SCOURING AGENTS WITH A BLEACHING AND DISINFECTING ACTION

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U.S. Cl. 252—99 9 Claims

ABSTRACT OF THE DISCLOSURE

Scouring agents having a bleaching and disinfecting action comprising a major amount of water-insoluble scouring components and a minor amount of essentially water-soluble components including a solid water-soluble per-compound and an effective amount of acylated activator compounds wherein the acyl is selected from the group consisting of N-acyl compounds, O-acyl compounds, carbonic acid esters and pyrocarnoic acid esters.

Cleaning and scouring agents which contain an additive with both a bleaching and disinfecting action are known already. In particular, bleaching and disinfecting detergents and scouring agents with a content of active chlorine-liberating compounds have been described. However, since such substances have the disadvantage of emitting an unpleasant and lasting chlorine odor, it has already been suggested to replace the active chlorine-liberating compounds by an odor-free active oxygen-liberating compound. This substitution, however, gives rise to the necessity of adding an activator for the liberating of the active oxygen from the corresponding compound, since mostly such cleaning and scouring agents are supposed to display their entire effectiveness at low temperatures. All storable per-compounds which come into consideration as bleaching and disinfectant additives do not liberate sufficient active oxygen at these low temperatures. Therefore, cleaning and scouring agents with a content of per-compounds and an activator for the per-compound have already become known.

In accordance with German Auslegeschrift 1,280,456 the addition of an inert carrier substance impregnated with solutions of metal ions, particularly Co²⁺, Mn³⁺, Ni²⁺, Cr³⁺, Mo⁶⁺, Cu²⁺, is recommended. The disadvantages of these activators is that on the one hand, a sequestration agent is required simultaneously, in order to avoid undesired discolorations caused by the mentioned metal ions, and on the other hand, those condensed phosphates normally employed in cleaners, owing to their satisfactory cleansing action, with the exception of hexametaphosphate, decrease the catalytic effectiveness of the activator.

OBJECTS OF THE INVENTION

An object of the present invention is the obtention of scouring agents having a bleaching and disinfecting action comprising a major amount of water-insoluble scouring components and a minor amount of essentially water-soluble components including a solid water-soluble per-compound and an effective amount of an acylated activator compound wherein the acyl is selected from the group consisting of alkanoyl having 2 to 4 carbon atoms, benzoyl and substituted benzoyl, said acylated compounds are selected from the group consisting of N-acyl compounds, O-acyl compounds, carbonic acid esters and pyrocarnoic acid esters.

A further object of the present invention is the obtention of scouring agents having a bleaching and disinfecting action consisting essentially of (A) from 60% to 95% by weight of water-insoluble scouring components having a mechanical cleaning action and (B) from 40% to 5% by weight of essentially water-soluble components consisting essentially of (1) from 5% to 100% by weight, of said water-soluble components, of a combination of a solid, water-soluble per-compound containing bound H₂O₂ and a water-soluble acylated activator compound in a ratio such that from 10 to 0.1 acyl groups are present per molecule of bound H₂O₂, said acylated activator compound is selected from the group consisting of:

(a) N-diacylated amines having the formula

wherein R₁ and R₂ are selected from the group consisting of alkyl having 1 to 3 carbon atoms and phenyl, and X is selected from the group consisting of alkyl having 1 to 3 carbon atoms, phenyl and

(b) N-alkyl-N-sulfonyl-carbamidates having the formula

wherein R₁ and R₂ have the above-assigned values and m is an integer from 0 to 2,

(c) N-acyl-hydantoins having the formula

wherein R₁ is selected from the group consisting of alkyl having 1 to 3 carbon atoms and haloalkyl having 1 to 3 carbon atoms, R₂ is alkyl having 1 to 3 carbon atoms and R₃ is selected from the group consisting of alkyl having 1 to 8 carbon atoms and phenyl,

(d) N-acylimidates having the formula

wherein D is selected from the group consisting of a double bond and two hydrogens and R₄ is selected from
the group consisting of alkanoyl having 2 to 4 carbon atoms, benzoyl, alkoxy carbonyl having 1 to 4 carbon atoms in the alkoxy, alky sulfonyl having 1 to 4 carbon atoms and benzenesulfonyl.
(e) Cyclic N-acyl-hydrazides having the formula 

\[ \text{N-COR}_{A} \]

wherein the two nitrogen atoms are part of a heterocyclic ring selected from the group consisting of maleic hydrazide, phthalic acid hydrazide, triazole and urazole and \( \text{R}_{A} \) is selected from the group consisting of alkyl having 1 to 4 carbon atoms and phenyl,
(f) 1,4-diformyl-2,3,5,6-tetraalkanoyloxy-piperazines having the formula

\[ \text{O} - \text{C} = \text{N} - \text{CHO} \]

wherein \( \text{R}_{A} \) is alkanoyl having 2 to 4 carbon atoms,
(g) Phenyl esters having the formula

\[ \text{OH} - \text{C} - \text{OR}_{A} \]

wherein \( \text{R}_{A} \) is selected from the group consisting of alkyl having 1 to 4 carbon atoms and phenyl,
(h) Acylated polyhydroxy compounds having the formula

\[ \text{Y(COR}_{A})_{n} \]

wherein \( \text{Y} \) is selected from the group consisting of a mono-saccharide residue, a di-saccharide residue and a lower alkanepolyol having at least 3 hydroxyl groups, \( \text{R}_{A} \) is alkyl having 1 to 4 carbon atoms and \( n \) is an integer of at least 3,
(i) Carbonic acid esters having the formula

\[ \text{R}_{A} - \text{O} - \text{CO} - \text{O} - \text{R}_{A} \]

wherein \( \text{R}_{A} \) is selected from the group consisting of p-carboxyphenyl, sodium-p-sulfophenyl and alkoxy carbonyl having 1 to 4 carbons in the alkoxy, and \( \text{R}_{A} \) is selected from the group consisting of alkyl having 1 to 4 carbon atoms, phenyl and cycloalkyl having 5 to 6 carbon atoms,
(j) Tricarboxylic anhydrides having the formula

\[ \text{R}_{A} - \text{O} - \text{CO} - \text{OR}_{A} \]

wherein \( \text{R}_{A} \) is alkaneoyl having 2 to 3 carbon atoms,
(k) Benzoic acid anhydride, and
(l) Phthalic acid anhydride, and
(2) from 0 to 95% by weight, of said water-soluble components, of water-soluble scavenging components selected from the group consisting of surface-active anionic compounds, surface-active non-ionic compounds, surface-active amphipathic compounds, inorganic builders, organic complex-forming compounds, dirt carriers, antimicrobial compounds, skin protecting compounds, superfatting compounds, corrosion inhibitors, enzymes, dyestuffs and perfumes.

Another object of the invention is the combination of solid, water-soluble per-compounds containing bound \( \text{H}_{2}\text{O}_{2} \) and the water-soluble acylated activator compounds.

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

DESCRIPTION OF THE INVENTION

The present invention provides scavenging agents having a bleaching and disinfecting action comprising a major amount of water-insoluble scavenging components and a minor amount of essentially water-soluble components including a solid water-soluble per-compound and an effective amount of acylated activator compounds.

The following N-acyl or O-acyl compounds, or carbonic acid or pyrocarbonic acid esters can be used as water-soluble organic acylated scavengers according to the invention:

(a) N-diacylated amines of Formula I:

\[ X - \text{N} - \text{COR}_{A} - \text{COR}_{B} \]

in which \( \text{R}_{A} \) and \( \text{R}_{B} \) represent an alkyl residue with 1 to 3 carbon atoms, or an optionally substituted aryl residue, preferably phenyl, and \( X \) represents an alkyl residue having 1 to 3 carbon atoms, an aryl residue, preferably phenyl, or one of the groups

\[ -\text{OH} - \text{N} - \text{COR}_{A} \text{ or } -\text{CHO} - \text{N} - \text{COR}_{A} \text{ or } -\text{N} - \text{COR}_{A} \]

such as \( \text{N,N-diacyl-ethylamine, N,N-dipropionylphenylamine, tetaacetylethylendiamine, tetrapropionylethaminediamine, tetrapropionylethaminediamine, and tetracyclohexylamine;} \)

(b) N-acyl-N-sulfonfuryl-carbonamides of Formula II:

\[ \text{R}_{A} - \text{CO} - \text{N} - \text{OR}_{A} \]

in which \( \text{R}_{A} \) represents an alkyl residue or halogenated alkyl residue having 1 to 3 carbon atoms or an optionally substituted aryl residue, preferably phenyl, \( \text{R}_{A} \) represents an alkyl residue having 1 to 3 carbon atoms, and \( \text{R}_{A} \) represents an alkyl residue having 1 to 8 carbon atoms or an optionally substituted aryl residue, preferably phenyl, such as \( \text{N-methyl-N-benzene-sulfonfyl-acetamide, N-ethyl-N-ethanesulfonfyl-proponamide, N-methyl-N-methanesulfonfyl-acetamide and N-methyl-N-methanesulfonfyl-benzamide;} \)

(c) N-acyl-hydantoins of Formula III:

\[ \text{R}_{A} - \text{N} - \text{COR}_{A} - \text{N} - \text{COR}_{B} \]

in which \( \text{R}_{A} \) represents an alkyl residue having 2 to 4 carbon atoms, an alkyl residue having 1 to 4 carbon atoms, or an optionally substituted benzoyl residue, or an aryl residue, preferably phenyl, \( \text{R}_{A} \) represents an alkyl residue having 2 to 4 carbon atoms, an alkyl residue having 1 to 4 carbon atoms, an aryl residue, preferably phenyl, or an optionally esterified carboxymethyl residue, preferably carboxymethyl or alkoxy carbonylmethyl having 1 to 4 carbon atoms in the alkoxy, and the compounds of Formula III at least one of the residues \( \text{R}_{A} \) and \( \text{R}_{A} \) represents an alkyl, group, and \( \text{R}_{A} \) and \( \text{R}_{A} \) represent hydrogen or an alkyl residue having 1 or 2 carbon atoms, such as 1,3-dipropionyl-hydantoin, 1-ethy1-3-butyryl-5,5-dimethyl-hydantoin, 1-methyl-3-benzoyl-hydantoin, 1-propionyl-3-phenyl - hydantoin, and 1-methoxycarbomethyl-3-propionyl-hydantoin;
3,730,902

(d) N-acyl-succinimides and maleic acid imides of Formula IVa or IVb:

in which R_{41} and R_{42} represent an alkanoyl residue having 2 to 4 carbon atoms, an optionally substituted benzoyl residue, an alkoxyacyl residue having 1 to 4 carbon atoms in the alkoxy residue or an alkan-sulfonyl residue having 1 to 4 carbon atoms, or an optionally substituted benzenesulfonyl residue, such as N-acetyl-succinimide, N-propionyl-maleic acid imide, N-benzoyl-maleic acid imide, N-ethoxycarbonylsuccinimide, N-benzenesulfonyl-maleic acid imide and N-methanesulfonylsuccinimide;

(e) Cyclic N-acylhydrazides of Formula V:

in which the two nitrogen atoms are part of a 5- or 6-membered heterocyclic ring from the group of maleic hydrazide, phthaloyl hydrazide, triazole or urazole, and R_{43} represents an alkyl residue having 1 to 4 carbon atoms, or an optionally substituted phenyl residue, such as N-acetyl-maleic hydrazide, N-benzoylphthaloyl hydrazide, N-propionyl-triazole, and acetylanazole;

(f) 1,4-diformyl-2,3,5,6-tetraalkanoyloxy - piperazines of Formula VI:

in which R_{44} represents an alkanoyl residue having 2 to 4 carbon atoms, such as 1,4-diformyl-2,3,5,6-tetraacetoxypiperazine;

(g) Phenol esters, optionally substituted in the phenol residue, of Formula VII:

(h) O-acyl derivatives of mono- and di-saccharides and of aliphatic polyhydroxyalkohols of Formula VIII:

in which Y represents a mono- or di-saccharide residue or the residue of an aliphatic polyhydroxyalcohol, preferably a lower alkanesol having at least 3 hydroxy groups, R_{45} represents an alkyl residue having 1 to 4 carbon atoms, preferably a methyl residue, and n is at least the number 3 and at most the number corresponding to the per-O-acyl compound, such as glucose pentaacetate and pentaerythritol tetaacetate;

(i) Carbolic acid esters of Formula IX:

in which R_{45} represents an electron-attracting residue, preferably from the group of p-carboxyphenyl, sodium p-sulfophenyl and alkoxyacarbonyl having 1 to 4 carbon atoms in the alkoxy, and R_{46} represents an optionally substituted alkyl, aryl, preferably phenyl, or cycloalkyl residue, such as diethyl pyrocarbonate, O-p-carboxyphenyl-O'-ethyl-carbonate, O - sodium-p-sulfophenyl-O'-cyclohexyl-carbonate, etc.;
per-compounds such as urea and melamine per-hydrates and, in particular, inorganic per-salts, such as, for instance, alkali metal perborates, percarbonates, perpyrophosphates and persilicates. Among the preferable inorganic per-compounds containing $H_2O_2$ to be used, sodium perborate tetrahydrate is of specific practical importance. Instead, partially or completely dehydrated perborates may be used as well, that is, dehydrated to the approximate composition: $NaBO_2\cdot H_2O_2$. Finally, borates containing active oxygen, $NaBO_2\cdot H_2O_2$ in which the proportion $NaO:BO_2^-:H_2O_2$ is less than 0.5:1 and is preferably in the range from 0.4 to 0.15:1, and in which the proportions $H_2O_2:Na$ is in the range from 0.5 to 4:1 are also useful. These products are described in German Pat. No. 901,287 and in United States Pat. No. 2,491,789.

The perborates may be wholly or partly replaced by the above-identified inorganic per-compounds. These peroxide hydrates are preferably soluble in water and are ordinarily utilized in the form of their alkali metal salts, such as their sodium salts.

The anionic, amphoteric or nonionic surface-active compounds contain in the molecule at least one hydrophobic group consisting of 8 to 26, preferably 10 to 20, and in particular, 12 to 18 carbon atoms and at least one anionic or nonionic or amphoteric water-solubilizing group. The preferably saturated hydrophobic residue may be of aliphatic or alicyclic nature, and be combined with the water-solubilizing groups directly or through intermediate members. Suitable intermediate members are, for example, benzene rings, carboxylic acid ester or carbonamide groups, ether or ester-like bound residues of polyvalent alcohols, such as ethylene glycol or propylene glycol, glycerine or corresponding polyether residues.

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

Soaps are useful as anionic detergents which are derived from natural or synthetic fatty acids, and possibly also from resin or naphthenic acids, particularly if these acids have iodine numbers of 30 at the most and preferably of less than 10.

Of the synthetic anionic surface-active compounds, the sulfonates are of special practical importance.

The sulfonates include, for example, the alkyaryl sulfonates, especially the alkylbenzene sulfonates, which are obtained among others from preferably straight-chain aliphatic hydrocarbons with 9 to 15, preferably 10 to 14, carbon atoms by chlorination and alkylation of benzene or from corresponding olefins with terminal or non-terminal double bonds by alkylation of benzene and sulfonation of the alkylbenzenes. Further, aliphatic sulfonates are of interest, such as, for example, as are obtainable from preferably saturated hydrocarbons containing 8 to 18 and preferably 12 to 18 carbon atoms in the molecule by sulfochlorination with sulfur dioxide and oxygen and conversion of the products thereby obtained into the sulfonates. Furthermore, mixtures of alkenesulfonates, hydroxyalkanesulfonates and disulfonates, such as are obtained, for example, from terminal or central $C_6-C_{14}$ and preferably $C_3-C_{14}$ olefins by sulfonation with sulfur trioxide and acid or alkaline hydrolysis of the sulfonation products, are useable as aliphatic sulfonates.

In the aliphatic sulfonates so prepared, the sulfonate group is often found on a secondary carbon atom, but by reacting terminal olefins with bisulfite, sulfonates with terminal sulfonate groups may be prepared.

Salts, preferably dialkali salt of $\alpha$-sulfo-fatty acids as well as those containing 1 to 4 and preferably 1 or 2 carbon atoms also belong to the sulfonates to be used according to the invention.

Further utilizable sulfonates are the fatty acid esters of hydroxyethanesulfonic acid and dihydroxypropansulfonic acid, the salts of fatty alcohol esters of lower aliphatic or aromatic sulfo-mono- and di-carboxylic acids containing 1 to 8 carbon atoms, the alklyglyceryl ethersulfonates, as well as the salts of the amide-like condensation products of fatty acids or sulfonic acids with aminoethane-sulfonic acid.

Suitable surface-active compounds of the sulfone type are fatty alcohol sulfates, especially those derived from coconut fatty acids, tallow fatty acids or oleyl alcohol. Useful sulfonation products of the sulfone type can also be prepared from C$_4$ to C$_{18}$ olefins with terminal or non-terminal double bonds. Furthermore, this group of surface-active compounds includes sulfated fatty acid alkylamidates, sulfated monoglycerides and sulfated products of ethoxylated and/or propoxylated fatty alcohols, alkylphenols with 8 to 15 carbon atoms in the alkyl residue, fatty acid amides, fatty acid alkylamidates and so on, where 0.5 to 2, preferably 1 to 8, and especially 2 to 4 mols of ethylene oxide and/or propylene oxide are added on to one mol of the said compounds to be ethoxylated and/or propoxylated.

Suitable as anionic surface-active agents of the carboxylate type are, for example, the fatty acid esters or fatty alcohol ethers of hydroxy carboxylic acids as well as the amide-like condensation products of fatty acids or sulfonic acids with aminoethane-sulfonic acid, for example, with glycoll, sarscine or albumin hydrolysates.

The nonionic surface-active agents useful in the scouring agents are the so-called "Nonionics" which are products which owe their water solubility to the presence of polyether chains, amineoxide, sulfoxide or phosphonooxide groups, alkylamide groupings as well as in general to a large number of hydroxyl groups.

Of special practical interest are products which are obtainable through the addition of ethylenoxide and/or glize to fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty acid or sulfonic acid amides. These "Nonionics" may contain from 4 to 100, preferably 6 to 40 and especially 8 to 20, ether radicals, and above all, ethyleneglycol ether radicals per molecule. Furthermore, these polyether radicals may contain central or terminal propylene- or butylene-glycol ether radicals as polyether chains.

Products known by the trade names of "Pluronsics" and "Tetronics" are also included among the nonionics. They are obtained from polypropylene glycols, themselves water-insoluble, or water-insoluble higher aliphatic alcohols containing 1 to 8, preferably 3 to 6, carbon atoms and/or from water-insoluble propoxylated alkyleneamines. These water-insoluble (i.e., hydrophobic) propylene oxide derivative are converted into the said nonionics by ethoxylation until the product is soluble in water. Finally, the still water-soluble reaction products of the above mentioned aliphatic alcohols with propylene oxide known as "Ucon-Fluid" are also useful as nonionics.

Other suitable "Nonionics" are fatty acid or sulfonic acid alkylamidates which are derived, for instance, from mono- or diethanolamine, from dihydroxypropylamine or other polyhydroxyalkylamines, e.g., the glycamines. They may be replaced by amides from higher primary or secondary alkylamines and polyhydroxycarboxylic acids.

To the capillary active amineoxides belong, for instance, those products which are derived from higher tert. amines which possess a hydrophobic alkyl radical and two shorter alkyl and/or alkyl radicals with up to 4 carbon atoms.

Amphoteric surface-active agents contain both acid and basic hydrophilic groups in the molecule. Among the acid groups are carboxylic acid groups, sulfonic acid groups, sulfuric acid half-ester groups, phosphate acid groups and phosphoric acid partial ester groups. Among the basic groups are primary, secondary, tertiary and quaternary ammonium groupings. Amphoteric com-
pounds with quaternary ammonium groups belong to the betaine type. Owing to their good compatibility with other surface-active agents, carboxy, sulfonate and sulfonate betaines are of special practical interest. Suitable sulfobetaines are obtained, for instance, through reaction of tert. amines, containing at least one hydrophobic alkyl radical, with sulfones, for instance, propane or butane sulfone. Corresponding carboxybetaines are obtained through reaction of the above-identified tert. amines with chloroacetic acid, its salts or with chloroacetic acid esters and cleavage of the ester bond.

The foaming properties of the surface-active agents may be increased or decreased by means of combination of suitable surface-active agent types as well as being modified by addition of non-surface-active organic substances. Particularly well suited as foam stabilizers for surface-active agents of the sulfonate or sulfate type are capillary active carboxy or sulfobetaines as well as the above-mentioned nonionics of the alkylamidol type. Equally well suited for this purpose are fatty alcohols or higher terminal alkanediols.

Suitable builders are weakly acid, neutral and alkaline-reacting inorganic or organic salts, especially inorganic or organic complex-forming substances.

Weakly acid, neutral or alkaline reacting salts utilisable in the compositions of the present invention are, for example, the borates, bicarbonates, carbonates or silicates of the alkali metals, and mono-, di- or tri-alkali metal orthophosphates, di- or tetra-alkali metal pyrophosphates, and metaphosphates known as complex-forming substances, alkali metal sulfates and the alkali metal salts of organic, non-surface-active sulfonic acids, carboxylic acids and sulfohydrocarboxylic acids containing 1 to 8 carbon atoms. These include, for example, water-soluble salts of benzenesulphonic acid, naphthalenesulphonic acids, water-soluble salts of sulftocetic acid, sulfonbenzoic acid or salts of sulfodioxacarboxylic acids, as well as 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 polymerizes of maleic acid, itaconic acid, mesaconic acid, fumaric acid, acetic acid, methylenmalonic acid and citric acid. Copolymerizes of these acids with one another or with other polymerizable monomers as, for example, ethylene, propylene, acrylic acid, methacrylic acid, crotonic acid, 3-butene-2-carboxylic acid, 3-methyl-3-butenecarboxylic acid and also vinylmethylether, vinyl acetate, isobutyrene, acrylamide and styrene are also utilisable.

Other suitable complex-forming builders are the weakly acid-reacting metaphosphates, as well as the alkaline-reacting polyphosphates, especially tripolyphosphate. They may be wholly or partly replaced by organic complex-forming substances.

Usable organic complex-forming compounds are the alkali metal salts of nitrolactoacetic acid, ethylenediaminetetraacetic acid, N-hydroxyethyl-ethylenediaminetetraacetic acid, polyalkylene-polyamine-N-polycarboxylic acids as well as other known organic complex-forming compounds. Combinations of several complex-forming compounds may be employed as well. Di- and poly-phosphonic acids of the following constitutions also belong to the other known complex-forming compounds:

\[
\begin{align*}
O & \quad X \quad O \\
O & \quad P \quad O \quad P \\
\end{align*}
\]

in which \(R\) represents alkyl and \(R'\) represents alkylene residues with 1 to 8, preferably 1 to 4, carbon atoms, \(X\) and \(Y\) represent hydrogen atoms or alkyl residues with 1 to 4 carbon atoms and \(Z\) represents the groups —OH, —NH\(_2\) or —NHR. For practical use the following compounds are of particular value:

- methylendiphosphonic acid
- 1-hydroxyethane-1,1-diphosphonic acid
- 1-aminoethane-1,1-diphosphonic acid
- amino-tri-(methylenephosphonic acid)
- methylamino- or ethylamino-di-(methylene-phosphonic acid)

As well as ethylendiamino-tetra-(methylenephosphonic acid).

All these complex-forming compounds may be present as the free acids, but preferably as the alkali metal salts.

The said inorganic builders and organic complex-forming substances may be replaced partly by neutral-reacting diluents or blending agents, for example, sodium sulfate or sodium chloride. Other scouring agent components comprise antimicrobial substances, skin-protective substances or super-fattening agents, corrosion inhibitors, enzymes possibly cooated or stabilized as well as dyestuffs and perfumes.

The scouring compositions according to the invention may be prepared by mixing the solid constituents in the usual way, or by preparing first a pulverulent product in known way from the water-soluble constituents suitable for spray drying and admixing with the other solid constituents of the composition, or by mixing the solid constituents and spraying on the solid particles of the mixture any liquid or pasty constituents possibly present in known way, owing to which the preparations have excellent non-dust-producing properties.

The compositions of some of the preparations of the present invention will be further described by way of reference to the following examples. These are, however, not to be deemed limiting in any respect.

**EXAMPLES**

The salt components, salt of surface-active agents, other organic salts as well as inorganic salts which are contained therein, are sodium salts. The terms used in the examples are as follows:

- "Alkylbenzenesulfonate" represents the sodium salt of an alkylbenzenesulfonic acid with from 10 to 15, preferably 11 to 13, carbon atoms in the alkyl chain which is obtained by condensation of straight-chain olefin with benzene and sulfonation of the thus obtained alkylbenzene.

- "Fatty alcohol+EO" represents the addition products of ethylene oxide (EO) to technical oleyl alcohol. The number indicates the molar amount of ethylene oxide added per 1 mol of alcohol.

- "Olefin sulfonate" represents a sulfonate obtained from olefin mixtures with from 12 to 18 carbon atoms through sulfonation with SO\(_4\) and hydrolyzation of the sulfonation product with sodium hydroxide solution. This sulfonate mainly consists of aikenesulfonates and hydroxyalkanesulfonates as well as small amounts of disulfonates. Each of the olefin sulfonate-containing preparations was prepared from two different olefin sulfonate types. One of these had been prepared from a mixture of straight-chain terminal olefins, the other from a mixture of nonterminal olefins.

- "Fatty alcohol—EO-sulfate" represents a sulfated addition product of 2 mols of ethyleneoxide to 1 mol of coconut fatty alcohol.

- "Fatty alcohol sulfate" represents a sulfated coconut fatty alcohol.

- "Fatty acid diethanol amide" represents the amide from coconut fatty acid and diethanolamine.

- "Aikenesulfonate" represents a sulfonate obtained from paraffins with from 12 to 16 carbon atoms by means of sulfonation.
"Soap" represents the sodium salts of a fatty acid mixture of the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Sodium salts</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12 fatty acids</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>C14 fatty acids</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>C16 fatty acids</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>C18 fatty acids</td>
<td>43</td>
<td>4</td>
</tr>
</tbody>
</table>

"Perborate" represents an approximate 10% active oxygen containing product of the approximate NaBO2·H2O2·SH2O.

The explanations for the terms can be taken from the above context whereby the expression "fatty acid" is always to be interpreted as coconut fatty acid mixture.

### Table I

<table>
<thead>
<tr>
<th>Example</th>
<th>Ingredient</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alkylbenzenesulfonate</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol plus 1 EO</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Sodium pyrophosphate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Alkylbenzenesulfonate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Perborate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2,2-Tetramethyl-4,4-diaminomethylene (Formula II)</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>Quartz flour</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Alkylbenzenesulfonate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol sulfate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Bicarbonate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Perborate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2-(2-hydroxyethyl)-2,2-dimethylpropionic acid (Formula III)</td>
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</tr>
<tr>
<td>3</td>
<td>Marble dust</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Soap</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>Orthophosphate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Perborate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Benzene acid anhydride</td>
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</tr>
<tr>
<td>5</td>
<td>Quartz flour</td>
<td>20</td>
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<td></td>
<td>Alkylbenzenesulfonate</td>
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<tr>
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<td>Fatty alcohol plus 1 EO</td>
<td>2.5</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>Triethylglycerol (Formula X)</td>
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</tr>
<tr>
<td>6</td>
<td>Quartz flour</td>
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<td></td>
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<td>Sodium pyrophosphate</td>
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<tr>
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<td>Sodium bicarbonate</td>
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</tr>
<tr>
<td></td>
<td>Perborate</td>
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</tr>
<tr>
<td></td>
<td>Sodium oleate-hydrazide (Formula V)</td>
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<tr>
<td></td>
<td>Marble dust</td>
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</tr>
<tr>
<td></td>
<td>Fungicide</td>
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</tr>
<tr>
<td></td>
<td>Olefinsulfonate</td>
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<td></td>
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<tr>
<td></td>
<td>Triphosphate</td>
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<tr>
<td></td>
<td>Perborate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1,4-dihydroxy-3,3,5,5-tetramethoxy-piperazine (Formula VI)</td>
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<tr>
<td>7</td>
<td>Quartz flour</td>
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<td></td>
<td>Alkylbenzenesulfonate</td>
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</tr>
<tr>
<td></td>
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<td>2</td>
</tr>
<tr>
<td></td>
<td>Sodium sulfate</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Perborate</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2-(2-hydroxyethyl)-2,2-dimethylpropionic acid (Formula VIII)</td>
<td>2</td>
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<tr>
<td>8</td>
<td>Quartz flour</td>
<td>85</td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Dirt</th>
<th>Time of action in minutes</th>
<th>Bleaching action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Tea</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>Carrots</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>Carrots (oil)</td>
<td>2</td>
<td>4.5</td>
</tr>
</tbody>
</table>

### Examples

**Example 9**

Using a scouring composition according to Example 6, a dispersion is prepared which consists of 3 parts of scouring composition and 2 parts of water. In each case 3 gm. of this dispersion are applied to pottery dishes which have been artificially dirtied with coffee, tea and carrot juice, respectively. The bleaching treatment was effected at 20° C. After different times of action the scouring composition is rinsed off and the bleaching action expressed in test values. Value 1 is given for a complete bleaching action, and for an imperceivable bleaching action value 6 is given. The values given in the following Table II are average values from three individual determinations.

A comparative experiment is carried out with a scouring composition of the same composition in which, however, the activator to be used according to the invention is replaced by the same amount by weight of pumice flour.

### Table II

<table>
<thead>
<tr>
<th>Dirt</th>
<th>Time of action in minutes</th>
<th>Bleaching action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Tea</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>Carrots</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>Carrots (oil)</td>
<td>2</td>
<td>4.5</td>
</tr>
</tbody>
</table>

### Example 10

Scouring compositions with various contents of perborate and activator are tested in comparison with corresponding mixtures without activator for their anti-microbial activity according to the surface disinfection test. For this purpose 6 x 6 cm. in size samples of rough wood or glazed tiles are uniformly infected with 3 drops of germ suspension and the suspension is allowed to dry. The germ suspensions are prepared by floating 24-hour old cultures on Merck Standard I agar in normal size Petri dishes with 5 ml. each of sterile Merck Standard I broth, shaking with sterile glass beads and filtering through sterile glass wool. The surfaces are then evenly moistened with the test product premixed with water at 20° C. (test dilution 5 gm. product + 5 ml. water). The removal of the sample was effected by rubbing off in each case a quarter of the surface of the sample with a slightly moistened cotton plug, spreading this on Merck Standard I broth and inoculating the swab in broth. The incubation is carried out at 37° C. up to a maximum of 8 days. The test organisms used were *Escherichia coli* (bacterial count: 117 x 10^5/ml), *Pseudomonas aeruginosa* (115 x 10^5/ml) and *Staphylococcus aureus* (122 x 10^5/ml).

The following scouring compositions were tested:

1. A scouring composition according to Example 3;
2. A scouring composition with:
   1. 1% by weight of perborate,
   2. 1% by weight of 1,3-dipropionyl-hydantoin,
   3. 2% by weight of quartz flour,
3. The remainder being of the same composition as the scouring composition according to Example 3;
4. A scouring composition with:
   1. 0.5% by weight of perborate,
   2. 0.5% by weight of 1,3-dipropionyl-hydantoin,
   3% by weight of quartz flour,
   the remainder being of the same composition as the scouring composition according to Example 3.

Scouring compositions of the same composition in which, however, the activator was replaced by the same amounts by weight of quartz flour served as control. In the following Table III the killing times for the test organisms used are given in minutes.
### TABLE III

<table>
<thead>
<tr>
<th>Example</th>
<th>Product</th>
<th>Sta. unoss E. coli</th>
<th>Ps. aeruginosus</th>
<th>Sta. unoss E. coli</th>
<th>Ps. aeruginosus</th>
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</thead>
<tbody>
<tr>
<td>10a.</td>
<td>1% perborate</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>10b.</td>
<td>1% activator</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>10c.</td>
<td>0% perborate</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>10d.</td>
<td>0% activator</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Control</td>
<td>0% perborate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0% quats flour</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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:

I. Scouring agents having a bleaching and disinfecting action consisting essentially of (A) from 60% to 95% by weight of water-insoluble, finely ground mineral scouring components having a mechanical cleaning action and (B) from 40% to 5% by weight of essentially water-soluble components consisting essentially of (1) from 5% to 25% of 100% by weight, of said water-soluble components, of a combination of a solid, water-soluble per-compound containing bound H₂O₂ and a water-soluble acylated activator compound in a ratio such that from 10 to 0.1 acyl groups are present per molecule of bound H₂O₂, said acyl activator compound is selected from the group consisting of:

(a) N-diacylated amines having the formula

\[
\text{COR}_1 \quad \text{COR}_2
\]

wherein R₁ and R₂ are selected from the group consisting of alkyl having 1 to 3 carbon atoms and phenyl, and X is selected from the group consisting of alkyl having 1 to 3 carbon atoms, phenyl and

\[
-(CH₂)_n
\]

wherein R₁₁ and R₁₂ have the above-assigned values and m is an integer of 0 to 2.

(b) N-alkyl - N-sulfonyl-carbamides having the formula

\[
\text{R}_2 \text{O} \equiv \text{N} \equiv \text{COR}_3
\]

wherein R₂ is selected from the group consisting of alkyl having 1 to 3 carbon atoms (and haloalkyl having 1 to 3 carbon atoms), R₃ is alkyl having 1 to 3 carbon atoms and R₁ is selected from the group consisting of alkyl having 1 to 8 carbon atoms and phenyl.

(c) N-acyl-hydantoins having the formula

\[
\text{R}_3 \equiv \text{C} \equiv \text{N} \equiv \text{COR}_2
\]

wherein R₃ and R₂ are selected from the group consisting of hydrogen and alkyl having 1 to 2 carbon atoms. R₃ is selected from the group consisting of alkanyl having 2 to 4 carbon atoms, alkyl having 1 to 4 carbon atoms, phenyl, and benzyl, and R₂ is selected from the group consisting of alkanyl having 2 to 4 carbon atoms, phenyl, carboxymethyl, and alkoxy-carbomethyl wherein the alkoxy has 1 to 3 carbon atoms, with the proviso that at least one of R₂₁ and R₂₂ is alkoxy, and

(d) N-acyl-imides having the formula

\[
\text{CH} - \text{CO} \quad \text{D} \quad \text{N} \equiv \text{R}_3
\]

wherein D is selected from the group consisting of a double bond and two hydrogens and R₄ is selected from the group consisting of alkoxy having 2 to 4 carbon atoms, benzyl, alkoxy-carbonyl having 1 to 4 carbon atoms in the alkoxy, alkyloxynyl having 1 to 4 carbon atoms and benzenesulfonyl.

(e) Cyclic N-acyl-hydrazides having the formula

\[
\text{N} \equiv \text{CO} \equiv \text{R}_3
\]

wherein the two nitrogen atoms are part of a heterocyclic ring selected from the group consisting of mstie hydrazide, phthalhydrazide, triazole, and urazole and R₃ is selected from the group consisting of alkyl having 1 to 4 carbon atoms and phenyl.

(f) 1,4 - diformyl - 2,3,5,6 - tetraalkanoyloxy-piperazines having the formula

\[
\text{O} \equiv \text{R}_4 \quad \text{O} \equiv \text{R}_4
\]

wherein R₄ is alkanyl having 2 to 4 carbon atoms.

(g) Phenyl esters having the formula

\[
\text{O} \equiv \text{R}_4 \quad \text{O} \equiv \text{R}_4
\]

wherein R₄ is alkanyl having 2 to 4 carbon atoms and phenyl.

(h) Acylated polyhydroxy compounds having the formula

\[
\text{Y(COR}_2\text{)}_n
\]

wherein Y is selected from the group consisting of a mono-saccharide residue, a di-saccharide residue and a lower alkanepolyl having at least 3 hydroxyl groups, R₂₁ is alkyl having 1 to 4 carbon atoms and n is an integer of at least 3.

(i) Carbonic acid esters having the formula

\[
\text{R}_3 \equiv \text{O} \equiv \text{CO} \equiv \text{O} \equiv \text{R}_2
\]

wherein R₃ is selected from the group consisting of p-carboxyphenyl, sodium-p-sulfophenyl and alkoxy-carbonyl having 1 to 4 carbons in the alkoxy, and R₂ is selected from the group consisting of alkyl having 1 to 4 carbon atoms, phenyl and cycloalkyl having 5 to 6 carbon atoms.
(i) Triacyl cyanurates having the formula

\[
\begin{array}{c}
\text{O} \quad \text{R}_{1,0} \\
\text{C} \quad \text{N} \\
\text{N} \quad \text{C} \quad \text{O} \quad \text{R}_{2,1} \\
\text{R}_{1,0} \quad \text{O} \\
\end{array}
\]

wherein \( R_{1,0} \) is alkanoyl having 2 to 3 carbon atoms,
(k) benzoic acid anhydride, and
(l) phthalic acid anhydride,

(2) from 0 to 95% by weight, of said water-soluble components, of surface-active agents selected from the group consisting of surface-active anionic compounds, surface-active non-ionic compounds, and surfactants with amphoteric properties, (3) from 0 to 95% by weight, of said water-soluble components, of inorganic builders selected from the group consisting of alkaline metal bicarbonates, carbonates, borates, silicates, orthophosphates, pyrophosphates and metaphosphates and organic complex-forming compounds, and (4) from 0 to 20% by weight, of said water-soluble components, of neutral inorganic salts.

2. The scouring agent of claim 1 wherein said acylated activator compound is tetraacetylmethylenediamine.

3. The scouring agent of claim 1 wherein said acylated activator compound is O-p-carboxyphenyl-O'-ethylcarboxylate.

4. The scouring agent of claim 1 wherein said acylated activator compound is 1,3-propionyl-hydantoin.

5. The scouring agent of claim 1 wherein said acylated activator compound is benzoic acid anhydride.

6. The scouring agent of claim 1 wherein said acylated activator compound is triacetyl-cyanuric acid.

7. The scouring agent of claim 1 wherein said acylated activator compound is N-acetyl-maleic hydrazide.

8. The scouring agent of claim 1 wherein said acylated activator compound is 1,4-diformyl-2,3,5,6-tetraacetoxy-piperazine.

9. The scouring agent of claim 1 wherein said acylated activator compound is glucose pentaacetate.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Classification</th>
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<tbody>
<tr>
<td>3,630,921</td>
<td>12/1971</td>
<td>Disch et al.</td>
<td>202—95</td>
</tr>
<tr>
<td>3,058,916</td>
<td>10/1962</td>
<td>Sinner et al.</td>
<td>252—95 X</td>
</tr>
<tr>
<td>3,163,606</td>
<td>12/1964</td>
<td>Viveen et al.</td>
<td>252—99 X</td>
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<tr>
<td>3,349,035</td>
<td>10/1967</td>
<td>Dithmar et al.</td>
<td>252—99</td>
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<td>3,272,750</td>
<td>9/1966</td>
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<td>3,183,242</td>
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<td>3,177,148</td>
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<td>Bright et al.</td>
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MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—95, 186