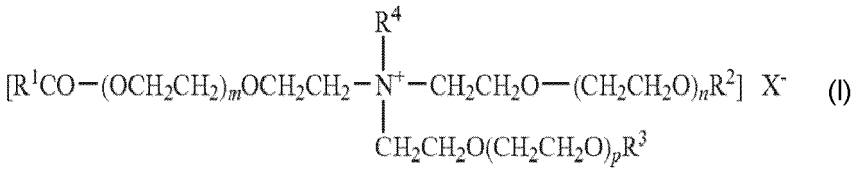
**[0015]** Among the appropriate nonionic surfactants are the alkoxylates, in particular ethoxylates and/or propoxylates, of saturated or mono- to polyunsaturated linear or branched-chain alcohols having 10 to 22 carbon atoms, by preference 12 to 18 carbon atoms. The degree of alkoxylation of the alcohols is as a rule between 1 and 20, by preference between 3 and 10. They can be manufactured, in known fashion, by reacting the corresponding alcohols with the corresponding alkylene oxides. The derivatives of the fatty alcohols are particularly suitable, although their branched-chain isomers, in particular so-called oxo alcohols, can also be used to manufacture usable alkoxylates. The alkoxylates, in particular the ethoxylates, of primary alcohols having linear, in particular dodecyl, tetradecyl, hexadecyl, or octadecyl radicals, and mixtures thereof, are accordingly usable. Also usable are corresponding alkoxylation products of alkylamines, vicinal diols, and carboxylic acid amides that correspond to the aforesaid alcohols in terms of the alkyl portion. Additionally suitable are the ethyleneoxide and/or propylene-oxide insertion products of fatty acid alkyl esters, as well as fatty acid polyhydroxyamides. So-called alkylpolyglycosides suitable for incorporation into the detergents according to the present invention are compounds of the general formula $(G)_n$-$OR^{12}$ , in which $R^{12}$ denotes an alkyl or alkenyl radical having 8 to 22 carbon atoms, G denotes a glycose unit, and n denotes a number between 1 and 10. The glycoside component (G)n refers to oligomers or polymers from naturally occurring aldose or ketose monomers, among which are included, in particular, glucose, mannose, fructose, galactose, talose, gulose, altrose, allose, idose, ribose, arabinose, xylose, and lyxose. The oligomers made up of glycosidically linked monomers of this kind are characterized not only by the nature of the sugars contained in them but also by their number (the so-called degree of oligomerization). The degree of oligomerization n, constituting a magnitude to be ascertained analytically, generally assumes fractional numerical values; its value is between 1 and 10, below 1.5 for the glycosides used by preference, in particular between 1.2 and 1.4. Because of its good availability, glucose is a preferred monomer module. The alkyl or alkenyl portion $R^{12}$ of the glycosides preferably derives likewise from easily accessible derivatives of renewable raw materials, in particular from fatty alcohols, although their branched-chain isomers, in particular so-called oxo alcohols, can also be used for the manufacture of usable glycosides. The primary alcohols having linear octyl, decyl, dodecyl, tetradecyl, hexadecyl, or octadecyl radicals, and mixtures thereof, are accordingly usable. Particularly preferred alkyl glycosides contain a coconut oil alkyl radical, i.e. mixtures with substantially $R^{12}$ = dodecyl and $R^{12}$ = tetradecyl.

**[0016]** Nonionic surfactant is contained in detergents according to the present invention, that are used according to the present invention, or that are utilized in the method according to the present invention, by preference in quantities from 1 wt % to 30 wt %, in particular from 1 wt % to 25 wt %; quantities in the upper part of this range are more likely to be encountered in liquid laundry detergents, and particulate laundry detergents preferably contain rather smaller quantities of up to 5 wt %.

**[0017]** The detergents can, instead or additionally, contain further surfactants, by preference synthetic anionic surfactants of the sulfate or sulfonate type, such as e.g. alkyl benzenesulfonates, in quantities by preference not above 20 wt %, in particular from 0.1 wt % to 18 wt %, based in each case on the entire detergent. Synthetic anionic surfactants that may be mentioned as particularly suitable for use in such detergents are the alkyl and/or alkenyl sulfates, having 8 to 22 carbon atoms, which carry an alkali-, ammonium-, or alkyl- or hydroxyalkyl-substituted ammonium ion as countercation. The derivatives of the fatty alcohols having, in particular, 12 to 18 carbon atoms, and their branched-chain analogs (the so-called oxo alcohols), are preferred. The alkyl and alkenyl sulfates can be manufactured in known fashion by reacting the corresponding alcohol component with a usual sulfating reagent, in particular sulfur trioxide or chlorosulfonic acid, and subsequent neutralization with alkali-, ammonium-, or alkyl- or hydroxyalkyl-substituted ammonium bases. Also included among the usable surfactants of the sulfate type are the sulfated alkoxylation products of the aforesaid alcohols (so-called ether sulfates). Such ether sulfates contain by preference 2 to 30, in particular 4 to 10 ethylene glycol groups per molecule. Included among the suitable anionic surfactants of the sulfonate type are the $\alpha$-sulfo esters obtainable by reacting fatty acid esters with sulfur trioxide and subsequent neutralization, in particular the sulfonation products deriving from fatty acids having 8 to 22 carbon atoms, by preference 12 to 18 carbon atoms, and linear alcohols having 1 to 6 carbon atoms, by preference 1 to 4 carbon atoms, and the sulfo-fatty acids generated therefrom by formal saponification.

**[0018]** Further optional surfactant ingredients that are appropriate are soaps; saturated fatty acid soaps such as the salts of lauric acid, myristic acid, palmitic acid, or stearic acid, as well as soaps derived from natural fatty acid mixtures, for example coconut, palm-kernel, or tallow fatty acids, are suitable. Those soap mixtures that are made up of 50 wt % to 100 wt % saturated C12 to C18 fatty acid soaps and up to 50 wt % oleic acid soap are particularly preferred. Soap is contained by preference in quantities from 0.1 wt % to 5 wt %. Greater quantities of soap, as a rule up to 20 wt %, can, however, also be contained in particular in liquid detergents that contain a polymer used according to the present invention.

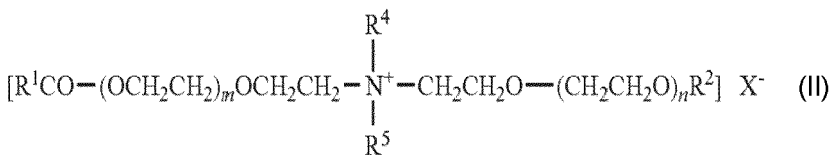
**[0019]** If desired, the detergents can also contain betaines and/or cationic surfactants, which are used (if present) by preference in quantities from 0.5 wt % to 7 wt %. Among these, esterquats are particularly preferred. Esterquats are quaternized fatty acid triethanolamine ester salts that conform to formula (I):



(I)

in which $R^1CO$ denotes an acyl radical having 6 to 22 carbon atoms, $R^2$ and $R^3$, mutually independently, denote hydrogen or $R^1CO$, $R^4$ denotes an alkyl radical having 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group, m, n, and p in total denote 0 or numbers from 1 to 12, q denotes numbers from 1 to 12, and $X^-$ denotes a charge-equalizing anion such as a halide, alkyl sulfate, or alkyl phosphate. Typical examples of esterquats that can be used in the context of the invention are products based on hexanoic acid, octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, isostearic acid, stearic acid, oleic acid, elaidic acid, arachidic acid, behenic acid, and erucic acid, and technical mixtures thereof, such as those occurring upon high-pressure cleavage of natural fats and oils. By preference, technical $C_{12/18}$ coconut oil fatty acids, and in particular partially hardened $C_{16/18}$ tallow or palm oil fatty acids, as well as elaidic-acid-rich C16/18 fatty acid cuts, are used. For manufacture of the quaternized esters, as a rule the fatty acids and the triethanolamine can be used at a molar ratio from 1.1:1 to 3:1; a utilization ratio from 1.2:1 to 2.2:1, by preference 1.5:1 to 1.9:1, has proven particularly advantageous. The esterquats preferred for use represent technical mixtures of mono-, di-, and triesters having an average degree of esterification from 1.5 to 1.9 and are derived from technical $C_{16/18}$ tallow or palm fatty acid (iodine number 0 to 40). Quaternized fatty acid triethanolamine ester salts of formula (I) in which $R^1CO$ denotes an acyl radical having 16 to 18 carbon atoms, $R^2$ denotes $R^1CO$, $R^3$ denotes hydrogen, $R^4$ denotes a methyl group, m, n, and p denote 0, and X denotes methyl sulfate, have proven particularly advantageous.

**[0020]** Also suitable as esterquats, in addition to the quaternized carboxylic acid triethanolamine ester salts, are quaternized ester salts of carboxylic acids with diethanolalkylamines, of formula (II):

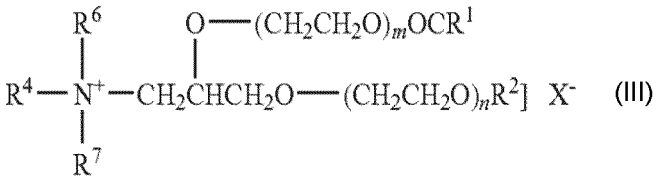


(II)

in which $R^1CO$ denotes an acyl radical having 6 to 22 carbon atoms, $R^2$ denotes hydrogen or $R^1CO$, $R^4$ and $R^5$, mutually

independently, denote alkyl radicals having 1 to 4 carbon atoms, m and n in total denote 0 or numbers from 1 to 12, and X denotes a charge-equalizing anion such as halide, alkyl sulfate, or alkyl phosphate.

**[0021]** Lastly, a further group of suitable esterquats that may be mentioned are the quaternized ester salts of carboxylic acids with 1,2-dihydroxypropyldialkylamines, of formula (III):



(III)

in which $R^1CO$ denotes an acyl radical having 6 to 22 carbon atoms, $R^2$ denotes hydrogen or $R^1CO$, $R^4$, $R^6$ , and $R^7$, mutually independent, denote alkyl radicals having 1 to 4 carbon atoms, m and n in total denote 0 or numbers from 1 to 12, and $X^-$ denotes a charge-equalizing anion such as halide, alkyl sulfate, or alkyl phosphate.

**[0022]** With regard to selection of the preferred fatty acids and of the optimum degree of esterification, the indications given by way of example for (I) also apply analogously to the esterquats of formulas (II) and (III). The esterquats are usually brought to market in the form of 50- to 90-weight-percent alcohol solutions, which can also be diluted with water without difficulty; ethanol, propanol, and isopropanol are the usual alcohol solvents.

**[0023]** Among the preferred embodiments of detergents according to the inventions are those that comprise 14 % by weight to 17 % by weight, preferably 15.3 % by weight, of surfactant, preferably anionic surfactant, 0.09 % by weight to 0.2 % by weight of said polyethylene oxide), 0.002 % by weight to 0.01 % by weight of fumed silica, and/or up to 0.006 % by weight, preferably 0.001 % by weight to 0.005 % by weight, of calcium salt.

**[0024]** The detergents may contain water-soluble and/or water-insoluble builders, selected in particular from alkali aluminosilicate, crystalline alkali silicate having a modulus above 1, monomeric polycarboxylate, polymeric polycarboxylate, and mixtures thereof, in particular in quantities in the range from 2.5 wt % to 60 wt %.

**[0025]** The detergent contains by preference 20 wt % to 55 wt % water-soluble and/or water-insoluble organic and/or inorganic builders. Included among the water-soluble organic builder substances are, in particular, those from the class of the polycarboxylic acids, in particular citric acid and sugar acids, as well as the polymeric (poly)carboxylic acids, in particular the polycarboxylates, accessible by oxidation of polysaccharides, of International Patent Application WO 93/16110, polymeric acrylic acids, methacrylic acids, maleic acids, and mixed polymers thereof, which can also contain small proportions of polymerizable substances, without carboxylic acid functionality, polymerized in. The relative molecular weight of the homopolymers of unsaturated carboxylic acids is generally between 5000 and 200,000, that of the copolymers between 2000 and 200,000, by preference 50,000 to 120,000, based on free acid. A particularly preferred acrylic acid/maleic acid copolymer has a relative molecular weight from 50,000 to 100,000. Suitable, although less preferred, compounds of this class are copolymers of acrylic acid or methacrylic acid with vinyl ethers such as vinylmethyl ethers, vinyl esters, ethylene, propylene, and styrene, in which the proportion of acid is at least 50 wt %. Terpolymers that contain as monomers two carboxylic acids and/or salts thereof, and vinyl alcohol and/or a vinyl alcohol derivative or a carbohydrate as a third monomer, can also be used as water-soluble organic builder substances. The first acid monomer or salt thereof is derived from a monoethylenically unsaturated $C_3$ to $C_8$ carboxylic acid and by preference from a $C_3$ to $C_4$ monocarboxylic acid, in particular from (meth)acrylic acid. The second acid monomer or salt thereof can be a derivative of a $C_4$ to Ca dicarboxylic acid, maleic acid being particularly preferred. The third monomeric unit is constituted in this case by vinyl alcohol and/or preferably an esterified vinyl alcohol. Vinyl alcohol derivatives that represent an ester of short-chain carboxylic acids, for example of $C_1$ to $C_4$ carboxylic acids, with vinyl alcohol, are particularly preferred. Preferred terpolymers contain 60 wt % to 95 wt %, in particular 70 wt % to 90 wt %, (meth)acrylic acid or (meth)acrylate, particularly preferably acrylic acid or acrylate, and maleic acid or maleinate, as well as 5 wt % to 40 wt %, by preference 10 wt % to 30 wt % vinyl alcohol and/or vinyl acetate. Very particularly preferred in this context are terpolymers in which the weight ratio of (meth)acrylic acid or (meth)acrylate to maleic acid or maleate is between 1:1 and 4:1, by preference between 2:1 and 3:1 and in particular 2:1 and 2.5:1. Both the quantities and weight ratios are based on the acids. The second acid monomer or salt thereof can also be a derivative of an allyl sulfonic acid that is substituted in the 2-position with an alkyl radical, by preference with a $C_1$ to $C_4$ alkyl radical, or with an aromatic radical that is preferably derived from benzene or benzene derivatives. Preferred terpolymers contain 40 wt % to 60 wt %, in particular 45 to 55 wt %, (meth)acrylic acid or (meth)acrylate, particularly preferably acrylic acid or acrylate, 10 wt % to 30 wt %, by preference 15 wt % to 25 wt % methallyl sulfonic acid or methallyl sulfonate, and as a third monomer 15 wt % to 40 wt %, by preference 20 wt % to 40 wt % of a carbohydrate. This carbohydrate can be, for example, a mono-, di-, oligo-, or polysaccharide, mono-, di-, or oligosaccharides being preferred; sucrose is particularly preferred. The use of the third monomer is presumed to incorporate into the polymer defined break points that are responsible for the polymer's good biodegradability. These terpolymers generally have a relative molecular weight between 1000 and

200,000, by preference between 200 and 50,000, and in particular between 3000 and 10,000. Especially for the manufacture of liquid detergents, they can be used in the form of aqueous solutions, by preference in the form of 30- to 50-weight-percent aqueous solutions. All the aforesaid polycarboxylic acids are used as a rule in the form of their water-soluble salts, in particular their alkali salts.

**[0026]** Organic builder substances of this kind are contained by preference in quantities of up to 40 wt %, particularly up to 25 wt %, and particularly preferably from 1 wt % to 5 wt %. Quantities close to the aforesaid upper limit are used by preference in pasty or liquid, in particular water-containing, detergents.

**[0027]** Crystalline or amorphous alkali aluminosilicates may be used in particular as water-insoluble, water-dispersible inorganic builder materials, in quantities of up to 50 wt %, by preference not above 40 wt %, and in liquid detergents in particular from 1 wt % to 5 wt %. Among these, the crystalline aluminosilicates of laundry-detergent quality, in particular zeolite NaA and if applicable NaX, are preferred. Quantities close to the aforesaid upper limit are used by preference in solid, particulate detergents. Suitable aluminosilicates comprise, in particular, no particles having a particle size above 30 $\mu$m, and by preference comprise at least 80 wt % of particles having a size below 10 $\mu$m. Their calcium binding ability is in the range from 100 to 200 mg CaO per gram. Suitable substitutes or partial substitutes for the aforesaid aluminosilicates are crystalline alkali silicates, which can be present alone or mixed with amorphous silicates. The alkali silicates usable in the detergents as detergency builders have by preference a molar ratio of alkali oxide to $SiO_2$ below 0.95, in particular from 1:1.1 to 1:12, and can be present in amorphous or crystalline fashion. Preferred alkali silicates are the sodium silicates, in particular the amorphous sodium silicates, having a $Na_2O:SiO_2$ molar ratio from 1:2 to 1 :2.8. Amorphous alkali silicates of this kind are obtainable commercially, for example, under the name Portil®. They are added in the context of manufacture preferably as a solid, and not in the form of a solution. Crystalline sheet silicates of the general formula $Na_2Si_xO_{2x+1} \cdot y\ H_2O$, in which x, the so-called modulus, is a number from 1.9 to 4 and y is a number from 0 to 20, and preferred values for x are 2, 3, or 4, are preferred for use as crystalline silicates, which can be present alone or mixed with amorphous silicates. Preferred crystalline sheet silicates are those in which x in the aforesaid general formula assumes the values 2 or 3. In particular, both $\beta$- and $\delta$-sodium disilicates ($Na_2Si_2O_5 \cdot y\ H_2O$) are particularly preferred. The alkali silicate content of the detergent is by preference 1 wt % to 50 wt %, and in particular 5 wt % to 35 wt %, based on anhydrous active substance. If alkali aluminosilicate, in particular zeolite, is also present as an additional builder substance, the alkali silicate content is by preference 1 wt % to 15 wt %, and in particular 2 wt % to 8 wt %, based on anhydrous active substance. The weight ratio of aluminosilicate to silicate, based in each case on anhydrous active substances, is then by preference 4:1 to 10:1. In detergents that contain both amorphous and crystalline alkali silicates, the weight ratio of amorphous alkali silicate to crystalline alkali silicate is by preference 1:2 to 2:1, and in particular 1:1 to 2:1.

**[0028]** In addition to the aforesaid inorganic builders, further water-soluble or water-insoluble inorganic substances can be contained in the detergents according to the present invention, that are to be used according to the present invention, or that are utilized in methods according to the present invention. The alkali carbonates, alkali hydrogen carbonates, and alkali sulfates, and mixtures thereof, are suitable in this context. Additional inorganic material of this kind can be present in quantities of up to 70 wt %.

**[0029]** In addition, the detergents can contain further constituents that are usual in laundry detergents and cleaning agents. Included among these optional constituents are, in particular, enzymes, enzyme stabilizers, complexing agents for heavy metals, for example aminopolycarboxylic acids, amino-hydroxypolycarboxylic acids, polyphosphonic acids, and/or aminopolyphosphonic acids, foam inhibitors, for example organopolysiloxanes or paraffins, solvents, and optical brighteners, for example stilbenedisulfonic acid derivatives. By preference, up to 1 wt %, in particular 0.01 wt % to 0.5 wt %, optical brighteners, in particular compounds from the class of the substituted 4,4'-bis(2,4,6-tri-amino-s-triazinyl)stilbene-2,2'-disulfonic acids, up to 5 wt %, in particular 0.1 wt % to 2 wt % complexing agents for heavy metals, in particular aminoalkylenephosphonic acids and salts thereof, and up to 2 wt %, in particular 0.1 wt % to 1 wt % foam inhibitors, are contained in detergents according to the present invention or that are used according to the present invention, the aforesaid weight proportions referring here and in each other case to the entire detergent.

**[0030]** Solvents, which can be used in particular with liquid detergents, are (in addition to water) preferably those that are miscible with water. Included among these are the lower alcohols, for example ethanol, propanol, isopropanol, and the isomeric butanols, glycerol, lower glycols, for example ethylene glycol and propylene glycol, and the ethers derivable from the aforesaid classes of compounds.

**[0031]** Enzymes that may be present are by preference selected from the group encompassing protease, amylase, lipase, cellulase, hemicellulase, oxidase, peroxidase, or mixtures thereof. Protease, recovered from microorganisms such as bacteria or fungi, is especially suitable. Proteases are obtainable commercially, for example, under the names BLAP®, Savinase®, Esperase®, Maxatase®, Optimase®, Alcalase®, Durazym®, or Maxapem®. Usable lipases may be recovered from Humicola lanuginosa, from Bacillus species, from Pseudomonas species, from Fusarium species, from Rhizopus species, or from Aspergillus species. Suitable lipases are obtainable commercially, for example, under the names Lipolase®, Lipozym®, Lipomax®, Lipex®, Amano® Lipase, Toyo-Jozo® Lipase, Meito® Lipase, and Diosynth® Lipase. Suitable amylases are commercially available, for example, under the names Maxamyl®, Termamyl®, Duramyl®, and Purafect® OxAm. Usable cellulases are recoverable from bacteria or fungi, which exhibits a pH optimum preferably

in the weakly acid to weakly alkaline range from 6 to 9.5. Cellulases of this kind are commercially available under the names Celluzyme®, Carezyme®, and Ecostone®.

**[0032]** Included among the usual enzyme stabilizers present if applicable, in particular in liquid detergents, are aminoalcohols, for example mono-, di-, triethanol- and -propanolamine and mixtures thereof, lower carboxylic acids, boric acid or alkali borates, boric acid/carboxylic acid combinations, boric acid esters, boronic acid derivatives, and/or sulfur-containing reducing agents.

**[0033]** Included among the suitable foam inhibitors are long-chain soaps, in particular behenic soap, fatty acid amides, paraffins, waxes, microcrystalline waxes, organopolysiloxanes, and mixtures thereof, which can furthermore contain microfine, optionally silanized or otherwise hydrophobized silicic acid. For use in particulate detergents, foam inhibitors of this kind are preferably bound to granular, water-soluble carrier substances as described.

**[0034]** In a preferred embodiment, the detergent is particulate, and contains up to 25 wt %, in particular 5 wt % to 20 wt % bleaching agent, in particular alkali percarbonate, up to 15 wt %, in particular 1 wt % to 10 wt % bleach activator, 20 wt % to 55 wt % inorganic builders, up to 10 wt %, in particular 2 wt % to 8 wt % water-soluble organic builders, 10 wt % to 25 wt % synthetic anionic surfactant, 1 wt % to 5 wt % nonionic surfactant, and up to 25 wt %, in particular 0.1 wt % to 25 wt % inorganic salts, in particular alkali carbonate and/or alkali hydrogen carbonate.

**[0035]** In a further preferred embodiment, a detergent into which cellulose derivative to be used according to the present invention is incorporated is liquid, and contains 10 wt % to 25 wt %, in particular 12 wt % to 22.5 wt % nonionic surfactant, 2 wt % to 10 wt %, in particular 2.5 wt % to 8 wt % synthetic anionic surfactant, 3 wt % to 15 wt %, in particular 4.5 wt % to 12.5 wt % soap, 0.5 wt % to 5 wt %, in particular 1 wt % to 4 wt % organic builders, in particular polycarboxylate such as citrate, up to 1.5 wt %, in particular 0.1 wt % to 1 wt % complexing agents for heavy metals, such as phosphonate, and in addition to an optionally contained enzyme, enzyme stabilizer, dye and/or fragrance, water and/or water-miscible solvent.

**[0036]** Also possible, in addition to the aforesaid combination, is the use of a polyester-active soil-release-enabling polymer made up of a dicarboxylic acid and an optionally polymeric diol, to intensify the cleaning performance of bleaching-agent-containing laundry detergents when washing textiles. Such addition of a polyester-active soil-release-enabling polymer are also possible in the context of detergents according to the present invention and of the method according to the present invention.

**[0037]** Included among the soil-release-enabling polymers known to be polyester-active, are copolyesters of dicarboxylic acids, for example adipic acid, phthalic acid, or terephthalic acid, diols, for example ethylene glycol or propylene glycol, and polydiols, for example polyethylene oxide. Included among the soil-release-enabling polyesters preferred for use are those compounds that are accessible formally by the esterification of two monomer parts, the first monomer being a dicarboxylic acid HOOC-Ph-COOH and the second monomer being a diol HO-$(CHR^{11}\text{-})_a$OH, which can also be present as a polymeric diol H-$(O\text{-}(CHR^{11}\text{-})_a)_b$OH, in which Ph denotes an o-, m-, or p-phenylene radical that can carry 1 to 4 substituents selected from alkyl radicals having 1 to 22 carbon atoms, sulfonic acid groups, carboxyl groups, and mixtures thereof, $R^{11}$ denotes hydrogen, an alkyl radical having 1 to 22 carbon atoms, and mixtures thereof, a is a number from 2 to 6, and b is a number from 1 to 300. By preference, both monomer diol units -O-$(CHR^{11}\text{-})_a)_b$O- and polymer diol units -$(O\text{-}(CHR^{11}\text{-})_a)_b$O- are present in the polyesters obtainable therefrom. The molar ratio of monomer diol units to polymer diol units is by preference 100:1 to 1:100, in particular 10:1 to 1:10. In the polymer diol units, the degree of polymerization b is preferably in the range from 4 to 200, in particular from 12 to 140. The molecular weight or average molecular weight, or the maximum of the molecular weight distribution, of preferred soil-release-enabling polyesters is in the range from 250 to 100,000, in particular from 500 to 50,000. The acid on which the Ph radical is based is selected by preference from terephthalic acid, isophthalic acid, phthalic acid, trimellitic acid, mellitic acid, the isomers of sulfophthalic acid, sulfoisophthalic acid, and sulfoterephthalic acid, and mixtures thereof. If their acid groups are not part of the ester bonds in the polymer, they are preferably present in salt form, in particular as an alkali or ammonium salt. Among these, the sodium and potassium salts are particularly preferred. If desired, instead of the HOOC-Ph-COOH monomer, small proportions - in particular no more than 10 mol % based on the proportion of Ph having the meaning indicated above - of other acids that comprise at least two carboxyl groups can be contained in the soil-release-enabling polyester. Included among these are, for example, alkylene and alkenylene dicarboxylic acids such as malonic acid, succinic acid, fumaric acid, maleic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid. Included among the preferred diols HO-$(CHR^{11}\text{-})_a$OH are those in which $R^{11}$ is hydrogen and a is a number from 2 to 6, and those in which a has the value of 2 and $R^{11}$ is selected from hydrogen and the alkyl radicals having 1 to 10, in particular 1 to 3, carbon atoms. Among the last-named diols, those of the formula HO-CH2-$CHR^{11}$-OH, in which $R^{11}$ has the meaning indicated above, are particularly preferred. Examples of diol components are ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,2-decanediol, 1,2-dodecanediol, and neopentyl glycol. Polyethylene glycol having an average molar weight in the range from 1000 to 6000 is particularly preferred among the polymeric diols.

**[0038]** If desired, the polyesters having the composition as described above can also be end-capped, alkyl groups having 1 to 22 carbon atoms and esters of monocarboxylic acids being suitable as terminal groups. The terminal groups,

bound via ester bonds, can be based on alkyl, alkenyl, and aryl monocarboxylic acids having 5 to 32 carbon atoms, in particular 5 to 18 carbon atoms. Included among these are valeric acid, hexanoic acid, oenanthic acid, octanoic acid, pelargonic acid, decanoic acid, undecanoic acid, undecenoic acid, lauric acid, lauroleic acid, tridecanoic acid, myristic acid, myristoleic acid, pentadecanoic acid, palmitic acid, stearic acid, petroselic acid, petroselaidic acid, oleic acid, linoleic acid, linolaidic acid, linolenic acid, eleostearic acid, arachidic acid, gadoleic acid, arachidonic acid, behenic acid, erucic acid, brassidic acid, clupanodonic acid, lignoceric acid, cerotic acid, melissic acid, benzoic acid, that can carry 1 to 5 substituents having a total of up to 25 carbon atoms, in particular 1 to 12 carbon atoms, for example tert.-butylbenzoic acid. The terminal groups can also be based on hydroxymonocarboxylic acids having 5 to 22 carbon atoms, included among which are, for example, hydroxyvaleric acid, hydroxyhexanoic acid, ricinoleic acid, its hydrogenation product hydroxystearic acid, and o-, m-, and p-hydroxybenzoic acid. The hydroxymonocarboxylic acids can in turn be connected to one another via their hydroxyl group and their carboxyl group, and thus be present more than once in a terminal group. By preference, the number of hydroxymonocarboxylic acid units per terminal group, i.e. their degree of oligomerization, is in the range from 1 to 50, in particular from 1 to 10. In a preferred embodiment of the invention, polymers of ethylene terephthalate and polyethylene oxide terephthalate, in which the polyethylene glycol units have molecular weights from 750 to 5000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 50:50 to 90:10, are used.

**[0039]** The soil-release-enabling polymers are preferably water-soluble; the term "water-soluble" is to be understood as a solubility of at least 0.01 g, by preference at least 0.1 g of the polymer per liter of water at room temperature and pH 8. Polymers preferred for use exhibit under these conditions, however, a solubility of at least 1 g per liter, in particular at least 10 g per liter.

Examples

**[0040]** Solid detergents according to the present invention (D1 and D2) and a comparative detergent (C1) were prepared by mixing the ingredients given in the following table 1 in the amounts also given there.

Table 1: Detergent compositions [wt %]

| | D1 | D2 | C1 |
|---|---|---|---|
| Sodium ABS | 15.3 | 15.3 | 15.3 |
| Sodium carbonate | 20 | 20 | 20 |
| Sodium silicate | 5.9 | 5.9 | 5.9 |
| Sodium HEDP | 0.3 | 0.3 | 0.3 |
| CMC | 0.3 | 0.3 | 0.3 |
| Perfume | 0.25 | 0.25 | 0.25 |
| Dye | 0.155 | 0.155 | 0.155 |
| Sodium sulfate | 53 | 53 | 53 |
| Polyethylene oxide), Mw 5,000,000 g/mol | 0.095 | 0.19 | 0 |
| fumed silica | 0.003 | 0.006 | 0 |
| calcium sulfate / calcium carbonate | 0.002 | 0.004 | 0 |
| Water | ad 100 | | |

**[0041]** With each detergent, hand washing trials were performed, using 100 g of detergent in 41 l of water, and washing fabrics soiled with the standardized stains given in the following table 2. After drying, the brightness (L) of the fabrics was determined and is also given in table 2.

Table 2: Brightness values after washing

| stain | L (C1) | L (D1) |
|---|---|---|
| frying fat (tinted blue) on cotton | 49,3 | 52,3 |
| mascara on cotton | 24,8 | 35,1 |
| creamy red curry sauce on cotton | 60,9 | 63,4 |

(continued)

| stain | L (C1) | L (D1) |
|---|---|---|
| frying fat (tinted blue) on polyester | 51,6 | 55,6 |
| lard (tinted blue) on polyester | 47,8 | 50,8 |
| mascara on polyester | 25,5 | 29,9 |
| butter (browned) on polyester | 71,5 | 72,7 |

## Claims

1. Solid laundry detergent in powder form, comprising surfactant and a combination of polyethylene oxide) in which the medium polymerization degree of the ethylene oxide is in the range of from 22,000 to 228,000, fumed silica, and at least one calcium salt.

2. Detergent according to claim 1, **characterized in that** the mean molecular weight (weight average, $M_w$) of said polyethylene oxide) preferably is in the range of from 1,000,000 g/mol to 10,000,000 g/mol.

3. Detergent according to claim 1 or 2, **characterized in that** it comprises 14 % by weight to 17 % by weight of surfactant, preferably anionic surfactant, 0.09 % by weight to 0.2 % by weight of said polyethylene oxide), 0.002 % by weight to 0.01 % by weight of fumed silica, and/or up to 0.006 % by weight, preferably 0.001 % by weight to 0.005 % by weight, of calcium salt.

4. Detergent according to any of claims 1 to 3, **characterized in that** the weight ratio of said poly(ethylene oxide) to fumed silica is in the range of from 25 : 1 to 40 : 1, and/or that the weight ratio of said poly(ethylene oxide) to calcium salt is in the range of from 55 : 1 to 40 : 1.

5. Detergent to any of claims 1 to 4, **characterized in that** said calcium salt comprises any of the anions acetate, benzoate, borate, bromide, butyrate, carbonate, chloride, citrate, formate, fumarate, gluconate, iodide, lactate, malate, maleate, malonate, nitrate, oxalate, phosphate, propionate, salicylate, silicate, succinate, sulfate, tartrate, or mixtures thereof.

6. Process of hand washing laundry, by manually contacting laundry in need of washing with an aqueous laundry liquor comprising 2.2 g/l to 2.7 g/l of a detergent according to any of claims 1 to 5.

7. Process of claim 6, **characterized in that** it is carried out by using water of a temperature in the range of from 20 °C to 35 °C, more preferred from 20 °C to 30 °C, and/or **characterized in that** it is carried out by applying manual force to the laundry immersed in the laundry liquor for a period of from 5 minutes to 20 minutes, more preferred from 5 minutes to 10 minutes.

8. Use of a combination of polyethylene oxide) in which the medium polymerization degree of the ethylene oxide is in the range of from 22,000 to 228,000, fumed silica, and at least one calcium salt to prevent accumulation of stains on fabrics by applying said combination in water to the fabrics.

9. Use of a combination of polyethylene oxide) in which the medium polymerization degree of the ethylene oxide is in the range of from 22,000 to 228,000, fumed silica, and at least one calcium salt to increase the detergency of detergents.

10. Use according to claim 8 or 9, **characterized in that** the combination is part of a detergent according to any of claims 1 to 5.

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# EUROPEAN SEARCH REPORT

Application Number
EP 23 15 6278

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