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WASHING AGENTS CONTAINING A TEXTILE SOFTENER

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ABSTRACT OF THE DISCLOSURE

Detergent compositions containing textile softeners consisting essentially of:

(1) from 5% to 100% by weight of a mixture of surface-active agents consisting essentially of:
  (a) from 20% to 90% by weight of customary surface-active compounds utilizable in neutral to alkaline textile washing baths selected from the group consisting of anionic surface-active compounds, amphoteric surface-active compounds, non-ionic surface-active compounds, and mixtures thereof, and
  (b) from 80% to 10% by weight of a textile softener composition consisting essentially of
    (i) from 100% to 20% by weight of a fatty acid - hydroxyalkylpolyamine condensation product of glyceride of higher fatty acids having from 8 to 24 carbon atoms with at least 50% of said higher fatty acids having from 16 to 24 carbon atoms, with a hydroxyalkyl-alkylpolyamine having at least one hydroxyalkyl selected from the group consisting of hydroxyethyl, hydroxypropyl and dihydroxypropyl and at least two hydrogen atoms bonded to nitrogen atoms, said condensation product containing from 5% to 40% by weight of fatty acid partial glycerides, and
    (ii) from 0 to 80% by weight of quaternary ammonium compounds containing two alkyls having 14 to 26 carbon atoms and at least one quaternary nitrogen atom in the molecule, and

(2) from 95% to 0 of other customary components of detergent compositions.

THE PRIOR ART

After drying washed textiles, especially those of cotton or similar cellulose fibers, a distinct harshening of the handle is to be noted especially when these textiles have been washed in drum washing machines. This phenomenon is particularly unpleasant in the case of laundered articles which come in contact with human skin during use, particularly underwear, bed linen and towels. In addition, considerable value is also attached to a pleasant handle in the case of other laundered articles such as, for example, table linen.

It is known that this undesired harshening of the handle can be avoided during laundering by adding cationic substances which contain at least two high molecular weight fatty residues in the molecule to the last rinsing bath. In practice, dialkyl-dimethyl-ammonium salts suspendable in water have been utilized for this purpose. Since these cationic textile softeners give water-insoluble precipitates with anionic detergent substances, they cannot be added

to the washing agent itself. Even when they are added to the last rinsing bath, precipitates may be formed from the reaction of the cationic textile softeners with the residues of anionic detergent substances which are still present in the rinsing water or on the fibers of the washed textiles. In the British patent specification No. 1,052,847 it was proposed to add cationic textile softeners to washing compositions based on anionic surface-active compounds. However, an improvement of the handle of the washed articles cannot be obtained in this way. The reason for this probably lies in the formation of the above-mentioned water-soluble precipitates.

OBJECTS OF THE INVENTION

An object of the invention is the obtention of textile softeners which are substantive and compatible with neutral to alkaline textile washing agents.

Another object of the invention is the obtention of detergent compositions containing textile softeners consisting essentially of:

(1) from 5% to 100% by weight of a mixture of surface-active agents consisting essentially of:
  (a) from 20% to 90% by weight of customary surface-active compounds utilizable in neutral to alkaline textile washing baths selected from the group consisting of anionic surface-active compounds, amphoteric surface-active compounds, non-ionic surface-active compounds, and mixtures thereof, and
  (b) from 80% to 10% by weight of a textile softener composition consisting essentially of: (i) from 100% to 20% by weight of a fatty acid-hydroxyalkylpolyamine condensation product of glyceride of higher fatty acids having from 8 to 24 carbon atoms with at least 50% of said higher fatty acids having from 16 to 24 carbon atoms, with a hydroxyalkyl-alkylpolyamine having at least one hydroxyalkyl selected from the group consisting of hydroxyethyl, hydroxypropyl and dihydroxypropyl and at least two hydrogen atoms bonded to nitrogen atoms, said condensation product containing from 5% to 40% by weight of fatty acid partial glycerides, and; (ii) from 0 to 80% by weight of quaternary ammonium compounds containing two alkyls having 14 to 26 carbon atoms and at least one quaternary nitrogen atom in the molecule, and

(2) from 95% to 0 of other customary components of detergent compositions.

These and other objects of the invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

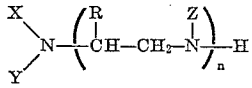
The invention is based on the discovery that the handle of the laundered fabrics is improved, if in the detergents or auxiliary used for the laundry in addition to anionic, non-ionic and/or amphoteric surface-active agents, and possibly traditional components of such agents, also reaction products of glycerides of higher fatty acids with hydroxyalkyl polyamines as textile softeners are present. Such textile fabric softeners may partly be substituted by quaternary ammonium compounds, containing two long-chain alkyl residues in the molecule.

The detergent compositions of the present invention containing the aforementioned textile softeners comprise:

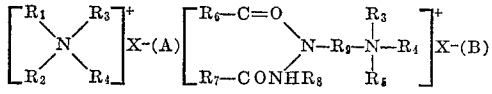
(1) from 5% to 100%, preferably from 5% to 80%, and in particular from 8% to 40% by weight of a mixture of surface-active agents consisting of:
  (a) from 20% to 90%, preferably from 75% to 35% by weight of customary surface-active

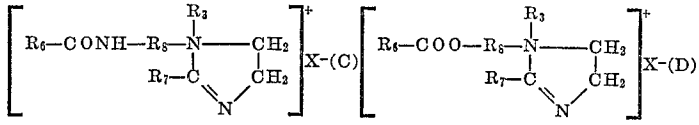
compounds utilizable in neutral to alkaline textile washing baths of the anionic and/or amphoteric and/or nonionic surface-active agents, particularly surface-active sulfonates and sulfates, soaps, surface-active polyethers, amine-oxides, sulfoxides, phosphineoxides, and surface-active carboxy, sulfate and sulfonate betaines, and

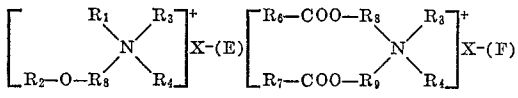
(b) from 80% to 10%, preferably from 25% to 65% by weight of a textile softener composition consisting of: (i) from 100% to 20% of a fatty acid-hydroxyalkyl-polyamine condensation product of a hydroxyalkyl-alkylpolyamine having at least one hydroxyalkyl selected from the group consisting of hydroxyethyl, hydroxypropyl and dihydroxypropyl and at least two hydrogen atoms bonded to nitrogen atoms, preferably of the formula



wherein X is a member selected from the group consisting of hydroxyethyl, hydroxypropyl and dihydroxypropyl, Y and Z are selected from the group consisting of hydrogen and X, with the proviso that at least one of Y and Z is hydrogen, *n* is an integer from 1 to 3, and R is a member selected from the group consisting of hydrogen and alkyl having 1 to 4 carbon atoms, with glycerides of higher fatty acids having from 16 to 24, preferably 16 to 22 carbon atoms in each fatty acid moiety, said condensation product containing from 5% to 40% preferably from 10% to 30% by weight of fatty acid partial glycerides such as mono-fatty acid glycerides and di-fatty acid glycerides, and (ii) from 0 to 80% by weight of quaternary ammonium compounds containing two hydrocarbonyls having 14 to 26, preferably 16 to 20, carbon atoms and a quaternary nitrogen atom, preferably having the formulas







wherein R_1 and R_2 are alkyl having 14 to 26, preferably 16 to 20 carbon atoms, R_3, R_4 and R_5 are lower alkyl and alkylol having 1 to 4 carbon atoms, R_6 and R_7 are alkyl with 13 to 21, preferably 15 to 19 carbon atoms and R_8 and R_9 are alkylene with 2 to 4 carbon atoms or hydroxyalkylene with 3 to 4 carbon atoms, and X represents the anion of an acid, said quaternary compound being water-dispersible, and

(2) from 0 to 95%, preferably from 20% to 95%, and in particular from 60% to 92% by weight of other customary components of detergent compositions selected from the group consisting of inorganic builders, organic builders, complexing compounds,

bleaches, foam stabilizers, foam inhibitors, dirt carriers, enzymes and water.

Preferably the fatty acid glycerides utilized in the condensation product are especially triglycerides of higher fatty acids with 16 to 24, preferably 16 to 22 carbon atoms in the fatty residues. Glycerides which have a content of fatty acid residues with 8 to 14 carbon atoms should have a proportion of the fatty acid residues with 16 to 22 carbon atoms in the mixed glycerides or glyceride mixtures of at least 50%. The fatty acid residues may be derived e.g. from caprylic, pelargonic, capric, undecylic, lauric, myristic, palmitic, stearic, oleic, arachidic or behenic acid. Preferably natural fats are employed, such as the fats of vegetable and land and sea animal origin such as coconut, palm, olive, linseed, cottonseed, soybean, peanut, rape, lard, tallow and especially the fully or partially hardened products of such fats and also hardened fish or whale oils.

Hydroxyalkylpolyamines are understood to mean compounds possessing at least one hydroxyethyl, hydroxypropyl or dihydroxypropyl group and at least two hydrogen atoms bonded to nitrogen, such as e.g. hydroxyethyl-ethylenediamine, di-(hydroxyethyl)-ethylenediamine, hydroxyethyl-diethylenetriamine, hydroxypropyl-diethylenetriamine, etc.

In the following the above-defined fatty acid-hydroxyalkylpolyamine condensation products are for reason of simplicity called "fatty-acid condensation products."

Such fatty-acid condensation products are obtained by the reaction of 1.3 to 4, preferably 1.5 to 3 mols of fatty acid radicals which are utilized in the form of the glycerides, particularly of the triglycerides, with one mol of the hydroxyalkylpolyamine where, however, not more fatty acid is present as can be bound by the amine nitrogen as an amide and/or to the hydroxyl groups as an ester. For instance, in the case of N-hydroxyethyl-ethylene diamine, 2 to 3 mols of fatty acid radicals are reacted.

If, owing to the use of fatty acid glycerides of natural origin, the fatty acid condensation products contain also fatty acid residues with 8 to 14 carbon atoms, these residues contribute only insignificantly to the fabric-softening effect of the fatty acid condensation products used in accordance with the invention, but they do not interfere with the total effect. It is preferable, however, as already mentioned, to use fatty acid glycerides with at least 50% fatty acid residues with 16 to 24, preferably 16 to 22 carbon atoms.

The fatty-acid condensation products are mixtures of varied compounds. The composition of these product mixtures depends to a large extent upon the mole ratio of the reaction components. The fatty acid condensation products corresponding to the said molar ratios of fatty acid residues amine have the following composition:

2% to 20%, preferably 5 % to 15% by weight of diamidoesters

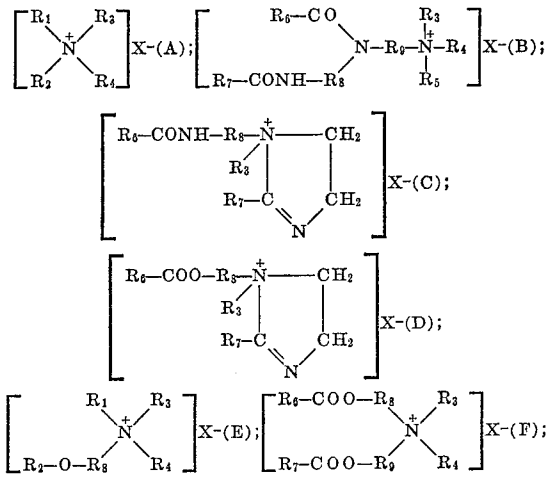
20% to 60%, preferably 25% to 45% by weight of diamides

5% to 40%, preferably 10% to 35% by weight of monoamides

5% to 40%, preferably 10% to 30% by weight of fatty acid partial glycerides such as mono-fatty acid glycerides and di-fatty acid glycerides.

The fatty acid condensation products may contain as reaction by-products further material such as triglycerides, free fatty acids, free amines, glycerol, water.

The textile fabric softening quaternary ammonium compounds are those containing two, preferably saturated, alkyl residues with 14 to 26, preferably 16 to 20 carbon atoms, and at least one quaternary nitrogen atom in the molecule and which correspond to the following formulas:



In these formulas R_1 and R_2 are, preferably saturated, alkyl residues with 14 to 26, preferably 16 to 20 carbon atoms, R_6 and R_7 alkyl residues with 13 to 21, preferably 15 to 19 carbon atoms, R_3, R_4 and R_5 lower alkyl and alkylol residues with 1 to 4 carbon atoms and R_8 and R_9 alkylene residues with 2 to 4 carbon atoms or hydroxyalkylene residues with 3 or 4 carbon atoms.

In the above-mentioned formulas, X^- represents the anion of an inorganic or non-capillary active organic acid with 2 to 7 carbon atoms. Examples of anion X^- are the hydrochloric acid, sulfuric acid, acetic acid, glycolic acid, lactic acid, methyl sulfuric acid, methane, ethane or toluene sulfonic acid residues, but the particularly preferred anion X^- is the chloride anion.

The invention relates to detergents and/or laundry compositions for textiles, especially for fine laundry articles and easy-care textiles, consisting of a combination of anionic and/or amphoteric and/or nonionic surfactants with the above-described textile fabric softeners and possibly traditional constituents of detergents and laundry auxiliaries. These laundry deteregnts and auxiliaries comprise (1) 5% to 100%, preferably 5% to 80%, and in particular 8% to 40%, by weight of a surfactant combination consisting of:

(a) 20% to 90%, preferably 75% to 35% by weight of a surfactant component having at least one surfactant of the anionic and/or amphoteric and/or non-ionic type, and

(b) 80% to 100%, preferably 25% to 65% by weight of a textile fabric softening component of the following composition: (i) 100% to 20% by weight of the above-mentioned fatty acid condensation product; (ii) 0 to 80% by weight of the above-mentioned quaternary ammonium compounds; and (2) 95% to 0, preferably 95% to 20%, and in particular 92% to 60% by weight of the other customary detergent constituents.

The surfactant component mentioned under (a) consists preferably of at least 50% of anionic surface-active agents.

Among the other traditional detergent constituents are, for example, neutral to alkaline reacting builders, complex formers, bleaching components, foam stabilizers, foam inhibitors, dirt carriers, enzymes etc. Preferably, sufficient alkali is present in the builders so that a 1% solution of the finished detergent or laundry auxiliary has a pH value in the range of 7 to 12, preferably 9 to 11.

In preferred laundry detergent compositions of the present invention, the extile softening component named above under (b) of the surfactant combinations comprises

80% to 20% by weight of the above-mentioned fatty acid condensation product, and

20% to 80% by weight of the above-mentioned quaternary ammonium compound.

If the products, in accordance with the invention, contain more than 45% by weight of the above surfactant combination, they are mostly not used as sole detergents, but they are generally supplied to industrial laundries or the txtile industry, where they are rarely used by themselves, but more frequently in combination with traditional additives. In such a concentrated product, by-products from the manufacture of the surfactants or the textile fabric softeners as well as traditional additives may also be present.

The quaternary products used in accordance with the invention are known products which are present as water-dispersable salts. Of particular practical importance are compounds of the Formula A, wherein the residues R_1 and R_2 are preferably alkyl residues with 16 to 20 carbon atoms, especially those originating from, preferably hardened, tallow fatty acids.

It is generally known that the above-mentioned textile softening quarternary ammonium compounds usually give undesirable precipitates with anionic surfactants in aqueous solution and are, therefore, not used in practice together with the common detergents containing anionic surface-active substances. This known incompatibility with anionic surface-active substances can be overcome suprisingly if, in accordance with the invention, detergents and laundry auxiliaries are used wherein the above-mentioned fatty acid condensation product serving as fabric softener is replaced in the said proportions by quaternary ammonium compounds of Formulas A to F.

The preparation of the fatty-acid condensation product used according to the invention is done in a simple manner by heating the hydroxyalkylamine with the glyceride at temperatures of from 90° to 150° C., preferably 90° to 130° C. Depending upon the temperature utilized, up to 15 hours, preferably up to 8 hours, are required to reach the reaction equilibrium. However, it is not absolutely necessary to reach this reaction equilibrium. For technical uses, products are acceptable in which the fatty-acid condensation product amounts to at least 50% and preferably 60% to 90% of the reaction product.

In order to finish the reaction, the reaction product is cooled and in a known manner converted, for example, by a cooling cylinder to flakes, or by an extrusion press to granulates, or by spraying to powder. According to a variant of the preparation, the reaction product is treated in the melt with a water-soluble organic or inorganic acid, adjusted to from slightly alkaline to slightly acidic, and subsequently subjected to the above-named forming processes. In the above forms, the fatty-acid condensation products are particularly capable of being stored or shipped. According to another variant, the product melt can also be dispersed in an aqueous phase, either by stirring the melt, after being adjusted to from slightly alkaline to slightly acidic with the water-soluble organic or inorganic acid, into an aqueous phase, or by stirring the melt into an aqueous phase which contains the organic or inorganic acid dissolved therein, or by stirring the melt into the aqueous phase and subsequently adding the organic or inorganic acid.

As water-soluble organic or inorganic acids which are used for the adjustment to from slightly alkaline to slightly acidic are organic acids, such as acetic acid, oxalic acid, glycolic acid, lactic acid, citric acid and tartaric acid and inorganic acids such as hydrochloric acid, sulfuric acid or phosphoric acid. Preferably glycolic acid is utilized.

If, for example in the preparation of the textile fabric softener, used in accordance with the invention, 3 mols fatty acid residue as triglyceride are reacted with 1 mol

N-hydroxyethyl-ethylenediamine, the resulting fatty acid condensation product has approximately the following composition:

5% to 15% by weight of diamidoesters
30% to 45% by weight of diamides
20% to 30% by weight of monoamides
15% to 30% by weight of fatty acid partial glycerides.

As by-products or accompanying substances, triglycerides, free fatty acids, free amine, glycerol, water and possibly organic or inorganic acid may be present in the reaction product in a total quantity of 0 to 25% by weight.

In accordance with the present invention, the preferred textile softeners used in the detergent compositions are the fatty acid condensation products of glycerides of higher fatty acids with N-hydroxyethyl-ethylene diamine, especially the product of 1 mol of hardened tallow (corresponding to 3 fatty acid residues) and 1 mol of N-hydroxyethyl-ethylenediamine. The invention will, therefore, be further described with reference to this product. The information given applies with due alteration of details equally well for derivatives of other hydroxyalkyl-polyamines, especially for hydroxyalkyl diethylenetriamines and also for glycerides of different origin and composition especially for fatty acid glycerides of fully or partly hardened fats.

In practice, the composition of particularly valuable heavy-duty washing agents generally lies within the range of the following formulation:

5% to 80%, preferably 8% to 40%, by weight of combinations of surface-active compounds, consisting of 0 to 80%, preferably 25% to 65%, by weight of synthetic surface-active compounds of the sulfonate and/or sulfate type with preferably 8 to 18 carbon atoms in the hydrophobic residue, 0 to 80%, preferably 5% to 40%, by weight of non-ionic surface-active compounds, 0 to 80%, preferably 10% to 50%, by weight of soaps, 10% to 80%, preferably 25% to 65%, by weight of the textile fabric softener component, 0 to 6%, preferably 0.5% to 3%, by weight of foam stabilizers. 0 to 8%, preferably 0.5% to 5%, by weight of foam inhibitors, preferably not a surface active compound.

20% to 95%, preferably 60% to 92%, by weight of builders, at least a part of this having an alkaline reaction and the quantity of alkaline and neutral reacting builders preferably constituting 0.5 to 7 times and especially 1 to 5 times, the amount of the total detergent substances.

0% to 30%, preferably 3% to 15%, by weight of other washing agent constituents, such as, for example, dirt carriers, enzymes, bleaching components, perfume, dye and water.

A further embodiment of the invention is a detergent concentrate composition comprising:

(a) From 10% to 60% by weight of a surfactant combination consisting of:

80% to 50% by weight of a surface-active component consisting essentially of anionic surface-active agents of the sulfonate and/or sulfate type with preferably 8 to 18 carbon atoms in the hydrophobic residue, possibly soaps and possible non-ionic surface active agents. The non-ionic surface active agents represent not more than 50% by weight and preferably not more than 35% by weight of this surface-active component.

20% to 50% by weight of the textile fabric softener component, 0 to 8%, preferably 0 to 6% by weight of non-surface-active foam inhibitors.

(b) from 90% to 40% by weight of other detergent constituents, especially alkaline to neutral reacting builders, dirt carriers, and possibly enzymes, optional bleaches, perfume, dyes and water.

The amounts of the detergent constituents within the above-mentioned ranges have been chosen so that the fatty acid condensation product serving as textile fabric softener amounts to from 3% to 30%, preferably 5% to 20% by weight of the total detergent.

In as far as the detergent compositions in accordance with the invention contain soaps the quantity ratio of the anionic surfactants of the sulfonate and/or sulfate type to soap lies in the range from 30:1 to 1:5, preferably 20:1 to 1:2.

The detergent compositions may also contain a bleaching component, which in the above recipes is regarded as forming part of the builders. The bleaching component, including optionally present stabilizers and/or activators therefor may amount to 2% to 35%, preferably 7% to 30% by weight of the whole detergent.

For the mixing of the textile fabric softener with the detergent substances various known methods may be used. For the optimum utilization of the textile fabric softening effect, it is recommended that the textile softener be finely distributed throughout in the detergent composition of the present invention. This desired distribution can be achieved by homogeneously mixing the finely powdered textile fabric softeners with the remaining detergent composition particles, or by spraying the melted textile fabric softener or the same dissolved or dispersed in suitable liquid carriers, onto the remaining solid detergent composition particles, so that these are wholly or partly coated, or the textile fabric softeners may be worked into a detergent paste which is to be spray dried. The latter method is particularly suitable for aqueous dispersions.

The detergent composition in accordance with the present invention is particularly suitable for the laundering of fine laundry articles and easy-care textiles especially those of cotton, polyester, polyacrylonitrile and polyamide, especially in the form of woven or knitted fabrics. It is preferred that the laundering be effected at a temperature in the range of 30 to 60° C. It is also possible though to launder at temperatures up to boiling temperature.

The anionic, amphoteric or non-ionic surface-active compounds contain in the molecule at least one hydrophobic residue mostly containing 8 to 26, preferably 10 to 20 and especially 12 to 18 carbon atoms, and at least one anionic, non-ionic or amphoteric water-solubilizing group. The preferably saturated hydrophobic residue is mostly aliphattc, but possibly also alicyclic in nature. It may be combined directly with the water-solubilizing group or through intermediate members. Suitable intermediate members are, for example, benzene rings, carboxylic acid ester or carbon amide groups, residues of polyhydric alcohols linked in ether- or ester-like form, such as for example, those of ethylene glycol, propylene glycol, glycerine or corresponding polyether residues.

The hydrophobic residue is preferably an aliphatic hydrocarbon residue having 10 to 18, preferably 12 to 18 carbon atoms, but deviations from this preferred range of numbers are possible, depending on the nature of the surface-active compound in question.

Soaps, which are derived from natural or synthetic fatty acids, possibly from resin or naphthenic acids, are utilizable as the anionic detergent substances, especially when these acids have iodine values of not more than 30 and preferably less than 10.

Among the synthetic anionic surface-active compounds, the sulfonates and sulfates possess particular practical importance.

The sulfonates include, for example, the alkylaryl-sulfonates, especially the alkylbenzene-sulfonates, which among others, are obtained from preferably straight chain, aliphatic hydrocarbons having 9 to 15, preferably 10 to 14, carbon atoms, by chlorination and condensation with benzene or from corresponding olefins with terminal or non-terminal double bonds by condensation with benzene, and sulfonation of the alkylbenzenes obtained. Furthermore, aliphatic sulfonates are of interest such as are obtainable, for example, from preferably saturated

hydrocarbons containing 8 to 18 and preferably 10 to 16, carbon atoms in the molecule by sulfochlorination with sulfur dioxide and chlorine or sulfoxidation with sulfur dioxide and oxygen and conversion of the products thereby obtained into the sulfonates. Mixtures of alkene sulfonates, hydroxyalkane sulfonates and alkane di-sulfonates are also useful as aliphatic sulfonates, such as are obtained, for example, from C_8 to C_{18}, preferably C_{12} to C_{16}, olefins with terminal or non-terminal double bonds by sulfonation with sulfur dioxide, and acid or alkaline hydrolysis of the sulfonation products. In the aliphatic sulfonates thus prepared, the sulfonate group is frequently attached to a secondary carbon atom. However, sulfonates with a primary, for example, terminal, sulfonate group can also be prepared by reacting terminal olefins with a bisulfite.

The sulfonates to be used according to the invention also include salts, preferably dialkali metal salts of α-sulfo-fatty acids as well as esters of α-sulfo-fatty acids with mono- or poly-hydric alcohols containing 1 to 4 and preferably 1 to 2 carbon atoms.

Further useful sulfonates are salts of fatty acid esters of hydroxyethanesulfonic acid or dihydroxypropane sulfonic acid, the salts of the fatty alcohol esters of lower aliphatic or aromatic sulfomono- or di-carboxylic acids containing 1 to 8 carbon atoms, alkylglycerylether sulfonates and the salts of the amide-like condensation products af fatty acids or sulfonic acids with aminoethanesulfonic acid.

Surface-active compounds of the sulfate type include fatty alcohol sulfates, especially those derived from coconut fatty alcohols, tallow fatty alcohols or from oleyl alcohol. Sulfonation products of the sulfate type utilizable according to the invention can also be prepared from C_8 to C_{18} olefins with terminal or non-terminal double bonds. In addition, belonging to this group of surface-active compounds are sulfated fatty acid alkylolamides, sulfated monoglycerides and sulfated products of ethoxylated and/or propoxylated compounds such as fatty alcohols, alkylphenols with 8 to 15 carbon atoms in the alkyl residue, fatty acid amides, fatty acid alkylolamides and so forth, where 0.5 to 20, preferably 1 to 8, and advantageously 2 to 4 mol of ethylene and/or propylene oxide are added to one mol of said compounds to be ethoxylated and/or propoxylated.

The washing agents according to the invention may also contain surface-active synthetic carboxylates, for example, the fatty acid esters or fatty alcohol ethers of hydroxy-carboxylic acids as well as the fatty acid amide condensation products of fatty acids or sulfonic acids with amino-carboxylic acids, for example, glycocoll, sarcosine or protein hydrolysates.

Products which owe their solubility in water to the presence of polyether chains, amineoxide, sulfoxide or phosphineoxide groups, alkylolamide groups, and very generally to a number of hydroxyl groups, belong to the non-ionic surface-active compounds, denoted here as "Non-ionics" for the sake of simplicity.

The products obtainable by addition of ethylene oxide and/or glycide to fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty acid amides and sulfonic acid amides are of special practical interest. These "Non-ionics" may contain, per molecule, 4 to 100, preferably 6 to 40 and especially 8 to 20, ether residues above all ethylene glycol ether residues. Moreover, propylene or butylene glycol ether residues may be present either in these polyglycol ether residues or at their ends.

Further, products known by the trade names of "Pluronics" and "Tetronics" belong to the "Non-ionics." They are obtained from water-insoluble polypropylene glycols or from water-insoluble propoxylated lower aliphatic alcohols containing 1 to 8, preferably 3 to 6 carbon atoms and/or from water-insoluble propoxylated alkylenediamines. These water-insoluble (for example, hydrophobic) propylene oxide derivaives are converted into the said "Non-ionics" by ethoxylation until they become soluble in water. Finally, the reaction products of the above-mentioned aliphatic alcohols with propylene oxide known as "Ucon-Fluid," some of which are still water-soluble, are useful as "Non-ionics."

Further useful "Non-ionics" are fatty acid or sulfonic acid alkylolamides, which are derived, for example, from mono- or di- ethanolamines, dihydroxypropylamine or other polyhydroxyalkylamines, for example, the glycamines. They can be replaced by amides of higher primary or secondary alkylamines and polyhydroxycarboxylic acids.

From the group of amineoxides, the "Non-ionics" derived from higher tertiary amines having a hydrophobic alkyl residue and two shorter alkyl and/or alkylol residues containing up to 4 carbon atoms each are of particular interest.

Amphoteric surface-active compounds contain in the molecule both acid and basic hydrophilic groups. To the acid groups belong carboxylic acid, sulfonic acid, sulfuric acid half ester, phosphonic acid and phosphoric acid partial ester groups. The basic groups may be primary, secondary, tertiary and quaternary ammonium groups.

Owing to their good compatibility with other surface-active compounds, carboxy, sulfate and sulfonate betaines have special practical interest. Suitable sulfobetaines are obtained, for example, by reacting tertiary amines containing at least one hydrophobic alkyl residue with sultones, for example propane- or butane- sultone. Corresponding carboxybetaines are obtained by reacting the said tertiary amines with chloroacetic acid, its salts or with chloroacetic acid esters and fission of the ester linkage.

The foaming capacity of the washing agents according to the invention may be increased or reduced by suitable combinations of different surface-active compounds as well as non-surface-active compounds.

Suitable foam stabilizers in the case of surface-active compounds of the sulfonate or sulfate type, are chiefly surface-active carboxy- or sulfo-betaines and also the above-mentioned non-ionics of the alkylolamide type. Moreover, fatty alcohols or higher terminal diols are utilizable for this purpose.

Products with a reduced foaming capacity are chiefly intended for use in washing and dish-washing machines, in which in some cases a limited inhibition of foam is sufficient, while in other cases a stronger anti-foaming effect may be desired. Products which still foam in the average range of temperatures up to about 65° C., but develop less and less foam as higher temperature (70–100° C.) are reached, are of particular practical importance.

A reduced foaming power is often obtained with combinations of different types of surface-active compound, especially with combinations of synthetic anionic surface-active compounds, above all of (1) sulfates and/or sulfonates or of (2) non-ionics on the one hand and (3) soaps on the other hand. With combinations of components (1) and (2) or (1), (2) and (3), the foaming behavior can be influenced by the respective soap used. In the case of soaps from preferably saturated fatty acids with 12 to 18 carbon atoms, the inhibition of foam is small, while a stronger anti-foaming effect is attained, especially in the higher temperature range, by soaps from saturated fatty acid mixtures with 20 to 26, preferably 20 to 22 carbon atoms, the amount of which may constitute 5 to 10% by weight of the total soap fraction present in the surface-active combination.

Among others, the addition products of propylene oxide to the above-described non-ionic polyethylene glycol ethers are marked by a small foaming capacity. By varying the number of ethylene glycols and propylene glycol residues present in the molecule, products with a large variety of turbidity points can be obtained. These "Non-ionics" act on other non-ionics as foam inhibitors at temperatures above their turbidity point. They can, therefore,

be used in the combinations of surface-active compounds according to the invention together with other "Non-ionics," and also in combination with other surface-active compounds, as for example, as the non-ionic constituent in the already mentioned combinations with sulfates and/or sulfonates, soaps and "Non-ionics."

The foaming capacity of the surface-active compounds, however, can also be reduced by additions of known, non-surface-active foam inhibitors. These include possibly chlorine-containing N-alkylated aminotriazines, which are obtained by reacting 1 mol of cyanuric acid chloride with 2 to 3 mol of a mono- and/or di-alkylamine with 6 to 20, preferably 8 to 18 carbon atoms in the alkyl residue. Amino-triazine- or melamine-derivatives, which contain polypropylene glycol or polybutylene glycol chains, while 10 to 100 of such glycol residues may be contained in the molecule, have a similar action. Such compounds are obtained for example, by addition of corresponding amounts of propylene and/or butylene oxide to aminotriazines, especially to melamine. Products preferably used are obtained, for example, by reacting 1 mol of melamine with at least 20 mol of propylene oxide or at least 10 mol of butylene oxide. Products have been found to be especially active which are obtained by addition of 5 to 10 mol of propylene oxide to 1 mol of melamine and further addition of 10 to 50 mol of butylene oxide to this propylene oxide derivative.

The tri- to hexa- alkylmelamines or di- to tetraalkyldiaminochlorotriazines so obtained have a remarkably broad active spectrum independent of the nature of the surface-active compound in question.

Other non-surface-active, water-insoluble, organic compounds, such as paraffins or haloparaffins with melting points below 100° C., aliphatic C_{18}- to C_{40}-ketones and aliphatic carboxylic acid esters, which contain at least 18 carbon atoms in the acid or in the alcohol residue, possibly also in both of these two residues (for example triglycerides or fatty acid-fatty alcohol esters), can also be used as foam inhibitors, especially in combination with anionic synthetic surface-active compounds and soaps.

The non-surface-active foam inhibitors are often only fully active at temperatures at which they are present in the liquid state, so that the foaming behavior of the products can be controlled by choice of suitable foam inhibitors in a similar way to the choice of soaps from fatty acids of suitable chain lengths.

When foam stabilizers are combined with foam inhibitors dependent upon temperature, readily foaming products are obtained at lower temperatures while progressively more weakly foaming products are obtained as the temperature approaches the boiling temperature.

Particularly weakly foaming non-ionics, which may be used both alone and in combination with anionic, amphoteric and non-ionic surface-active compounds and reduce the foaming power of more strongly foaming, especially non-ionic, surface-active compounds, are addition products of propylene oxide to the above-described surface-active polyethylene glycol ethers, and also the above-described "Pluronics," "Tetronics" and "Ucon" fluid.

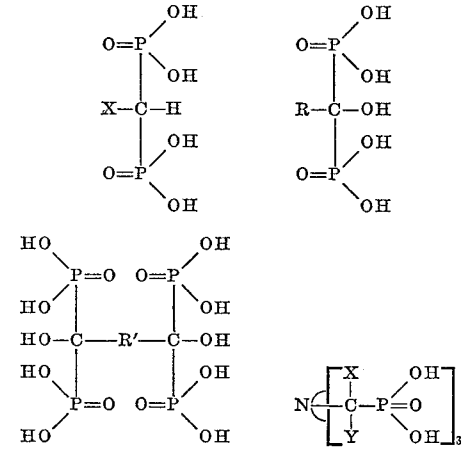
The complete washing compositions contain builders and inorganic salts as well as inorganic and organic complex-forming compounds.

Salts which are weakly acid, neutral or alkaline reacting are utilizable in the compositions of the invention, for example, the alkali metal bicarbonates, carbonates, silicates, orthophosphates, sulfates, di- or tetra-alkali metal pyrophosphates, complex forming alkali metal metaphosphates and the alkali metal salts of organic, non-surface-active sulfonic acids, carboxylic acids and sulfocarboxylic acids containing 1 to 8 carbon atoms. To the latter belong, for example, water-soluble salts of benzene-, toluene- or xylene-sulfonic acids, water-soluble salts of sulfoacetic acid, sulfobenzoic acid or salts of sulfodicarboxylic acids and the salts of acetic acid, lactic acid, citric acid and tartaric acid.

Further, the water-soluble salts of higher molecular weight polycarboxylic acids are useful as builders, especially polymerizates of maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, methylenemalonic acid and citraconic acid. Mixed polymerizates of these acids with one another or with other polymerizable substances, as for example with ethylene propylene, acrylic acid, methacrylic acid,, crotonic acid, 3-butenecarboxylic acid, 3-methyl-3-butane-carboxylic acid and also with vinyl methyl ether, vinyl acetate, isobutylene, acrylamide and styrene, are also useful.

Suitable complex forming builders are the weakly acid reacting metaphosphates and the alkaline reacting polyphosphates, especially the pyro-, tripoly- or tetrapolyphosphates. They may be replaced by known organic complex-forming compounds or be combined with them.

The latter include, for example, nitrilotriacetic acid, ethylenediaminetetraacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid, polyalkylene-polyamine - N - polyacetic acids and other known organic complex-forming compounds. Combinations of different complex-forming compounds may also be used. Di- and poly-phosphonic acids of the following constitutions also belong to the other known complex-forming compounds.



wherein R represents alkyl and R' represents alkylene radicals with 1 to 8, preferably 1 to 4, carbon atoms, and X and Y represent hydrogen atoms or alkyl radicals with 1 to 4 carbon atoms. Carboxy-methylenephosphonic acid ($HOOC—CH_2—PO(OH)_2$) is also useful as a complex-forming compound according to the invention. All these complex-forming compounds may be present as the free acids, but are preferably present as the alkali metal salts.

The washing agents according to the invention are preferably used as washing agents for white goods at boiling temperature or in the vicinity of the boiling temperature. They therefore often contain a bleaching component based on active oxygen or active chlorine.

The bleaching agents based on active oxygen are, especially, the inorganic percompounds, for example, perpyrophosphates, perpolyphosphates, percarbonates and perborates. The commercial sodium perborate of the approximate composition $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$ is of particular practical importance. Partly or completely dehydrated perborates, that is up to the approximate composition $NaBO_2 \cdot H_2O_2$, may also be used in its place. Finally, active oxygen containing borates, $NaBO_2 \cdot H_2O_2$, are also useful in which the ratio $Na_2O:B_2O_3$ is less than 0.5:1 and preferably lies in the region of 0.4 to 0.15:1, and in which the ratio H_2O_2:Na lies in the region of 0.5 to 4:1. These products are described in German Pat. No. 901,287 and in U.S. Pat. No. 2,491,789. The perborates may be wholly or partly replaced by other inorganic per-compounds, especially peroxyhydrates, such as for example, the peroxy-

hydrates of ortho-, pyro- or poly-phosphates, for example of tripolyphosphates, and also of the carbonates.

The active chlorine compounds useful as bleaching agents may be inorganic or organic. The inorganic active chlorine compounds include alkali metal hypochlorites, which may be used especially in the form of their mixed salts or addition compounds with orthophosphates or condensed phosphates, as for example, with pyro- and polyphosphates, or with alkali metal silicates. If the washing agents and washing agent adjuvants contain monopersulfates and chlorides, active chlorine is formed in aqueous solution.

Suitable organic active chlorine compounds are, in particular, the N-chloro-compounds in which one or two chlorine atoms are linked to a nitrogen atom, the third valency of the nitrogen atom being preferably linked to a negative group, especially a CO— or SO_2 group. These compounds include dichloro- and trichloro-cyanuric acid, chlorinated alkylguanides or alkylbiguanides, chlorinated hydantoin and chlorinated melamine.

The washing agents may also contain stabilizers for the bleaching component, especially for the percompounds. The above-indicated complex-forming compounds often have a stabilizing action. However, in their place or together therewith, different kinds of stabilizers may be present, for example, those which act through their large surface area. These customary water-soluble or water-insoluble stabilizers are utilized in amounts up to 10%, preferably from 0.25% to 8% by weight.

Suitable water-insoluble stabilizers for per-compounds are the different magnesium silicates, mostly obtained by precipitation from aqueous solutions, of composition $MgO:SiO_2=4:1$ to 1:4, preferably 2:1 to 1:2 and especially 1:1. These magnesium silicates may be replaced by the corresponding silicates of other alkaline earth metals or the corresponding silicates of cadmium or tin. Hydrated oxides of tin are also utilizable as stabilizers. These water-insoluble stabilizers are usually present in amounts from 1% to 8%, preferably 2% to 7% of the weight of the total preparation.

Suitable water-soluble stabilizers, which may be present together with water-insoluble stabilizers, are the above referred-to organic complex-forming compounds, the amount of which may constitute 0.25% to 5%, preferably 0.5% to 2.5% of the weight of the total preparation, depending on the strength of the complex formed.

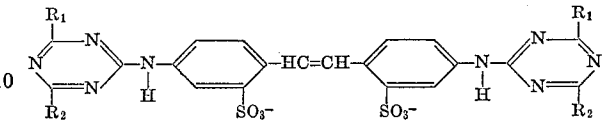
The action of the bleaching components and above all of the percompounds can be increased by known activators, such as small quantities of heavy metal ions, especially copper ions, which may preferably be present as mixed silicates of magnesium.

Furthermore, dirt carriers or soil suspension agents may be contained in the washing agents according to the invention, which keep the dirt, detached from the fiber, suspended in the washing bath and thus prevent graying. For this purpose water-soluble colloids of mostly organic nature are suitable, as for example, the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ethercarboxylic acids or ethersulfonic acids of starch or cellulose or salts of acid sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also suitable for this purpose. Further, soluble starch and starch products other than those named above can be used, as for example, degraded starch, aldehyde starches and so on. Polyvinylpyrrolidone is also utilizable.

The components of the washing compositions according to the invention, especially the builders, are usually selected so that the preparations have a neutral to distinctly alkaline reaction, so that the pH value of a 1% solution of the preparation usually lies in the region of 7 to 12. Fine washing compositions usually have a neutral to weakly alkaline reaction (pH value=7–9.5), while soaking, prewashing and boiling washing compositions are made more strongly alkaline (pH value=9.5–12, preferably 10–12.5).

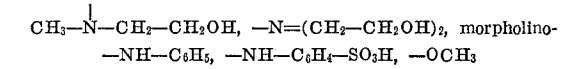
The brighteners which may be used are mostly, if not exclusively, derivatives of diaminostilbenesulfonic acid, diarylpyrazolines and aminocoumarins.

Examples of brighteners from the class of diaminostilbenesulfonic acid derivatives are compounds according to the formula



In the formula R_1 and R_2 signify halogen atoms or alkoxy groups, amino groups or residues of aliphatic, aromatic or heterocyclic, primary or secondary amines, or residues of aminosulfonic acids, while aliphatic residues present in the above groups preferably contain 1 to 4 and especially 2 to 4 carbon atoms, and in the heterocyclic ring systems, five- or six-membered rings are usually concerned. Aniline, anthranilic acid or anilinesulfonic acid residues are preferred as the aromatic amines. Brighteners derived from diaminostilbenesulfonic acid are mostly used as cotton brighteners. The following products derived from the above formula in which R_1 represents the residue —NH—C_6H_5 and R_2 may represent the following residues, are at present on the market:

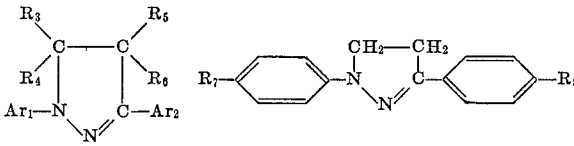
—NH_2, —NH—CH_3, —NH—CH_2—CH_2OH
—NH—CH_2—CH_2—O—CH_3, —NH—CH_2—CH_2—CH_2—O—CH_3



—NH—C_6H_5, —NH—C_6H_4—SO_3H, —OCH_3

Some of these brighteners are to be regarded as transitional types to the cotton brighteners as regards their affinity for the fiber, for example, the brightener in which R_2 equals —NH—C_6H_5. The compound 4,4′-bis-(4-phenyl-vicinal-triazolyl-2)-stilbenedisulfonic acid-2,2′ also belongs to the cotton brighteners of the diaminostilbenesulfonic acid type.

Diarylpyrazolines of Formulas II and III belong to the polyamide brighteners, of which again a few have a certain affinity for cotton fibers:



II III

In Formula II, R_3 and R_5 represent hydrogen atoms, or alkyl or aryl residues possibly substituted by carboxyl, carbonamide or ester groups.

R_4 and R_6 represent hydrogen or short-chain alkyl residues.

Ar_1 and Ar_2 represent aryl residues such as phenyl, diphenyl or naphthyl, which may carry further substituents such as hydroxy, alkoxy, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, carboxylic acid ester, sulfonic acid, sulfonamide and sulfone groups or halogen atoms.

Brighteners of this type found at present on the market are derived from the Formula III, and the residue R_7 may represent the groups Cl, —SO_2—NH_2,

—SO_2—CH=CH_2

and —COO—CH_2—CH_2—O—CH_2, while the residue R_8 in all cases represents a chlorine atom. 9-cyano-anthracene is also on the market as a polyamide brightener.

In addition, aliphatic or aromatic substituted amino coumarins belong to the polyamide brighteners, for example 4-methyl-7-dimethylamino- or 4-methyl-7-diethylamino-coumarin. Further useful polyamide brighteners are the compounds 1-(benzimidazolyl-2′)-2-(N-hydroxy-

ethyl-benzimidazolyl-2')-ethylene and 1-N-ethyl-3-phenyl-7-diethylamino-carbostyril. Suitable brighteners for polyester and polyamide fibers are the compounds 2,5-di-(benzoxazolyl-2')-thiophene and 1,2-di-(5'-methyl-benzoxazolyl-2')-ethylene.

If the brighteners are present together with other constituents of the products according to the invention as aqueous solutions or pastes and are converted into the solid state by spray drying, it is advisable to incorporate at least 0.1% and preferably 0.2% to 1% by weight of the solid products, of organic complex-forming compounds for the stabilization of the brighteners.

The enzymes which may be utilized may be obtained from animals, microorganisms such as bacteria or fungi, and plants, especially from digestive ferments, yeasts and strains of bacteria. They usually represent a complicated mixture composed of various enzymatic active substances. According to their action they are denoted as proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases. The enzymatic substances, particularly protease or amylases, obtained from strains of bacteria or fungi, such as *Bacillus subtilis* and *Streptomyces griseus*, are of special interest. Further useful enzymes are pepsin, pancreatin, trypsin, papain and diastases. The enzyme preparations obtained from *Bacillus subtilis*, however, have the advantage, as compared with the last-named enzymes, in that they are relatively stable with respect to alkali, percompounds and anionic detergents, and even at temperatures between 45° and 70° C. are still not appreciably inactivated.

The enzymes are marketed by the producers usually in the form of aqueous solutions of active substances or with addition of blending agents, as powders. Suitable blending agents are sodium sulfate, sodium chloride, alkali metal ortho-, pyro- or poly-phosphates, especially tripolyphosphates. The still moist enzyme preparations are frequently incorporated with calcined salts, which then, in some cases with agglomeration of the particles present to larger particles, bind the water present together with the enzymatic substance as water of crystallization.

If the enzymatic substances are present as dry products, liquid or paste-like or possibly solid non-ionic preferably surface-active, organic compounds, especially the above-described "Non-ionics," can also be used at room temperature for binding the enzymatic active substance to the respective preparation to be made. For this purpose, a mixture of the components of the combination of surface-active compounds or of the washing agent and the enzymatic substance, for example, is sprayed with these non-ionic products, or the enzymatic substance is dispersed in the said non-ionic substances and this dispersion is united with the other constituents of the product. If the other constituents of the products are solids, the dispersion of the enzymatic substances in the non-ionic component can be sprayed on the other solid constituents.

The enzymes, or combinations of enzymes with variable action, are generally used in quantities such that the finished products have protease activities of 50 to 5000, preferably 100 to 2500 LVE/g. and/or amylase activities of 20 to 5000, preferably 50 to 2000 SKBE/g. and/or lipase activities of 2 to 1000, preferably 5 to 500 IE/g.

The above data on the content of enzymes and activities of the preparations according to the invention are obtained from the activities of those enzyme preparations which are available at the present time, from the standpoint of economy, for use in the washing agent field. From the technical-chemical standpoint the enzyme activities of the preparations according to the invention can be increased, if feasible, so that the activities as regards proteases and amylases can be raised to 5 times, and as regards lipases, to 10 times the above given maximum values. Therefore, should, in the future, enzyme preparations with higher enzyme contents be supplied, which also appear suitable economically for use in washing agents, one has the choice either of keeping the enzyme activity of the preparation to the above given height by use of smaller amounts of enzymes or of increasing the enzyme activity with use of the same amount of enzymes.

The following references in the literature are referred to relative to the determination of the enzyme activities:

Determination of the activity of proteases by Lohlein-Volhard: A. Kunzel: "Gerbereichemisches Taschenbuch," 6th ed., Dresden and Leipzig, 1955.

Determination of the activity of amylases: J. Wohlmuth: "Biochemische Zeitschrift," 1908, vol. 9, pages 1–9; and R. M. Sandsteadt, E. Kneen and M. J. Blish: "Cereal Chemistry," 1949, vol. 16, pages 712–723.

Determination of the activity of lipases: R. Willstatter, E. Waldschmidt-Leitz and Fr. Memmen: "Hoppe-Seyler's Zeitschrift fur physiologische Chemie," 1923, vol. 125, pages 110–117; and

R. Boissonas: "Helvetia Chimica Acta," 1948, vol. 31, pages 1571–1576.

The following specific embodiments are illustrative of the practice of the invention without being limitative in any respect.

EXAMPLES

The following examples describe compositions of a few preparations according to the invention. The salt-like components contained therein, salt-like surface-active compounds, other organic salts and inorganic salts, are present as sodium salts, provided it is not expressly given otherwise, although other alkali metal and ammonium salts may be utilized. The notations and abbreviations used signify:

"ABS" is the salt of an alkylbenzenesulfonic acid with 10 to 15, preferably 11 to 13, carbon atoms in the alkyl chain, obtained by condensing straight chain olefins with benzene and sulfonating the alkylbenzene so obtained.

"Olefinsulfonate" is a sulfonate obtained from straight chain olefins (12 to 16 carbon atoms) with terminal or non-terminal double bonds by sulfonation with SO_3 and hydrolysis of the sulfonation product with an alkali liquor. The said sulfonate consists substantially of alkene sulfonate and hydroxyalkane sulfonate, but also contains small quantities of alkaline disulfonates. For olefinsulfonate-containing preparation was prepared using two different types of olefinsulfonate; one was from a mixture of straight-chain terminal olefins, and the other was prepared from a mixture of non-terminal olefins.

"Alkane sulfonate" is a sulfonate obtained from paraffins with 12 to 16 carbon atoms by the sulfoxidation method.

"Fatty acid ester sulfonates" (FA ester sulfonate) is a sulfonate obtained from the methyl ester of a hardened tallow fatty acid by sulfonating with SO_3.

"Oleyl alcohol ether sulfate" (OA-EO-sulfate) or "Tallow alcohol ether sulfate" (TA-EO-sulfate) or "Coconut alcohol ether sulfate" (CA-EO-sulafte) are the sulfated products of addition of 2 mols of ethylene oxide (EO) to 1 mol of oleyl alcohol or of 3 mols of ethylene oxide to 1 mol of tallow fatty alcohol or of 2 mols of ethylene oxide to 1 mol of coconut fatty alcohol.

"Tallow alcohol sulfate" (TA-sulfate) or "Coconut alcohol sulfate" (CA-sulfate) are the salts of the sulfated fatty alcohols prepared by reduction of tallow fatty acid or coconut fatty acid.

"Oleyl alcohol+5EO" (OA+5EO) or "Oleyl alcohol+10 EO" (OA+10 EO) are the products of addition of five or ten mols of ethylene oxide to one mol of a commercial oleyl alcohol.

"Coconut alcohol+20EO" (CA+20EO) is the product of addition of 20 mols of ethylene oxide to 1 mol of a fatty alcohol prepared from coconut fatty acid.

"Coconut alcohol+9EO+12PO" (CA+9EO+12PO) is the product of addition of 9 mols of ethylene oxide to 1 mol of a fatty alcohol prepared from coconut fatty acid, reacted with 12 mols of propylene oxide.

"Tallow alcohol+14EO" (TA+14EO) is the product of addition of 14 mols of ethylene oxide to 1 mol of a fatty alcohol prepared from tallow fatty acid.

"Nonylphenol+9.5EO" (NP+9.5EO) is the product of addition of 9.5 mols of ethylene oxide to 1 mol of nonylphenol.

"FA-amide+8EO" is the product of addition of 8 mols of ethylene oxide to 1 mol of a hardened tallow fatty acid amide.

"HEDP" is the salt of hydroxyethane-diphosphonic acid.

"EDTA" is the salt of ethylenediaminetetraacetic acid.

"NTA" is the salt of nitrilotriacetic acid.

"Perborate" is a product of the approximate composition $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$ containing about 10% of active oxygen.

"CMC" is the salt of carboxymethyl cellulose.

The compositions of the fatty acid mixtures from which the various soaps contained in the combinations of surface-active compounds or washing agents were produced, may be taken from the following Table I:

TABLE I.—COMPOSITION OF THE FATTY ACID MIXTURES CORRESPONDING TO THE SOAPS

Number of carbon atoms in the fatty acid	Weight percent of fatty acid component in the soap					
	1,018	1,218	1,222	1,222μ	1,622	1,822
C_{10}	1					
C_{12}	6	20	18	14		
C_{14}	5	12	8	6		
C_{16}	28	20	17	13	8	
C_{18}	60	48	32	60	32	9
C_{20}			4	3	12	14
C_{22}			21	4	48	77
Iodine value of the fatty acid mixture	7.5	15	12	76	4	3

As a foam inhibitor a mixture of approximately 45% of a di-(alkylamino)-monochlorothriazine and approximately 55% of an N-N'-N''-trialkyl melamine was used. In all these triazine derivatives the alkyl residues were present as a mixture of homologs with 8 to 18 carbon atoms. The monochloro triazine derivative or trialkylmelamine could also be used with similar success. Inasfar as the products described contained synthetic sulfates or sulfonates together with a soap, the other non-surfactant foam inhibitors mentioned in the description such as, for example, paraffin oil or paraffin could be used. In the preparation of the products, the foam inhibitor used dissolved in a suitable organic solvent or in melted condition, was sprayed through a nozzle onto the moving powdered preparation. The examples T1 to T21 describe surfactant combinations, which are supplied as special products especially for industrial laundries or the textile industry. The surfactant combinations described in the examples T1 to T21 mostly come onto the market in mixtures with sodium sulfate or with other traditional laundry additives, the surfactant combinations amounting to 90% to 50% by weight and the other constituents 10% to 50% by weight.

In all the examples the amounts indicated for the surfactants relate to pure active substances. In the textile fabric softeners, small quantities of by-products originating from the manufacture are also present.

In the following tables the sign "+" in the line

"Na_2SO_4"

means that small quantities of sodium sulfate as impurity are present, introduced by the anionic surfactants used. The "remainder" consists substantially of water, also dyes, and perfumes. Where the Na_2SO_4 quantity is given as "+" the remainder also comprises the existing sodium sulfate.

The examples described in the following tables up to W29 contain as textile fabric softener the fatty acid condensation product of hardened tallow and hydroxyethyl ethylenediamine corresponding to a molar ratio fatty acid residues:amine equals 3:1, prepared in accordance with the following specification:

900 gm. (about 1 mol) of hardened beef tallow were heated to 95° C. and 114 (about 1.1 mol) gm. of N-hydroxyethyl ethylenediamine were stirred in over a period of 35 minutes. Subsequently, the melt was agitated for another 4 hours at 100° C. Thereafter, the melt was cooled to 90° C. and 42.6 gm. of a 70% aqueous glycolic acid solution was added. After another 30 minutes of agitation at 90° C., the mixture was allowed to solidify by cooling in a thin layer. Yield: 1050 gm.

The product prepared in this way had the following composition:

	Percent
Tri-tallow fatty acid-diamindo-ester	[1] 5.6
Di-tallow fatty acid diamide	[1] 36.8
Tallow fatty acid-monoamide	[1] 20.5
Tallow fatty acid-triglyceride	13.6
Tallow fatty acid-diglyceride	8.2
Tallow fatty acid-monoglyceride	5.1
Glycolic acid	4.2
Free glycerine and free fatty acid	4.7

[1] Derivatives of N-hydroxyethyl ethylene diamine or fatty acid condensation product.

The detergent composition in accordance with the invention used in the examples with a content of textile fabric softeners are prepared by spraying the textile fabric softeners, in a manner similar to that of the above-mentioned foam inhibitors, in a melted condition through a nozzle in the form of very fine particles onto the detergent particles.

The examples W30 to W35 contain as textile fabric softener component the fatty acid condensation product of hardened tallow and hydroxyethyl ethylenediamine corresponding to a molar ratio fatty acid residue to amine of 3:1 (abbreviated FKP), and as quaternary ammonium compound dialkyl-dimethyl ammonium chloride, "dialkyl" meaning alkyl residues obtainable from hardened tallow acid (abbreviated QAV).

Component of surfactant combination	Percent by weight component in the surfactant combination according to Example—						
	T1	T2	T3	T4	T5	T6	T7
ABS	42	32		37	44	33	30
Alkane sulfonate			42				
Olefinsulfonate		10					
TA-sulfate						11	
OA plus 10 EO	14	14	14	17	14	14	
FA-amide plus 8 EO							13
Soap 1222μ							20
Soap 1622					4	4	
Soap 1822	6	6	6				
Fabric softener	38	38	38	43	38	38	32
Foam inhibitor				3			5

Component of surfactant combination	Percent by weight component in the surfactant combination according to Example—					
	T8	T9	T10	T11	T12	T13
ABS		49				34
Olefinsulfonate				32	32	
FA-ester sulfonate			35			
CA sulfate			14			8
TA sulfate						3
OA plus 10 EO		16	16	16	16	18
CA plus 20 EO	48					
CA plus 9 EO plus 12 PO	25					
Soap 1218				15		
Soap 1222					14	
Fabric softener	27	33	33	34	34	34
Foam inhibitor		2	2	3	4	3

Component of surfactant combination	Percent by weight component in the surfactant combination according to Example—							
	T14	T15	T16	T17	T18	T19	T20	T21
ABS	34	26						41
Alkane sulfonate				40				
Olefinsulfonate					20			
FA-ester sulfonate			18					
OA sulfate								
CA sulfate	9	7	11	9		10	5	9
TA sulfate		2			10		5	
OA-EO-sulfate						20		
CA-EO-sulfate		8						17
TA-EO-sulfate							25	
OA plus 5 EO			9			24	14	
OA plus 10 EO	11			14	14			
Soap 1018							14	
Soap 1218	9							
Soap 1222		22	28		27	23		
Fabric softener	34	35	34	35	29	23	34	31
Foam inhibitor	3			2			3	2

Component of the detergent	Percent by weight of the component in the detergent according to Example—						
	W1	W2	W3	W4	W5	W6	W7
Surfactant combination [1]	19.0	20.8	17.5	19.5	27.5	23.8	21.5
Na_3PO_4						1.8	2.3
$Na_4P_2O_7$				12.0		6.5	20.2
$Na_5P_3O_{10}$	45.0	32.8	19.5		32.0	38.0	23.8
NTA			18.0	19.0			
EDTA							1.3
HEDP			6.6	14.0	28.0		
$Na_2O.3.3\ SiO_2$	4.5	2.9	4.0	4.5	7.5	5.5	5.5
Perborate	16.0	31.8	21.0	16.0		17.0	17.0
$MgSiO_3$	1.0	2.5	1.6	1.0	1.6	2.0	2.0
CMC	1.5	0.8	1.3	1.5	1.3	1.2	1.2
Water	(2)	(2)	(2)	(2)	(2)	(2)	(2)

[1] As surfactant combination any combination according to Examples T1–T12 may be used.
[2] Remainder.

Component of the detergent	Percent by weight of the components in the detergent according to Example W... with surfactant combination according to Example T...				
	W8, T13	W9, T14	W10, T15	W11, T16	W12, T17
Surfactant combination	18.2	23.2	19.9	23.2	19.5
Na_2SO_4	+	+	+	+	+
Na_2CO_3				8.0	
$Na_5P_3O_{10}$	30.0	35.0	28.0	24.0	38.0
NTA			15.0	5.0	
EDTA	0.2	0.3		0.25	0.5
HEDP			0.22		
$Na_2O.3.3\ Si_4O_2$	6.0	4.5	5.0	4.0	3.8
Perborate	32.0	27.0	24.0	25.0	23.5
$MgSiO_3$	2.5		2.0		
CMC	2.0	1.8	1.3	1.9	1.2
Brightening agent	0.3	0.8	0.8	0.5	0.9
Water	(1)	(1)	(1)	(1)	(1)

[1] Remainder.

Component of the detergent	Percent by weight of the components in the detergent according to Example W... with surfactant combination according to Example T...				
	W13, T18	W14, T19	W15, T20	W16, T21	W17, T1–20
Surfactant combination	26.2	21.6	21.1	30.0	11.3
Na_2SO_4		5.0	18.0	10.0	22.0
$Na_5P_3O_{10}$	21.0	33.0	35.0	48.0	46.0
NTA	8.0		10.0		
EDTA	0.4				0.5
HEDP					
$Na_2O.3.3\ SiO_2$	4.2	3.5	3.7	4.5	4.0
Perborate	22.0	22.0			
$MgSiO_3$	3.0				
CMC	1.4	1.5	1.3	1.7	1.6
Brightening agent	1.2				0.3
Water	(1)	(1)	(1)	(1)	(1)

[1] Remainder.

No.	Detergent, single components (100%)	Percent by weight component of detergent according to Example—					
		W18	W19	W20	W21	W22	W23
1	ABS	7.0	7.0	10.0	10.0		5.0
2	Alkane sulfonate					7.0	
3	FA-ester sulfonate						2.0
4	Olefinsulfonate						
5	OA-EO-sulfate					2.5	
6	TA-EO-sulfate						2.5
7	CA-EO-sulfate	2.5	2.5	3.0	5.0		
8	TA plus 14 EO					0.5	
9	NP plus 9.5 EO						
10	OA plus 10 EO						
11	OA plus 5 EO						
12	CA-sulfate	2.0	2.0			2.0	2.–
13	Soap 1622	0.3			3.0		
14	Soap 1822					0.5	
15	Soap 1218						
16	Textile fabric softener	5.0	5.0	5.0	5.0	5.0	5.0
17	$Na_5P_3O_{10}$	48.0	48.0	48.0	48.0	50.0	40.0
18	$Na_2O.3.35\ SiO_2$	4.5	4.5	4.5	4.5	5.0	4.0
19	CMC	1.5	1.5	1.5	1.5	1.7	1.3
20	Perfume	0.1	0.0	0.1	0.1	0.1	0.15
21	Sodium sulfate and water			Remainder			

No.	Detergent, single components (100%)	Percent by weight component of detergent according to Example—					
		W24	W25	W26	W27	W28	W29
1	ABS			5.0		9.5	10.0
2	Alkane sulfonate		10.0				
3	FA-ester sulfonate			5.0			
4	Olefinsulfonate	8.0			10.0	0	
5	OA-EO-sulfate			5.0			
6	TA-EO-sulfate				5.0		
7	CA-EO-sulfate	2.5	3.0			4.5	5.0
8	TA plus 14 EO						
9	NP plus 9.5 EO	0.5					0.5
10	OA plus 10 EO			0.5			
11	OA plus 5 EO					0.5	
12	CA-sulfate	2.0					
13	Soap 1622			3.0			3.0
14	Soap 1822				4.0		
15	Soap 1218					5.5	
16	Fabric softener	5.0	5.0	5.0	5.0	5.0	5.0
17	$Na_5P_3O_{10}$	40.0	35.0	30.0	38.0	43.0	48.0
18	$Na_2O.3.35\ SiO_2$	4.0	3.5	3.0	3.8	4.3	4.5
19	CMC	1.3	1.1	0.9	2.0	2.3	1.5
20	Perfume	0.15	0.2	0.25	0.12	0.22	0.1
21	Sodium sulfate and water			Remainder			

Detergent, single components (100%)	Percent by weight component of detergent according to Example—					
	W30	W31	W32	W33	W34	W35
ABS	6.6		8.0	5.0		
Alkane sulfonate					8.0	
FA-ester sulfonate				4.0		7.0
Olefinsulfonate		7.5				
CA-sulfate	1.5		1.5		1.0	
TA-sulfate		1.5		2.0	1.0	2.0
OA-EO-sulfate	1.5		2.0		1.5	1.5
TA-EO-sulfate				3.5		
CA-EO-sulfate	2.0	2.5				
TA plus 14 EO			1.0			
NP plus 9.5 EO				1.5		
OA plus 10 EO						2.5
OA plus 5 EO					1.5	
Soap 1622	0.5					
Soap 1822					1.5	
Soap 1222				3.5		2.5
Fabric softener component:						
FKP	5.0	4.0	5.0	3.0	5.0	5.0
QAV	5.0	1.0	3.0	5.0	2.5	3.0
$Na_5P_3O_{10}$	45.5	48.0	45.0	48.0	52.0	45.0
$Na_2O.3.35\ SiO_2$	4.5	4.5	4.5	4.5	5.0	4.0
CMC	1.5	1.5	1.5	1.5	2.0	1.5
Remainder						

Instead of the fatty acid condensation products used in the examples, it is also possible, for example, to use the condensation product of hardened tallow and hydroxyethylenediamine (and reacted with glycolic acid) of the following composition:

	Molar ratio, fatty acid:amine	
	1.5:1	2:1
Tri-tallow fatty acid-diamido-ester, percent by weight	[1] 2.3	5.1
Di-tallow fatty acid-diamide, percent by weight	[1] 44.6	50.7
Tallow fatty acid-monoamide, percent by weight	[1] 25.9	11.8
Tallow fatty acid-triglyceride, percent by weight	0.5	2.6
Tallow fatty acid mono and diglyceride (fatty acid partial glycerides), percent by weight	9.2	17.5
Free tallow acid, amine, glycerol, glycolic acid, water	Remainder	

[1] Derivatives of N-hydroxyethyl-ethylenediamine or fatty acid condensation product.

Brighteners for cotton, polyamides or polyesters or combinations thereof are used, depending upon the purpose for which the washing composition is to be used.

The washing compositions described in Examples W1 to W35 were also prepared with addition of enzymes. The enzymes were commercial products which had been adjusted by the manufacturer to the following activities by addition of 7% to 15% by weight of sodium sulfate:

A protease with 125,000 LVE/g.
An amylase with 75,000 SKBE/g.
A lipase with 10,000 IE/g.

In the following list the enzyme activity, referred to 1 g. of the finished washing composition, is given in addition to the quantity of enzyme:

(I) A washing composition according to one of the Examples W1 to W35 contains:

0.3 to 1.5% by weight of protease
(375–1875 LVE/g.)

(II) A washing composition according to one of the Examples W1 to W35 contains: 1.2% by weight of lipase (120 IE/g.)

(III) A washing composition according to one of the Examples W1 to W35 contains:

0.4% by weight of protease (500 LVE/g.)
1.0% by weight of amylase (750 SKBE/g.)

(IV) A washing composition according to one of the Examples W1 to W35 contains: 2.0% by weight of amylase (1500 SKBE/g.)

(V) A washing composition according to one of the Examples W1 to W35 contains:

0.2% by weight of protease (250 LVE/g.)
0.5% by weight of amylase (375 SKBE/g.)
0.5% by weight of lipase (50 IE/g.)

(IV) A washing composition according to one of the Examples W1 to W35 contains:

1.0% by weight of protease (1250 LVE/g.)
0.3% by weight of amylase (225 SKBE/g.)
0.4% by weight of lipase (40 IE/g.)

The textiles washed with the washing compositions according to the invention at temperatures of 20° to 70° C., preferably at 30° to 60° C., especially fine laundry articles and easy-care textiles, for example of cotton, polyester, polyacrylonitrile and polyamide, manufactured in particular into woven and knitted fabrics, show, after drying, a remarkably pleasant and soft handle and, in the case of velvet textiles, a uniform pile. The treatment with the detergent composition in accordance with the invention imparts an antistatic effect to the textiles.

The desired reviving effect is achieved also if, as textile softeners, fatty acid condensation products of different composition are used, such as for example products containing fatty acid partial glycerides, corresponding to a different molar ratio lying in the range from 1.3 to 4 mols of fatty acid residues per mol of amine, or products which have been manufactured not from tallow but from other triglycerides such as coconut fat, hardened palm or rape oils or hardened fish oils, or of a mixture of such triglycerides, preferably a mixture of 20% coconut fat, 20% hardened rape oil and 60% hardened tallow.

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art or described herein may be employed without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. Detergent compositions containing textile softeners consisting essentially of:

(1) from 5% to 100% by weight of a mixture of surface-active agents consisting essentially of:
  (a) from 20% to 90% by weight of a mixture of (i) anionic surface-active compounds selected from the group consisting of surface-active sulfonates, surface-active sulfates and soaps, and (ii) nonionic surface active compounds, wherein at least 50% of said mixture is said anionic surface-active compounds, and
  (b) from 80% to 10% by weight of a textile softener composition consisting essentially of:
    (i) from 100% to 20% by weight of a fatty acid-hydroxyalkylpolyamine condensation product of one mol of a triglyceride of higher fatty acids having from 8 to 24 carbon atoms with at least 50% of said higher fatty acids having from 16 to 24 carbon atoms, with one mol of hydroxyethylethylenediamine, said condensation product containing from 5% to 40% by weight of fatty acid partial glycerides, and
    (ii) from 0 to 80% by weight of quaternary ammonium compounds containing two alkyls having 14 to 26 carbon atoms and at least one quaternary nitrogen atom in the molecule, and
(2) from 95% to 0 by weight of
  (a) inorganic builders, and (b) organic builders.

2. The detergent composition of claim 1 wherein said component (1) is present in an amount of from 8% to 40% by weight and said component (2) is present in an amount of from 92% to 60% by weight.

3. The detergent composition of claim 1 wherein said component (b) (i) is present in an amount of 100% by weight of component (b).

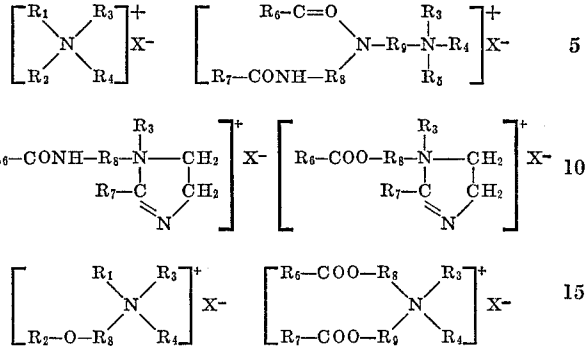
4. The detergent composition of claim 1 wherein, in said component (b) (i), said condensation product contains from 5% to 15% by weight of diamidoesters, from 30% to 45% by weight of diamides, from 20% to 30% by weight of monoamides and from 15% to 30% by weight of said fatty acid partial glycerides.

5. The detergent composition of claim 1 wherein at least part of said mixture of customary surface-active compounds of component (1) (a) is soap and the fatty acids present in said soap consist of at least 50% of saturated fatty acids with from 16 to 30 carbon atoms, wherein foaming of said combination of surface-active compounds in water is reduced at higher temperatures.

6. The detergent composition of claim 5, wherein at least 5% of said fatty acids in said soap have from 20 to 30 carbon atoms.

7. Detergent compositions containing textile softeners consisting essentially of:
(1) from 5% to 80% by weight of a mixture of surface-active compounds utilizable in neutral to alkaline washing baths consisting of:
  (a) from 75% to 35% of a mixture of (i) anionic surface active compounds selected from the group consisting of surface-active sulfonates, surface-active sulfates and soaps, and (ii) nonionic surface-active compounds, wherein at least 50% of said mixture is said anionic surface-active compounds, and
  (b) from 25% to 65% by weight of a textile softener composition consisting of:
    (i) from 100% to 20% of a fatty acid-hydroxyalkylpolyamine condensation product of one mol of hydroxyethylethylenediamine, with 1 mol of triglycerides of higher fatty acids having from 16 to 22 carbon atoms in each fatty acid moiety, said condensation product containing from 10% to 30% by weight of fatty acid partial glycerides, and
    (ii) from 0 to 80% by weight of quaternary ammonium compounds selected from the

group consisting of compounds having the formula

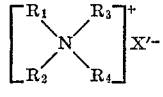


wherein R_1 and R_2 are alkyl having 16 to 20 carbon atoms, R_3, R_4 and R_5 are lower alkyl and alkylol having 1 to 4 carbon atoms, R_6 and R_7 are alkyl with 15 to 19 carbon atoms and R_8 and R_9 are alkylene with 2 to 4 carbon atoms or hydroxyalkylene with 3 to 4 carbon atoms, and X represents the anion of an acid, said quaternary compound being water-dispersible, and

(2) from 20% to 95% by weight of inorganic builders, and organic builders.

8. The composition of claim **7** wherein, in component (b), component (i) is present in an amount of from 80% to 20% by weight and component (ii) is present in an amount of from 20% to 80% by weight.

9. The composition of claim **8** wherein said component (ii) is a quaternary ammonium compound of the formula



wherein R_1 and R_2 are alkyl having 16 to 20 carbon atoms, R_3 and R_4 are lower alkyl and alkylol having 1 to 4 carbon atoms, and X' represents the anion of an acid selected from the group consisting of inorganic acids and non-capillary active organic acids with 2 to 7 carbon atoms.

10. The composition of claim **9** wherein R_1 and R_2 are alkyl derived from hardened tallow fatty acids and R_3 and R_4 are methyl.

11. The composition of claim **7** having a further content of enzymes selected from the group consisting of proteases, amylases, lipases and mixtures thereof wherein the enzymatic activity is in the range of 50 to 5000 LVE per gram of total washing agent in the case of proteases, of 20 to 5000 SKBE per gram of total washing agent in the case of amylases and of 2 to 1000 IE per gram of total washing agent in the case of lipases.

12. Detergent compositions containing textile softeners consisting essentially of

(A) from 8% to 40% by weight of a mixture of surface-active agents consisting essentially of:

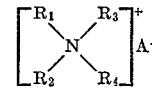
(1) 25% to 65% by weight of surface-active compounds selected from the group consisting of sulfonates and sulfates,

(2) 5% to 40% by weight of non-ionic surface-active compounds,

(3) 10% to 50% by weight of soap,

(4) 25% to 65% by weight of a fatty acid hydroxyalkylpolyamine condensation product of one mol of hydroxyethylethylenediamine, with 1 mol of triglyceride of higher fatty acids having from 16 to 24 carbon atoms, said condensation product containing from 10% to 30% by weight of fatty acid partial glycerides,

(5) 0 to 52% by weight of a textile softener of the formula



wherein R_1 and R_2 are alkyl having 14 to 26 carbon atoms, R_3 and R_4 are alkyl having from 1 to 4 carbon atoms and A is the anion of an acid, said softener being water-dispersible,

(6) 0.5% to 3% by weight of foam stabilizers, and

(7) 0.5 to 5% by weight of non-surface-active foam inhibitors effective at temperatures of 60° C. selected from the group consisting of higher alkylated aminotriazines, lower alkoxylated aminotriazines, aliphatic C_{18} to C_{40} ketones and aliphatic carboxylic acid esters having at least 18 carbon atoms in at least one of the acid and alcohol moieties;

(B) 92% to 60% by weight of inorganic builders, at least part of the builders being alkaline reacting, said builders weighing from 1 to 5 times that of component (A); and

(C) 3% to 30% by weight of bleaches and their stabilizers and activators.

13. The composition of claim **12** wherein component (A)(5) is absent.

14. The composition of claim **12** wherein component (A)(4) and component (A)(5) together comprise from 80% to 20% by weight of component (A)(4) and from 20% to 80% by weight of component (A)(5).

15. Prewashing agents containing a compatible textile softener consisting of:

(A) from 5% to 8% by weight of a combination of surface-active compounds consisting of:

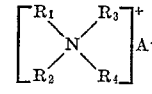
(1) 25% to 65% by weight of surface-active compounds selected from the group consisting of sulfonates and sulfates,

(2) 5% to 40% by weight of non-ionic surface-active compounds,

(3) 10% to 50% by weight of soap,

(4) 25% to 65% by weight of a textile softener fatty acid-hydroxyalkylpolyamine condensation product of one mol of hydroxyethylethylenediamine, with 1 mol of a triglyceride of higher fatty acids having from 16 to 24 carbon atoms, said condensation product containing from 10% to 30% by weight of fatty acid partial glycerides,

(5) 0 to 52% by weight of a textile softener of the formula



wherein R_1 and R_2 are alkyl having 14 to 26 carbon atoms, R_3 and R_4 are alkyl having from 1 to 4 carbon atoms and A is the anion of an acid, said softener being water-dispersible,

(6) 0.5% to 3% by weight of foam stabilizers, and

(7) 0.5 to 5% by weight of non-surface-active foam inhibitors effective at temperatures of 60° C. selected from the group consisting of higher alkylated aminotriazines, lower alkoxylated aminotriazines, aliphatic C_{18} to C_{20} ketones and aliphatic carboxylic acid esters having at least 18 carbon atoms in at least one of the acid and alcohol moieties; and

(B) from 95% to 92% of inorganic builders.

16. The prewashing agents of claim **15** having a further content of enzymes selected from the group consisting of proteases, amylases, lipases and mixtures thereof wherein the enzymatic activity is in the range of 50 to 5000 LVE

per gram of total washing agent in the case of proteases, of 20 to 5000 SKBE per gram of total washing agent in the case of amylases and of 2 to 1000 IE per gram of total washing agent in the case of lipases.

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