

[54] **DETERGENT COMPOSITIONS
CONTAINING A TEXTILE SOFTENER**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 745,952, July 18, 1968, abandoned.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**.....**C11d 1/04**, C11d 1/83, D06m 13/20

[58] **Field of Search**.....260/534 R, 410, 413, 417, 419; 252/8.6, 8.75, 8.8, 108, 109, 110, 132, 137, 367, 368; 117/139.5 F

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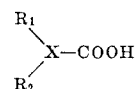
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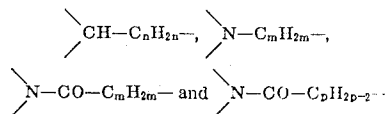
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[57] **ABSTRACT**

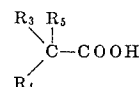
This invention relates to a combination of surface-active compounds utilizable in neutral to alkaline textile washing baths which comprises (a) from 20 to 90 percent by weight of customary surface-active compounds utilizable in neutral to alkaline textile washing baths selected from the group consisting 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 selected from the group consisting of (1) compounds of the formula



wherein R_1 and R_2 are alkyl having from six to 18 carbon atoms and X is a trivalent link selected from the group consisting of

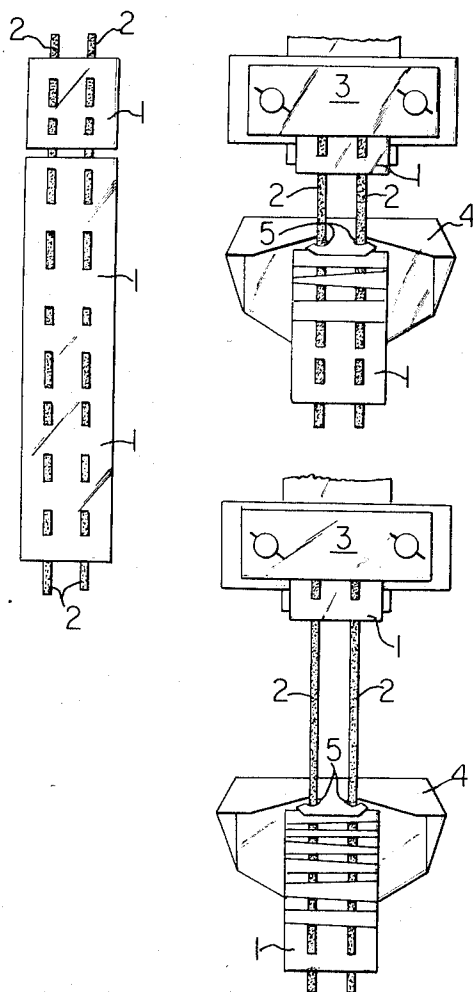


where n represents an integer from 0 to 2, m represents an integer from 1 to 2 and p represents an integer from 2 to 3, compounds of the formula



wherein R_3 and R_4 are members selected from the group consisting of alkyl having from one to 23 carbon atoms and cycloalkylalkyl having from seven to 23 carbon atoms and R_5 is a member selected from the group consisting of hydrogen, alkyl having from one to 23 carbon atoms and cycloalkylalkyl having from seven to 23 carbon atoms, with the proviso that the total number of carbon atoms in R_1 , R_2 and R_3 is from six to 24 carbon atoms and (2) water soluble salts thereof. Textile washing agents and textile auxiliary washing agents containing the above combinations of surface-active compounds, with or without a content of enzymes are also part of the invention.

18 Claims, 3 Drawing Figures



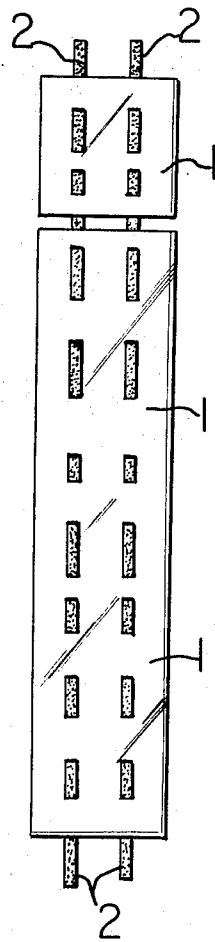


FIG. 1

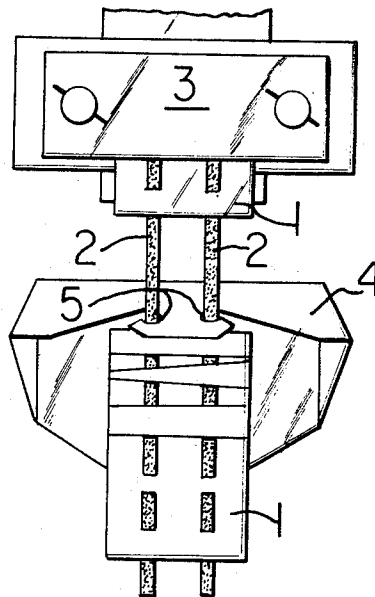


FIG. 2

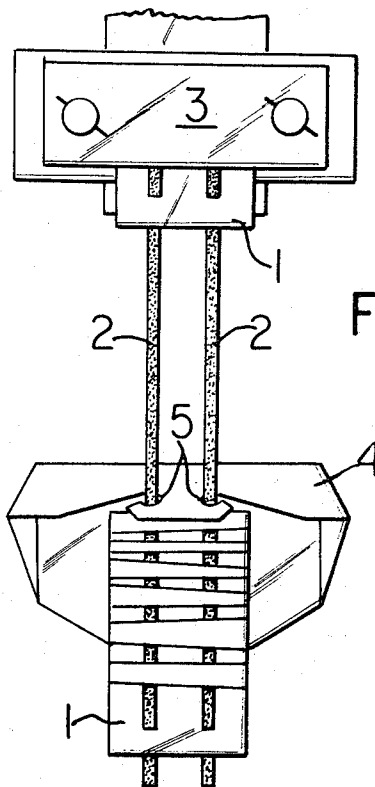


FIG. 3

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or its water-soluble salts, wherein R_3 and R_4 represent aliphatic and/or cycloaliphatic residues, such as alkyl and cycloalkylalkyl, preferably alkyl residues with one to 23, preferably one to 21 and in particular one to 19 carbon atoms and R_5 represents hydrogen or R_3 . The total number of carbon atoms in R_1 , R_2 and R_3 is from six to 24 carbon atoms, preferably from seven to 19 carbon atoms.

The invention further relates to washing agents and washing agent adjuvants containing such combinations of surface-active compounds with a content of other customary washing agent constituents, in which case the said combinations of surface-active compounds may constitute 5 to 80 percent, preferably 15 to 40 percent, by weight and the usual washing agent constituents may constitute 20 to 95 percent, preferably 85 to 60 percent by weight. Examples of the other customary washing agent constituents are neutral to alkaline reacting builders, complex-forming compounds, bleaching components, foam stabilizers, foam inhibitors and dirt carriers. Sufficient alkali is preferably present in the basic washing composition substance for a 1 percent solution of the finished washing composition or washing assistant to have pH value in the region of 8 to 12, preferably of 9 to 11.

If the products according to the invention contain more than 45 percent by weight of the above combination of surface-active compounds, they are mostly not used as domestic washing agents, but are chiefly used in industrial laundries and in the textile industry, where they are seldom used alone but more often in combination with the usual additives. In such products, by-products from the preparation of the surface-active compounds or the textile softeners may be present as well as the usual additives.

Finally, the invention relates to combinations of surface-active compounds and washing agents or washing agent adjuvants containing these, which also contain enzymes.

Suitable enzymes are chiefly proteases, amylases and lipases, which may be incorporated in the products according to the invention either alone or in conjunction with one another. Where finished washing agents or washing agent adjuvants are concerned, their protease content may correspond to activities of 50 to 5,000, preferably 100 to 2,500 LVE; their amylase content, to activities of 20 to 5,000, preferably 50 to 2,000 SKBE; and their lipase content, to activities of 2 to 1,000, preferably 5 to 500 i.e. per gram of said washing agent or washing agent adjuvant.

When the preparations according to the invention relate to combinations of surface-active compounds which are frequently used in combination with the usual builders and additives in industrial laundries, the enzyme content of these preparations can be so high that the product composed of the respective combination of surface-active compounds used and the other constituents of washing agent and washing agent adjuvant simultaneously used has the above given enzyme content. Since the combination of surface-active compounds may constitute 5 to 80 percent, preferably 15 to 40 percent, of a finished washing agent or washing agent adjuvant, enzyme activities are calculated for the combinations of surface-active compounds which correspond to 62.5 to 100,000 LVE in the case of proteases, 25 to 100,000 SKBE in the case of amylases and 2.5 to 20,000 IE in the case of lipases, per gram of the combinations of surface-active compounds. Of course, combinations of surface-active compounds with such high enzyme activities as are present in the upper limits, can only be prepared when very active enzyme preparations are available. Therefore, one is usually restricted to maximum values for activity of 50,000 LVE, 50,000 SKBE and 10,000 IE per gram of combinations of surface-active compounds. The enzyme activities are preferably in the range of 250 to 15,000 LVE, 125 to 15,000 SKBE, and 12.5 to 3,500 IE per gram of combinations of surface-active compounds.

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. Wohlgemuth: "Biochemische Zeitschrift," 1908, Vol. 9, pages 1-9; and

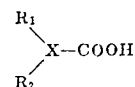
R. M. Sandsteadt, E. Kneen and M. J. Blish: "Cereal Chemistry," 1939, Vol. 16, pages 712-723.

Determination of the activity of lipases:

R. Willstätter, E. Waldschmidt-Leitz and Fr. Memmen: "Hoppe-Seyler's Zeitschrift für physiologische Chemie," 1923, Vol. 125, pages 110-117; and

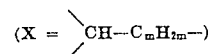
R. Boissonas: "Helvetica Chimica Acta," 1948, Vol. 31, pages 1571-1576.

The textile softeners of the formula



wherein R_1 , R_2 and X have the above values are readily available materials.

The nitrogen-free branched-chain carboxylic acids

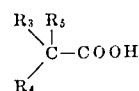


obtainable by known processes, for example, by malonic ester synthesis or by catalytic addition of olefins to carboxylic acids.

The Guerbet synthesis offers a further possible preparation. By this process, aliphatic alcohols, especially those with six or more carbon atoms, are heated in the presence of finely divided alkali metal hydroxide, then a condensation takes place with formation of a branched-chain alcohol, water being split off between the hydroxyl group of one alcohol molecule and a hydrogen atom on carbon atom 2 of a second alcohol molecule. This branched-chain alcohol can then be oxidized or dehydrogenated to give the corresponding carboxylic acid.

Similarly constructed aminocarboxylic acids or their salts can be prepared from the corresponding dialkylamines, for example, by reaction with methyl acrylate or chloroacetic acid esters and saponification of the product of addition, or by addition of chloroacetic acid or its salts. The compounds with carbonamide groups are obtained in a similar way from the corresponding dialkylamines by reaction with dicarboxylic acid anhydrides or by reaction with half ester chlorides of dicarboxylic acids and saponification of the ester group.

The textile softeners of the formula



wherein R_3 , R_4 and R_5 have the above values are likewise readily available materials.

Such carboxylic acids are commercially available in a simple way by addition of carbon monoxide and water to olefins by the Koch process (see H. Koch: "Brennstoff-chemie" (Fuel chemistry), 1955, vol. 26, pages 321-328). There are a number of variants of this synthesis: reference may be made to the publications, R.F. Goldstein and A. W. Waddams: "The Petroleum Chemicals Industry," London 1967, pages 207-209 and J. Falbe: "Syntheses with carbon monoxide," Berlin and Heidelberg, 1967, pages 120-128.

The synthesis does not consist only of an addition of carbon monoxide and water to the starting olefins; isomerizations also take place, so that the reaction products obtained represent a mixture of a variety of isomers, in which the residues R_3 to R_5 may be approximately the same with respect to their degree of branching and the number of carbon atoms contained therein, but may also be very different from one another. Such isomeric mixtures are obtained in particular from mixtures of aliphatic olefins with terminal or non-terminal double bonds, which differ from one another with regard to the carbon number and/or the position of the double bond in the molecule. In a similar way, cycloaliphatic olefins or cycloaliphatic-aliphatic olefins or mixtures thereof with purely aliphatic olefins can be converted into carboxylic acids of the above-indicated structure.

Among suitable carboxylic acids under the above formula are those sold under the trademark "Versatic" acids. These acids are saturated synthetic tertiary monocarboxylic acids. "Versatic" 911 acid contains a mixture of acids having C_9 , C_{10} and C_{11} chain lengths. "Versatic" 1519 acid contains a mixture of acids having C_{15} to C_{19} chain lengths and "Versatic" 1621 acid contains a mixture of acids having C_{16} to C_{21} chain lengths.

The invention is not restricted; however, to the carboxylic acids or their water-soluble salts prepared by the said process, according to the invention, carboxylic acids of the above given structure are also utilizable when they have been prepared by different processes.

All these compounds are denoted below, for the sake of simplicity, as "branched-chain carboxylic acids."

The above-described water-soluble salts of branched chain carboxylic acids serving as textile softeners in the composition according to the invention are surface-active compounds and resemble soap in their behavior. This applies especially to alterations in the foaming power of synthetic, especially anionic, surface-active compounds. Thus, salts of such branched chain carboxylic acids containing 20 and more carbon atoms in the molecule can reduce the foaming power of anionic surface-active compounds. Therefore, other surface-active or non-surface-active foam inhibitors may be used in correspondingly smaller amounts or be completely omitted.

The invention is of special practical importance for the so-called heavy-duty washing agents, that is for washing agents which are used in the main washing operation. Machine washing agents with foam-inhibiting properties are included thereby, but also all purpose washing agents, which show good foaming capacity at temperatures up to 60° C, while the development of foam abates more and more with the rise in temperature above 60° C. The surface-active components of such washing agents may simultaneously contain foam stabilizers and foam inhibitors with an action dependent on temperature.

Such surface-active components consist mostly of synthetic, anionic, amphoteric and/or non-ionic surface-active compounds as well as soaps with, for example, 12 to 18 carbon atoms in the fatty acid residue, or the soaps of corresponding free fatty acids. The soap fraction may be wholly or partly replaced by the "branched-chain carboxylic acids" used according to the invention. The surface-active sulfonates, and also the corresponding sulfates have special practical importance as the synthetic anionic surface-active compounds. The anionic surface-active component usually constitutes at

least 50 percent of all the types of synthetic surface-active compounds mentioned under (a) in the combination of surface-active compounds.

The foaming capacity of anionic and/or non-ionic surface-active compounds can be affected by choice of suitable fatty acid components. Inhibition of foaming, especially at temperatures from 60° to 60° C, increases with the number of carbon atoms and the degree of saturation of the fatty acid residue. A considerable anti-foaming effect can be attained in the case of synthetic anionic, amphoteric or non-ionic surface-active compounds by inclusion therein of soaps from fatty acid mixtures which contain at least 50 percent of fatty acids with 16 to 30 carbon atoms and at least 3, preferably more than 5 percent, of fatty acids with 20 or more carbon atoms. The saturated fatty acids containing at least 16 carbon atoms preferably constituting at least 50 percent of the total soap fraction. This soap fraction in the combination of surface-active compounds can be abolished, or replaced by synthetic detergent substances, provided the washing agent contains other foam-inhibiting substances, for example, those further defined under the said foam inhibitors.

When the heavy-duty washing agents according to the invention contain, in addition to the combinations of surface-active compounds, neutral to alkaline reacting builders, the amount of these usually lies in the region of 0.5 to 7 times, especially 1 to 5 times, the amount of the combination of surface-active compounds. Preferably alkalis are present in the builders in such amount that a 1 percent solution of the finished washing agent has a pH value in the region of 8 to 12, preferably 9 to 11.

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

5 to 80 percent, preferably 12 to 40 percent, by weight of combinations of surface-active compounds, consisting of 0 to 80 percent, preferably 25 to 65 percent, by weight of synthetic surface-active compounds of the sulfonate and/or sulfate type, 0 to 80 percent, preferably 5 to 40 percent, by weight on non-ionic surface-active compounds, 0 to 80 percent, preferably 10 to 50 percent, by weight of soap, 10 to 80 percent, preferably 25 to 65 percent, by weight of the "branched-chain carboxylic acids," 0 to 6 percent, preferably 0.5 to 3 percent, by weight of foam stabilizer, 0 to 8 percent, preferably 0.5 to 5 percent, by weight of foam inhibitor, preferably not a surface-active compound, 20 to 95 percent, preferably 60 to 85 percent, 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, 35 to 30 percent by weight of other washing agent constituents, such as, for example, bleaching components and water.

The anionic, amphoteric or non-ionic surface-active compounds present in the combinations of surface-active compounds or the washing agents containing them, according to the invention, contain in the molecule at least one hydrophobic radical having eight to 30 carbon atoms, and an anionic or non-ionic water-solubilizing group. The hydrophobic radical may be of aliphatic or alicyclic, saturated or unsaturated nature and be combined with the water-solubilizing group directly or through intermediate members. Suitable intermediate members are, for example, benzene rings, carboxylic acid ester or carboxylic acid amide groups, and ethylene glycol or propylene glycol residues.

The hydrophobic radical is preferably an aliphatic hydrocarbon radical with 10 to 18 carbon atoms, but deviations from this preferred range of number of carbon atoms are possible, according to 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 includes, for example, the alkyl-aryl-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 eight 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, hydroxyalkene sulfonates and hydroxyalkane sulfonates are also useful as aliphatic sulfonates, such as are obtained, for example, from C_8 to C_{18} 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, i.e., 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 esters of α -sulfo-fatty acids with mono- or polyhydric alcohols containing one to four and preferably one to two, carbon atoms.

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.

Further useful sulfonates are the fatty acid esters of hydroxyethanesulfonic acid and dihydroxypropanesulfonic acid, and the fatty acid amides of aminoethanesulfonic acid. 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 amides of amino-carboxylic acids, for example, of glycocoll or sarcosine.

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 glycidol 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.

In addition, the "Non-ionics" include the water-insoluble polypropylene glycols made water-soluble by addition of ethylene oxide and known by the trade-name of "Plurionics," "Tetronics" or "Ucon Fluid." Also addition products of propylene oxide to alkylenediamines or lower aliphatic alcohols containing one to eight and preferably three to six, carbon atoms are included as "Non-ionics."

Further useful "Non-ionics" are fatty acid or sulfonic acid alkylolamides, which are derived, for example, from mono- or di-alkylolamines, 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 last 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.

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 temperature up to about 65° C, but develop less and less foam as higher temperatures (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 percent 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 glycol 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 sur-

face-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 eight to 18 carbon atoms in the alkyl residue. Aminotriazine- 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 specially 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 tetra-alkyl-diaminochlorotriazines 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 C₁₈ - to C₄₀-ketones and aliphatic carboxylic acids, 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.

The combinations of surface-active compounds according to the invention may be put on the market as such, in order to combine them with washing alkalis, complex-forming compounds or other customary constituents of washing liquors, as is done, for example, in industrial laundries. The combinations of surface-active compounds, however, can also be processed together with these customary washing agent additives to a finished washing agent adjuvant.

Complete washing compositions usually also contain a bleaching component. The bleaching component inclusive of stabilizers and/or activators present, may constitute 2 to 35 percent, preferably 7 to 30 percent by weight of the total washing composition.

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

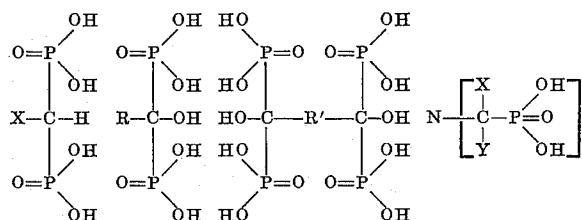
Salts which are weakly acid, neutral or alkaline reacting are utilizable in the compositions of the invention, for example, the alkali metal bicarbonates, carbonates, silicates, orthophosphates, sulfates and the alkali metal salts of organic,

non-surface-active sulfonic acids, carboxylic acids and sulfocarboxylic acids containing one to eight carbon atoms. To the latter belong, for example, water soluble salts of benzene-, toluene- or xylene-sulfonic acids, water-soluble salts of sulfacetic 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, methylenemalononic 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.

Of the usual washing agent additives, the water-soluble condensed phosphates, especially the pyro-, tripoly- or tetrapoly-phosphates have special practical importance. 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 complexforming compounds.



wherein R represents alkyl and R' represents alkylene radicals with one to eight, preferably one to four, carbon atoms, and X and Y represent hydrogen atoms or alkyl radicals with one to four carbon atoms. Carboxy-methylenephosphonic acid (HOOC-CH₂-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 NaBO₂·H₂O₂·3H₂O is of particular practical importance. Partly or completely dehydrated perborates that is up to the approximate composition NaBO₂·H₂O₂, may also be used in its place. Finally, active oxygen containing borates, MaBO₂·H₂O₂, are also useful in which the ratio Na₂O : B₂O₃ is less than 0.5:1 and preferably lies in the region of 0.4 to 0.15:1, and in which the ratio H₂O₂: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 percompounds, especially peroxy-hydrates, such as for example, the peroxyhydrates 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 poly- phosphates, 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 SO₂ 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 percent, preferably from 0.25 percent to 8 percent by weight.

Suitable water-insoluble stabilizers for per-compounds are the different magnesium silicates, mostly obtained by precipitation from aqueous solutions, of composition MgO: SiO₂ = 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-in-soluble stabilizers are usually present in amounts from 1 to 8 percent, preferably 2 to 7 percent 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 percent, preferably 0.5 percent to 2.5 percent 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 or 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, starch and starch products other than those named above can be used, as for example, degraded starch, aldehyde starches and so on. Polyvinyl-pyrrolidone is also utilizable. 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 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 diastase. 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. Their relatively great stability towards oxidizing agents possibly depends on their small content of free sulfhydryl groups.

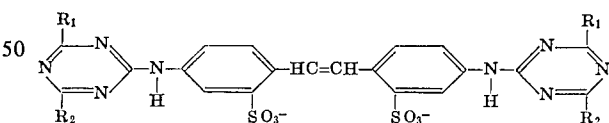
The enzymes are marketed by the producers usually with addition of blending agents. Suitable blending agents are sodium sulfate, sodium chloride, alkali metal ortho-, pyro- or polyphosphates, especially tripolyphosphates. The still moist enzyme preparations are frequently incorporated with calcined salts, 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 non-ionic organic compounds, as for example, ethylene glycol, polyethylene glycols, butylene glycol or polybutylene glycols, and also the known liquid to paste-like surface-active compounds, which are obtained for example, by adding ethylene oxide and possibly propylene oxide to the starting materials known for the preparation of such products, can also be used 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.

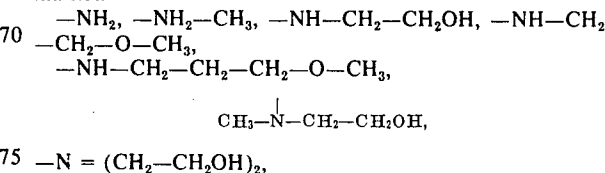
The components of the washing compositions according to the invention, especially the builders, are usually selected so that the preparations have a neutral to distinctly alkaline reaction, so that the pH value of a 1 percent solution of the preparation usually lies in the region of 7 to 12. Fine washing 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.



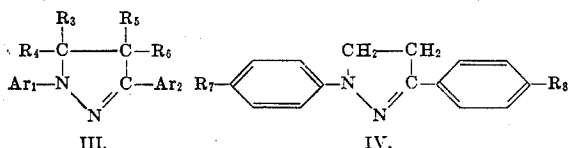
In the formula R₁ and R₂ signify halogen atoms or alkoxy groups, amino groups or residues of aliphatic, aromatic or heterocyclic, primary or secondary amines, or residues of aminosulfonic acids, while aliphatic residues present in the above groups preferably contain one to four and especially two to four 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 R₁ represents the residue —NH—C₆H₅ and R₂ may represent the following residues, are at present on the market:



morpholino-, $\text{—NH—C}_6\text{H}_5$, $\text{—NH—C}_6\text{H}_4\text{—SO}_3\text{H}$, —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 $\text{—NH—C}_6\text{H}_5$. The compound 4,4'-bis-(4-phenyl-5

vicinal-triazolyl-2-)-stilbenedisulfonic acid-2,2' also belongs to the cotton brighteners of the diaminostilbenesulfonic acid type.

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



In formula III, 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 IV, and the residue R_7 may represent the groups Cl , $\text{—SO}_2\text{—NH}_2$, $\text{—SO}_2\text{—CH=CH}_2$ and $\text{—COO—CH}_2\text{—CH}_2\text{—O—CH}_2$, 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-dimethylamino-coumarin. Further useful polyamide brighteners are the compounds 1-(benzimidazolyl-2')-2-(N-hydroxyethyl-benzimidazolyl-2')-ethylene and 1-N-ethyl-3-phenyl-7-diethylamino-carbostyryl. 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.

The following examples are illustrative of the practice of the invention. However, they are not to be deemed limitative in any manner.

EXAMPLES

The following examples describe the compositions of some of the combinations of surface-active compounds according to the invention or a few washing agents with a content of such surface-active combinations. In them:

"ABS" is the alkali metal salt of an alkylbenzene-sulfonic 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 an alkali metal 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 alkane disulfonates. Each 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 an alkali metal sulfonate obtained from paraffins with 12 to 16 carbon atoms by the sulfoxidation method.

"Fatty acid ester sulfonate" is an alkali metal sulfonate obtained from the methyl ester of a hardened tallow fatty acid by sulfonating with SO_3 .

"Oleyl alcohol ether sulfate" or "Tallow alcohol ether sulfate" or "Coconut alcohol ether sulfate" 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 2.5 mols of ethylene oxide to 1 mol of coconut fatty alcohol.

"Tallow alcohol sulfate" or "Coconut alcohol sulfate" are the alkali metal salts of the sulfated fatty alcohols prepared by reduction of tallow fatty acid or coconut fatty acid.

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

"Coconut alcohol + 20 EO" 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 + 9 EO + 12 PO" 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.

"Fatty acid monoethanolamide + 8 EO" is the product of addition of 8 mols of ethylene oxide to 1 mol of a monoethanolamide of coconut fatty acid.

"Diocetylacetate" is the alkali metal salt of di-octylacetic acid (α -n-octyl-capric acid).

"Dicoconut alkylaminopropionate" is the carboxylic acid salt of an alkali metal obtained from the corresponding dialkylamine (prepared from coconut fatty acid) by reacting with methyl acrylate and saponifying the reaction product.

"CMC" is the alkali metal salt of carboxymethyl-cellulose.

"EDTA" is the alkali metal salt of ethylenediaminetetraacetic acid.

"NTA" is the alkali metal salt of nitrilotriacetic acid.

"Waterglass" is a silicate of the composition $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$.

"Perborate" is a product of the approximate composition $\text{NaB}_2\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ containing about 10 percent of active oxygen.

"Cotton Brightener" is the commercial product "Blankophor BBH/SII".

"Polyamide Brightener" is the commercial product "Purwil p".

"Polyester Brightener I" is the commercial product "Uvitex SOF".

"Polyester Brightener II" is the commercial product "Calcofluor white ALF".

The composition 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

No. of carbon atoms in the fatty acid	Wt. percent of fatty acid component in the soap									
	818	1018	1022	1218	1222a	1222b	1222u	1622	1822	
C_9	2									
C_{10}	2	1	1							
C_{12}	16	6	19	20	18	16	14			
C_{14}	10	6	8	12	8	8	6			
C_{16}	25	28	17	20	17	6	13	8		
C_{18}	45	60	33	48	32	16	60	32	9	
C_{20}					4	7	3	12	14	
C_{22}				18	21	47	4	48	77	
Iodine value of the fatty acid mixture.....	10	7.5	5	15	12	8	76	4	3	

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Unless specified to the contrary, the anionic surface-active compounds and the other salts are present as the sodium salts. All percentages given are by weight.

In the examples, the foam inhibitor is associated with the combination of surface-active compounds. This is incorrect in so far as the special foam inhibitors mentioned in the description are not regarded as surface-active compounds. They are nevertheless listed together with the combinations of surface-active compounds because they do of course influence the foaming capacity of the surface-active compounds. In the preparation of the products, the foam inhibitor used in each case, dissolved in a suitable organic solvent or in the molten state, was sprayed by means of a jet nozzle on the agitated pulverulent combination of surface-active compounds or on the agitated pulverulent washing agent. If combinations of surface-active compounds which contain synthetic sulfates or sulfonates together with soap are concerned, paraffin or paraffin oil, for example, are suitable foam inhibitors. In Examples 1-8, an N,N',N''-trialkylmelamine was used as foam inhibitor. This foam inhibitor could be replaced, with a similar result, by a bis-(alkylamino)-monochlorotriazine or by a mixture of 10 percent to 90 percent of the melamine derivative and 90 to 10 percent of the chlorotriazine derivative. In all these triazine derivatives, the alkyl residues were present as mixtures of homologs with eight to 18 carbon atoms. Their foam inhibiting action commenced at temperatures of about 50° C and was present to the full extent after a temperature of 65° C was exceeded.

In the preparations according to Examples 9 to 21, a mixture of about 45 percent of a di(alkylamino)-monochlorotriazine and about 55 percent of an N,N',N''-trialkylmelamine was used as foam inhibitor. In all these triazine derivatives the alkyl residues were present as a mixture of homologs with eight to 18 carbon atoms. If the combinations of surface-active compounds described in the examples contain synthetic sulfates and/or sulfonates together with soap, the said aminotriazine derivatives can be replaced by the other above-mentioned foam inhibitors which are non-surface-active compounds.

If the preparations herein described — the enzyme-free and also the enzyme-containing preparations — are prepared in a pourable state (i.e., as powder, granules, agglomerates), it is advisable to mix the non-surface-active foam inhibitors with the pourable preparations or parts thereof. This can also be carried out by spraying the foam inhibitor present in the liquid state on the agitated pourable product or a part thereof. The foam inhibitors may then be mixed as discrete particles with the other constituents of the product, while they are also combined with the particles of the preparation and can wholly or partly cover these. If the said preparations are prepared as pastes, it is then advisable to incorporate the foam inhibitors as solid powder or granules in the pastes without their granular size being thereby substantially reduced.

The following Examples 1 to 21 describe different combinations of surface-active compounds with a content of textile softeners according to the invention.

EXAMPLE 1a

42% ABS
14% Oleyl alcohol + 10 EO
6% Soap 1822
38% Dioctylacetate

EXAMPLES 1b AND 1c

If in the combination of surface-active compounds according to Example 1a, the ABS is replaced (b) to 25 percent of its weight by Olefin sulfonate, (c) completely by Alkane sulfonate, a similarly utilizable product is obtained.

EXAMPLE 2

37% ABS
17% Oleyl alcohol + 10 EO
46% Dioctylacetate

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EXAMPLE 3

44% ABS
14% Oleyl alcohol + 10 EO
4% Soap 1622
38% Dioctylacetate

EXAMPLE 4

34% ABS
13% Fatty acid ethanolamide + 8 EO
20% Soap 1222 μ
33% Dioctylacetate

EXAMPLE 5

48% Coconut fatty alcohol + 20 EO
25% Coconut fatty alcohol+9 EO+12 PO
27% Dioctylacetate

EXAMPLE 6

49% ABS
16% Oleyl alcohol + 10 EO
33% Dioctylacetate
2% Foam inhibitor

EXAMPLE 7

32% Olefin sulfonate
16% Oleyl alcohol + 10 EO
15% Soap 1218
34% Dioctylacetate
3% Foam inhibitor

EXAMPLE 8

32% Olefin sulfonate
16% Oleyl alcohol + 10 EO
14% Soap 1222 α
34% Dioctylacetate
4% Foam inhibitor

EXAMPLE 9

37% ABS
17% Oleyl alcohol + 10 EO
43% Branched-chain tertiary carboxylic acid
textile softener
3% Foam inhibitor

EXAMPLE 10

33% ABS
11% Tallow alcohol sulfate
14% Oleyl alcohol + 10 EO
4% Soap 1622
38% Branched-chain tertiary carboxylic acid textile
softener.

EXAMPLE 11

30% ABS
13% Fatty acid monoethanolamide + 8 EO
20% Soap 1222 μ
32% Branched-chain tertiary carboxylic acid textile
softener
5% Foam inhibitor

EXAMPLE 12

35% Fatty acid ester sulfonate
14% Coconut alcohol sulfate
16% Oleyl alcohol + 10 EO
33% Branched-chain tertiary carboxylic acid textile
softener
2% Foam inhibitor

EXAMPLE 13

34% ABS
8% Coconut alcohol sulfate
3% Tallow alcohol sulfate
18% Oleyl alcohol + 10 EO
34% Branched-chain tertiary carboxylic acid textile
softener
3% Foam inhibitor

EXAMPLE 14

34% ABS
9% Coconut alcohol sulfate
10% Oleyl alcohol + 10 EO

- 9% Soap 1218
34% Branched-chain tertiary carboxylic acid textile softener
3% Foam inhibitor

EXAMPLE 15

- 26% ABS
7% Coconut alcohol sulfate
2% Tallow alcohol sulfate
8% Coconut alcohol ether sulfate
22% Soap 1222
35% Branched-chain tertiary carboxylic acid textile softener

EXAMPLE 16

- 18% Fatty acid ester sulfonate
11% Coconut alcohol sulfate
9% Oleyl alcohol + 5 EO
28% Soap 1222
34% Branched-chain tertiary carboxylic acid textile softener

EXAMPLE 17

- 40% Alkane sulfonate
9% Coconut alcohol sulfate
14% Oleyl alcohol + 10 EO
35% Branched-chain tertiary carboxylic acid textile softener
2% Foam inhibitor

EXAMPLE 18

- 20% Olefin sulfonate
10% Tallow alcohol sulfate
14% Oleyl alcohol + 10 EO
27% Soap 1222
29% Branched-chain tertiary carboxylic acid textile softener

EXAMPLE 19

- 10% Coconut alcohol sulfate
20% Oleyl alcohol ether sulfate
24% Oleyl alcohol + 5 EO
23% Soap 1222
23% Branched-chain tertiary carboxylic acid textile softener

EXAMPLE 20

- 5% Coconut alcohol sulfate
5% Tallow alcohol sulfate
25% Tallow alcohol ether sulfate
14% Oleyl alcohol + 5 EO
14% Soap 1018
34% Branched-chain tertiary carboxylic acid textile softener
3% Foam inhibitor

EXAMPLE 21

- 41% ABS
9% Coconut alcohol sulfate
17% Coconut alcohol ether sulfate
31% Branched-chain tertiary carboxylic acid textile softener
2% Foam inhibitor

The dioctylacetate used in Examples 1 to 8 and the branched-chain tertiary carboxylic acid used in Examples 9 to 21 are interchangeable and each can also be replaced with similar results by the nitrogen-containing branched-chain carboxylic acids.

The combinations of surface-active compounds described in the Examples 9 to 21 contain as textile softeners, salts of carboxylic acid mixtures with the carbon number indicated below, which were prepared by addition of carbon and water to mixtures of substantially aliphatic olefins.

Textile softener C_{8-11}^- : salt of a C_{8-11} carboxylic acid

Textile softener C_{15-19}^- : salt of a C_{15-19} carboxylic acid

Textile softener C_{16-21}^- : salt of a C_{16-21} carboxylic acid

The Examples 1 to 21 describe combinations of surface-active compounds which are provided as special products preferably for the laundry trade or the textile industry. The

combinations of surface-active compounds described in Examples 1 to 21 come on the market mostly in admixture with sodium sulfate or with other customary washing composition additives, and the combinations of surface-active compounds may constitute 90 to 50 percent by weight and the other constituents 10 to 50 percent by weight.

In all the Examples the data for the surface-active compounds relate to the pure active substance; in the case of the textile softeners, small amounts of by-products from the preparation may also be present.

In the following Examples the sign "+" in the lines " Na_2SO_4 " means that small amounts of sodium sulfate which have been introduced by the anionic surface-active compounds used are present as impurity. The "residue" consists substantially of water, and also includes dyes and perfumes. When the amount of Na_2SO_4 is indicated with "+," the residue also includes the sodium sulfate present.

The following examples describe a few washing agents which contain combinations of builders and additives in addition to the combinations of surface-active compounds according to Examples 1 to 21.

EXAMPLE 22

- 19% Combinations of surface active compounds according to Examples 1 to 12
45% $Na_3P_3O_{10}$
4.5% $Na_2O \cdot 3.3 SiO_2$
1.0% $MgSiO_3$
1.5% CMC
16% Perborate
Remainder: Brightener, perfume, sodium sulfate and water.

EXAMPLE 23

- 20.8% Combination of surface-active compounds according to Examples 1 to 12
32.8% $Na_3P_3O_{10}$
2.9% $Na_2O \cdot 3.3 SiO_2$
2.5% $MgSiO_3$
0.8% CMC
31.3% Perborate
Remainder: Brightener, perfume, sodium sulfate and water

EXAMPLE 24

- 17.5% Combination of surface-active compounds according to Examples 1 to 12
18.0% NTA
6.6% Hydroxyethanediphosphonate
19.0% $Na_3P_3O_{10}$
4.0% $Na_2O \cdot 3.3 SiO_2$
1.6% $MgSiO_3$
1.3% CMC
21.0% Perborate
Remainder: Brightener, perfume, sodium sulfate and water.

EXAMPLE 25

- 19.5% Combination of surface-active compounds according to Examples 1 to 12
19.0% NTA
14.0% Hydroxyethanediphosphonate
12.0% $Na_3P_3O_{10}$
4.5% $Na_2O \cdot 3.3 SiO_2$
1.0% $MgSiO_3$
1.5% CMC
16.0% Perborate
Remainder: Brightener, perfume, sodium sulfate and water.

EXAMPLE 26

- 27.5% Combination of surface-active compounds according to Examples 1 to 12
32.0% $Na_3P_3O_{10}$
28.0% Hydroxyethanediphosphonate
7.5% $Na_2O \cdot 3.3 SiO_2$
1.6% $MgSiO_3$
1.3% CMC
Remainder: Brightener, perfume, sodium sulfate and water.

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EXAMPLE 27

23.8% Combination of surface-active compounds according to Examples 1-12
 1.8% Na_3PO_4
 6.5% $\text{Na}_4\text{P}_2\text{O}_7$
 38.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 5.5% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 2.0% MgSiO_3
 1.2% CMC
 17.0% Perborate
 Remainder: Brightener, perfume, sodium sulfate and water.

EXAMPLE 28

21.5% Combination of surface-active compounds according to Examples 1-12.
 2.3% Na_3PO_4
 20.2% $\text{Na}_4\text{P}_2\text{O}_7$
 23.8% $\text{Na}_5\text{P}_3\text{O}_{10}$
 1.3% EDTA
 5.5% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 20% MgSiO_3
 1.2% CMC
 17.0% Perborate
 Remainder: Brightener, perfume, sodium sulfate and water.

EXAMPLE 29

18.2% Composition of Example 13
 + Na_2SO_4
 30.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 0.2% EDTA
 6.0% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 2.5% MgSiO_3
 2.0% CMC
 0.3% Brightener
 Remainder: Perfume, sodium sulfate and water

EXAMPLE 30

23.2% Composition of Example 14
 + Na_2SO_4
 35.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 0.3% EDTA
 4.5% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 1.8% CMC
 0.8% Brightener
 27.0% Perborate
 Remainder: Perfume, sodium sulfate and water

EXAMPLE 31

19.9% Composition of Example 15
 + Na_2SO_4
 28.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 15.0% NTA
 0.22% Hydroxyethane diphosphonate
 5.0% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 2.0% MgSiO_3
 1.3% CMC
 0.8% Brightener
 24.0% Perborate
 Remainder: Perfume, sodium sulfate and water

EXAMPLE 32

23.2% Composition of Example 16
 + Na_2SO_4
 8.0% Na_2CO_3
 24.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 5.0% NTA
 0.25% EDTA
 4.0% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 1.9% CMC
 0.4% Brightener
 25.0% Perborate
 Remainder: Perfume, sodium sulfate and water

EXAMPLE 33

19.5% Composition of Example 17
 + Na_2SO_4
 38.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 0.5% EDTA
 3.8% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$

20

1.2% CMC
 0.9% Brightener
 23.5% Perborate
 Remainder: Perfume, sodium sulfate and water

EXAMPLE 34

26.2% Composition of Example 18
 21.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 8.0% NTA
 0.4% EDTA
 4.2% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 3.0% MgSiO_3
 1.4% CMC
 1.1% Brightener
 22.0% Perborate
 Remainder: Perfume and water

EXAMPLE 35

21.6% Composition of Example 19
 5.0% Na_2SO_4
 33.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 3.5% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 1.5% CMC
 22.0% Perborate
 Remainder: Perfume and water

EXAMPLE 36

21.1% Composition of Example 20
 18.0% Na_2SO_4
 35.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 10.0% NTA
 3.7% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 1.7% CMC
 Remainder: Perfume and Water

EXAMPLE 37

35 30.0% Composition of Example 21
 10.0% Na_2SO_4
 48.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 4.5% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 1.7% CMC
 Remainder: Perfume and water

EXAMPLE 38

11.3% Combination of surface-active compounds according to Examples 1-20
 22.0% Na_2SO_4
 46.0% $\text{Na}_5\text{P}_3\text{O}_{10}$
 0.5% EDTA
 4.0% $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$
 1.6% CMC
 0.4% Brightener
 Remainder: Perfume and water

50 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 22 to 38 were 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 percent by weight of sodium sulfate:

A protease with 125,000 LVE/g

60 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:

65 I. A washing composition according to one of the Examples 22 to 38 contains

0.3 to 1.5 percent by weight of protease (375-1875 LVE/g)

70 II. A washing composition according to one of the Examples 22 to 38 contains

1.2 percent by weight of lipase (120 IE/g)

III. A washing composition according to one of the Examples 22 to 38 contains

0.4 percent by weight of protease (500 LVE/g)

75 1.0 percent by weight of amylase (750 SKBE/g)

- IV. A washing composition according to one of the Examples 22 to 38 contains
2.0 percent by weight of amylase (1,500 SKBE/g)
- V. A washing composition according to one of the Examples 22 to 38 contains
0.2 percent by weight of protease (250 LVE/g)
0.5 percent by weight of amylase (375 SKBE/g)
0.5 percent by weight of lipase (50 IE/g)
- VI. A washing composition according to one of the Examples 22 to 38 contains
1.0 percent by weight of protease (1,250 LVE/g)
0.3 percent by weight of amylase (225 SKBE/g)
0.4 percent by weight of lipase (40 IE/g)

The textiles washed with the washing compositions according to the invention, especially those of cotton or linen, show a remarkably pleasant and soft handle; cotton towelling is more voluminous than when it is washed without use of the textile softeners according to the invention.

All the combinations of surface-active compounds or washing agents with a content of such surface-active combinations described in the Examples have a low foaming power and are therefore suitable for use in washing machines. However, it may occasionally happen, depending on the local conditions, which cannot be influenced by the washing agent manufacturer, as for example, the concentration of the washing agent used, hardness of the water, quantity and nature of the dirt in the laundry to be washed and so on, that the combinations of surface-active compounds or the washing agents containing them foam somewhat more than is desirable. In such cases the foaming power of the preparations of the Examples can be reduced still further by addition of larger amounts of foam inhibitor and/or by increasing the content of soaps of saturated fatty acids with 18 to 22, preferably 20 to 22, carbon atoms.

Textiles washed with the combinations of surface-active compounds according to the invention or with washing agents containing these surface-active combinations, especially those made of cotton or linen, show a remarkably pleasant and soft handle. Cotton terry cloth is more voluminous than when it is washed without the use of the textile softener according to the invention.

EXAMPLES 39 to 50

The technical effect obtained according to the invention can be demonstrated numerically in a test method developed specially for this case. This method depends on the measurement of the resistance to traction when a curtain tape is frilled or gathered. The curtain tape shown in FIG. 1 consists of a woven band 1 about 2 cm in width. Through it in the longitudinal direction are drawn the interwoven cotton cords 2. If the cords at one end of the band are held fast and the cloth is pushed along on the cords, a specific force has thereby to be applied. This force increases with the hardness of the curtain tapes used.

The pieces of band about 20 cm long intended for the test were first washed successively 20 times, with a bath ratio of 1:15 and a concentration of washing agent of 5 g per liter in water of 17° dH, at a maximum temperature of 98° C. An impeller washing machine was used for these experiments, and the curtain tape was immersed in the bath during the whole time of treatment.

By this pre-treatment, the dressing, which is usually applied during the finishing of the textile, was removed without residue from the curtain tapes. Since the washing agents contained no textile softener, the curtain tapes were also hardened by the pre-treatment. Then some of the curtain tapes so pre-treated were washed in the same way successively 5 times with the washing agents according to the invention, while in the case of the remainder a washing agent of similar composition was used for comparison, which of course contained, instead of the textile softener, the same amount by weight of sodium sulfate. Each curtain tape, therefore, had to pass through 25 washing operations.

The curtain tapes were dried and, before the test measurements, were conditioned at 65 percent relative humidity and

20° C. Before measurement, the tape, but not the two cords, was cut at about 2 cm from one end of the band (see FIG. 1). This end of the band was now (see FIG. 2) inserted in the top clamp 3 of a tensile-testing machine, while the lower clamp 5 was replaced by the gripper 4, which was inverted over the lower cut edge of the cut mentioned. The two inter-woven cords 2 were passed through two notches 5 in the gripper. The gripper was then pulled down 5 cm in the tensile testing machine. The tape then slipped along on the cords, and the force thereby applied was measured on the top clamp. For each washing agent tested, drawing experiments on 20 tapes were made and the values thus obtained were averaged. The difference between the values obtained with the comparative washing agent and with the washing agents including the softeners according to the invention is a measure of the softening effect obtained.

The composition of the washing agent used in the Examples and the softness the tapes attained when treated according to the invention are grouped in the following Table II. The values so obtained are only comparable when the treatment with the different washing agents has taken place as far as possible under constant conditions, and especially when the separate pieces of the curtain tape come from a single manufactured web. If curtain tapes from webs of different manufacturers are used for the test, or as was the case in Examples 39+40, 41-44, 45+46 and 47-50, curtain tapes of different origin or character are used, a comparison is only admissible in the case of results coming from the one series of experiments. In the following Table the comparative experiments made with washing agents without a softener are denoted as "V," and as an index, the numbers of those examples in which a comparison is allowable are associated with this letter.

TABLE II

Composition of the Washing Agents Used in the Comparative Experiments and the Results of the Experiments

		Percent wt. of component in washing agent according to example								
Washing agent component		39	40	V 39+40	41	42	43	44	V 41-44	
40	Combination of surface- active compounds:									
	ABS	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	
	Oleyl alcohol plus									
	EO	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	
45	Soap 1222	7.5		7.5	7.5		7.5		7.5	
	(C ₈ H ₁₇) ₂ CH									
	-COONa	7.5	7.5							
	(Coconut) ₂ >CH									
	-COONa*				7.5	7.5				
	(C ₁₂ H ₁₉) ₂ >N						7.5	7.5		
50	NaOOC-C ₂ H ₄ CO									
	Washing agent builders:									
	Na ₂ PO ₄		1.8					2.3		
	Na ₂ P ₂ O ₇		6.5					20.2		
	Na ₂ P ₂ O ₆		38.0					23.8		
	Na ₂ O-3.3 SiO ₂		5.5					5.5		
	MgSiO ₃		2.0					2.0		
	CMC		1.2					1.2		
	NaBO ₂ -H ₂ O-3 H ₂ O		17.0					17.0		
	Na ₂ SO ₄ , brightener, perfume, water		Remainder					Remainder		
55	Improvement of the softness	454	342		174	61	95	37		

*"Coconut" means here an alkyl residue formed by reduction of the fatty acids derived from coconut fat.

Composition of the Washing Agents Used in the Comparative Experiments and the Results of the Experiments

		Percent by wt. of component in the washing composition according to example								
Washing composition component		45	46	V 45+46		47	48	49	50	V 45-50
65	Surface-active combination:									
	ABS	6.0	6.0	6.0	6.0	6.0		6.0	6.0	6.0
	Oleyl alcohol plus									
	10 EO	2.8	2.8	2.8	2.8	2.8		2.8	2.8	2.8
	Soap 1222	7.5		7.5	7.5			7.5		7.5
	Textile softener									
	C ₁₂₋₁₁	7.5	7.5							
	Textile softener									
	C ₁₅₋₁₉				7.5	7.5				
	Textile softener									
70	C ₁₅₋₂₁							7.5	7.5	
	Basal washing composition:									
	Na ₂ PO ₄		1.8					2.3		

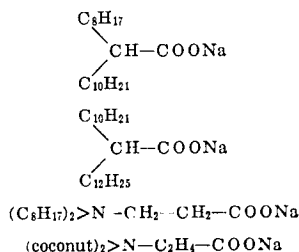
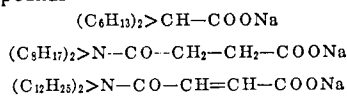
Table II - Continued

Composition of the Washing Agents Used in the Comparative Experiments and the Results of the Experiments

Washing composition component	Percent by wt. of component in the washing composition according to example							
	45	46	45+46	47	48	49	50	45-50
Na ₄ P ₂ F ₇		6.5				20.2		
Na ₃ P ₃ O ₁₀		38.0				23.8		
Na ₂ O·3.3 SiO ₂		5.5				5.5		
MgSiO ₃		2.0				2.0		
CMC.....		1.2				1.2		
NaBO ₂ ·H ₂ O·3H ₂ O.....		17.0				17.0		
Na ₂ SO ₄ , brightener, perfume, water...	Remainder			Remainder				
Improvement in the softness.....	490	369		873	657	1,215	915	

It is clearly apparent, however, that the softness attained increases with the chain length of the branched chain carboxylic acids used as textile softeners, at least in the carbon number range of 9 to 21. The desired effect is further improved by simultaneous presence of soaps of higher fatty acids, especially those containing 18 to 22 carbon atoms.

If the textile softener contained in the combinations of surface-active compounds in the Examples is replaced by the following compounds



similar results are obtained. "Coconut" here means an alkyl residue formed by reduction of the fatty acids derived from coconut fat.

The following examples demonstrate the washing preparations containing the combination of surface-active compounds of the invention in combination with enzyme systems.

As enzymes, the following commercial products were used which were adjusted by the manufacturer to the following activities by addition of sodium sulfate in amounts of about 7-15 percent:

- A protease with 120,000 LVE/gm
- An amylase with 75,000 SKBE/gm
- A lipase with 10,000 IE/gm

In the Examples, in addition to the amount of enzyme, the enzyme activity is also given, based on 1 gm of washing agent.

EXAMPLE 51

An all purpose washing agent, which at temperatures of about 45° C has a certain development of foam, but with increasing temperature shows inhibition of foaming which becomes greater and greater, so that it can be used even at boiling temperatures, has the following composition:

- 6.7% ABS
- 0.5% Tallow alcohol sulfate
- 1.5% Coconut alcohol sulfate
- 3.0% Oleyl alcohol + 10 EO
- 0.5% Foam inhibitor
- 6.0% Dioctylacetate
- 2.0% CMC
- 0.2% EDTA
- 30.0% Na₃P₃O₁₀
- 6.0% Waterglass
- 2.5% MgSiO₃
- 0.25% Cotton Brightener
- 0.03% Polyamide Brightener
- 32.0% Perborate
- 0.8% Protease (1000 LVE/g)
- Remainder: blue dyestuff, perfume and water

EXAMPLE 52

All purpose washing agent as example 51

- 8.1% ABS
- 2.0% Coconut alcohol sulfate
- 2.5% Oleyl alcohol + 10 EO
- 2.0% Soap 818
- 0.6% Foam inhibitor
- 8.0% Dioctylacetate
- 1.8% CMC
- 0.3% EDTA
- 35.0% Na₃P₃O₁₀
- 4.5% Waterglass
- 0.3% Cotton Brightener
- 0.02% Polyamide Brightener
- 0.5% Polyester Brightener I
- 27.0% Perborate
- 1.2% Lipase (120 IE/g)
- Remainder: Green dyestuff, perfume and water

EXAMPLE 53

All purpose washing agent as example 51

- 5.5% ABS
- 1.5% Coconut alcohol ether sulfate
- 0.3% Tallow alcohol sulfate
- 1.2% Coconut alcohol sulfate
- 4.2% Soap 1222 b
- 7.2% Dicoconut alkyl-aminopropionate
- 1.3% CMC
- 0.22% EDTA
- 15.0% NTA
- 28.0% Na₃P₃O₁₀
- 5.0% Waterglass
- 2.0% MgSiO₃
- 0.5% Cotton Brightener
- 0.05% Polyamide Brightener
- 0.2% Polyester Brightener II
- 24.0% Perborate
- 0.4% Protease (500 LVE/g)
- 1.0% Amylase (750 SKBE/g)
- Remainder: perfume and water

EXAMPLE 54

All purpose washing agent as example 51

- 4.6% Fatty acid ester sulfonate
- 2.3% Coconut alcohol sulfate
- 2.0% Oleyl alcohol + 5 EO
- 6.3% Soap 1022
- 8.0% Dicoconut alkyl-aminopropionate
- 1.9% CMC
- 0.25% EDTA
- 5.0% NTA
- 24.0% Na₃P₃O₁₀
- 8.0% Na₂CO₃
- 4.0% Waterglass
- 0.4% Cotton Brightener
- 0.04% Polyamide Brightener
- 25.0% Perborate
- 1.5% Protease (1875 LVE/g)
- Remainder: perfume and water

EXAMPLE 55

All purpose washing agent as example 51

- 7.9% Alkane sulfonate
- 1.7% Coconut alcohol sulfate
- 2.7% Oleyl alcohol + 10 EO
- 0.4% Foam inhibitor
- 6.8% Dioctylacetate
- 1.2% CMC
- 0.5% EDTA
- 38.0% Na₃P₃O₁₀
- 3.8% Waterglass
- 0.18% Cotton Brightener
- 0.5% Polyamide Brightener
- 0.15% Polyester Brightener I
- 0.1% Polyester Brightener II
- 23.5% Perborate
- 2.0% Amylase (1500 SKBE/g)
- Remainder: Blue-green dyestuff, perfume and water.

EXAMPLE 56

All purpose washing agent as example 51

- 5.5% Olefin sulfonate
- 2.5% Tallow alcohol sulfate
- 3.5% Oleyl alcohol + 10 EO

7.2% Soap 1022
7.5% Dioctylacetate
1.4% CMC
0.4% EDTA
8.0% NTA
21.0% $\text{Na}_3\text{P}_3\text{O}_{10}$
4.2% Waterglass
3.0% MgSiO_3
0.35% Cotton Brightener
0.03% Polyamide Brightener
0.7% Polyester Brightener II
22.0% Perborate
0.8% Protease (1000 LVE/g)
Remainder: perfume and water

EXAMPLE 57

For use for washing colored and easy-care fabrics, washing agents specified for use at temperatures up to 60° C, but which also possess a sufficient inhibition of foaming at temperatures up to 100° C are preferred.

9.8% Oleyl alcohol ether sulfate
1.8% Coconut alcohol sulfate
5.0% Oleyl alcohol + 5 EO
5.0% Soap 1222 b
5.0% Dioctylacetate
1.5% CMC
33.0% $\text{Na}_3\text{P}_3\text{O}_{10}$
3.5% Waterglass
5.0% Na_2SO_4
22.0% Perborate
0.3% Protease (375 LVE/g)
Remainder: perfume and water

EXAMPLE 58

For washing easy-care textiles, washing agents specified for use at temperatures up to 60° C, but also safe from foaming at temperatures up to 100° C, are preferred.

5.6% Tallow alcohol ether sulfate
1.0% Tallow alcohol sulfate
1.0% Coconut alcohol sulfate
3.0% Oleyl alcohol + 5 EO
3.0% Soap 1018
0.5% Foam inhibitor
7.0% Dicoconut alkyl-aminopropionate
1.3% CMC
10.0% NTA
35.0% $\text{Na}_3\text{P}_3\text{O}_{10}$
3.7% Waterglass
18.0% Na_2SO_4
0.5% Protease (625 LVE/g)
Remainder: perfume and water

EXAMPLE 59

This washing agent has the same field of application as the product according to Example 58.

12.9% ABS
5.0% Coconut alcohol ether sulfate
2.5% Coconut alcohol sulfate
9.0% Dicoconut alkyl-aminopropionate
1.7% CMC
48.0% $\text{Na}_3\text{P}_3\text{O}_{10}$
4.5% Waterglass
10.0% Na_2SO_4
0.2% Protease (250 LVE/g)
0.5% Amylase (375 SKBE/g)
0.5% Lipase (50 IE/g)
Remainder: perfume and water

EXAMPLE 60

Prewashing agent, which can be used in case of need also at boiling temperatures without causing excessive foaming.

1.0% Oleyl alcohol + 5 EO
7.0% Oleyl alcohol + 10 EO
0.3% Foam inhibitor
3.0% Dioctylacetate
1.6% CMC
0.5% EDTA
46.0% $\text{Na}_3\text{P}_3\text{O}_{10}$
4.0% Waterglass
0.3% Cotton Brightener

0.05% Polyamide Brightener
22.0% Sodium sulfate
0.6% Protease (750 LVE/g)
0.3% Amylase (225 SKBE/g)
0.4% Lipase (40 IE/g)
Remainder: perfume and water

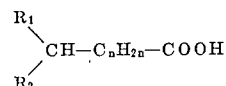
When textiles, especially cotton textiles, which are soiled with albumen, starch and fat-containing contaminations, are washed with the combinations of surface-active compounds or with the washing agents containing them according to the invention, the enzymes contained therein effect a more rapid removal of these contaminations, even at relatively low temperatures, especially when they are present as dried spots of blood, pus, gravy and so forth. The textile softeners contained in the products according to the invention can then act on the textiles at a relatively early state in the washing process. Therefore, a combined action of the enzymes and the textile softeners is attained.

It is quite possible to market the combinations of surface-active compounds with a content of enzymes, rather than the finished washing agents. The formulations of such enzyme-containing combinations of surface-active compounds follow directly from the above examples by omission of the builders and additives (CMC to perborate, as well as dyestuff and perfume). Of course, it is possible to incorporate builder components in smaller quantities, such as for example, dirt carriers (CMC), complex-forming compounds (EDTA) and brighteners, to be also present in the combinations of surface-active compounds. In the case of Example 29, these combinations of surface-active compounds are present as a paste, taking into consideration the large quantities of non-ionics in the formulation.

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 may be employed without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. A combination of surface-active compounds in granular or pasty form utilizable in neutral to alkaline textile washing baths which consists essentially of (a) from 20 to 90 percent by weight of customary surface-active compounds utilizable in neutral to alkaline textile washing baths consisting of a mixture of anionic surface active compounds selected from the group consisting of surface-active sulfonates, surface-active sulfates and straight-chain fatty acid soaps, and non-ionic surface-active compounds, and (b) from 80 to 10 percent by weight of a textile softener selected from the group consisting of (1) compounds of the formula



wherein R_1 and R_2 are alkyl having from six to 18 carbon atoms and n represents an integer from 0 to 2, and (2) water-soluble salts thereof.

2. The combination of surface-active compounds of claim 1 wherein components (a) are present in an amount of from 75 to 35 percent by weight and components (b) are present in an amount of from 25 to 65 percent by weight.

3. The combination of surface-active compounds of claim 1 wherein R_1 and R_2 are different and one of R_1 and R_2 contains not more than twice as many carbon atoms as the other of R_1 and R_2 .

4. The combination of surface-active compounds of claim 3 wherein one of R_1 and R_2 contains not more than 1.5 times as many carbon atoms as the other of R_1 and R_2 .

5. The combination of surface-active compounds of claim 1 wherein the sum of the carbon atoms in R_1 and R_2 is between 14 and 20.

6. The combination of surface-active compounds of claim 1 wherein at least 50 percent of said mixture of anionic surface-active compounds and non-ionic surface-active compounds of component (a) is said anionic surface-active compounds selected from the group consisting of surface-active sulfonates, surface-active sulfates and straight-chain fatty acid soaps.

7. The combination of surface-active compounds of claim 1 wherein at least part of said mixture of anionic surface-active compounds and non-ionic surface-active compounds of component (a) is said straight-chain fatty acid soap and the fatty acids present in said soap consist of at least 50 percent 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.

8. The combination of surface-active compounds of claim 7 wherein at least 3 percent of said fatty acids in said soap have from 20 to 30 carbon atoms.

9. The combination of surface-active compounds of claim 7 wherein at least 5 percent of said fatty acids in said soap have from 20 to 30 carbon atoms.

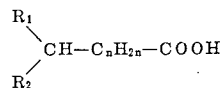
10. The combination of surface-active compounds of claim 1 wherein a further content of enzymes is present selected from the group consisting of proteases, amylases, lipases and mixtures thereof, wherein the enzymatic activity is in the range of 62.5 to 50,000 LVE per gram of the combination of surface-active compounds in the case of proteases, of 25 to 50,000 SKBE per gram of the combination of surface-active compounds in the cases of amylases and of 2.5 to 10,000 IE per gram of the combination of surface-active compounds in the case of lipases.

11. Washing agents and washing agent adjuvants containing from 5 to 80 percent by weight of the combination of surface-active compounds of claim 1 and from 20 to 95 percent by weight of a builder selected from the group consisting of neutral to alkaline reacting inorganic has been inserted therefor.

12. The washing agents and washing agent adjuvants of claim 11 containing from 15 to 40 percent by weight of said combination of surface-active compounds and from 85 to 60 percent by weight of said builders.

13. The washing agents and washing agent adjuvants of claim 12 wherein at least 30 percent by weight of said builder is selected from the group consisting of condensed alkali metal phosphates and organic builders.

14. Washing agents in powder to granular form containing a compatible textile softener consisting of (a) from 12 to 30 percent by weight of a combination of surface-active compounds consisting of (1) 25 to 65 percent by weight of surface-active compounds selected from the group consisting of sulfonates and sulfates, (2) 5 to 40 percent by weight of non-ionic surface-active compounds, (3) 10 to 50 percent by weight of straight-chain fatty acid soap, (4) 25 to 65 percent by weight of a textile softener selected from the group consisting of (i) compounds of the formula

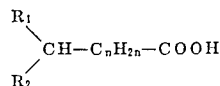


wherein R_1 and R_2 are alkyl having from six to 18 carbon atoms and n represents an integer from 0 to 2, and (ii) water-soluble salts thereof, (5) 0.5 to 5 percent by weight of non-surface-active foam inhibitors effective at temperatures of 60° C selected from the group consisting of N-alkylated aminotriazines and aminotriazine adducts with propylene oxide and/or butylene oxide containing from 10 to 100 polyglycol units; (b) 40 to 85 percent by weight of 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 percent by weight of soil suspension agents.

15. The washing agents of claim 14 wherein a further content of enzymes is present selected from the group consisting of proteases, amylases, lipases and mixtures thereof wherein the enzymatic activity is in the range of 50 to 5,000 LVE per gram of total washing agent in the case of proteases, of 20 to 5,000 SKBE per gram of total washing agent in the case of amylases and of 2 to 1,000 IE per gram of total washing agent in the case of lipases.

16. The washing agents of claim 14 wherein said non-surface-active foam inhibitors of component (a) (5) is incorporated with solid particles of the washing agent with said foam inhibitors surrounding at least partially said solid particles.

17. Prewashing agents in powder to granular form containing a compatible textile softener consisting of (a) from 5 to 8 percent by weight of a combination of surface-active compounds consisting of (1) 25 to 65 percent by weight of surface-active compounds selected from the group consisting of sulfonates and sulfates, (2) 5 to 40 percent by weight of non-ionic surface-active compounds (3) 10 to 50 percent by weight of straight-chain fatty acid soap, (4) 25 to 65 percent by weight of a textile softener selected from the group consisting of (i) compounds of the formula



wherein R_1 and R_2 are alkyl having from six to 18 carbon atoms and (ii) water-soluble salts thereof, (5) 0.5 to 5 percent by weight of non-surface-active foam inhibitors effective at temperatures over 60° C selected from the group consisting of N-alkylated aminotriazines and aminotriazine adducts with propylene oxide and/or butylene glycol containing from 10 to 100 polyglycol units and (b) from 95 to 92 percent of builders.

18. The prewashing agents of claim 17 wherein a further content of enzymes is present 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 5,000 SKBE per gram of total washing agent in the case of amylases and of 2 to 1,000 IE per gram of total washing agent in the case of lipases.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,676,338

Dated July 11, 1972

Inventor(s) Walter Fries, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 14, after "and (c)" it should read -- 2% to 35% by weight of bleaching components --.

Signed and sealed this 26th day of February 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents