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SYNERGISTIC BLEACHING TEXTILE TREATING COMPOSITIONS WITH AN ANTIMICROBIAL ACTION

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23 Claims

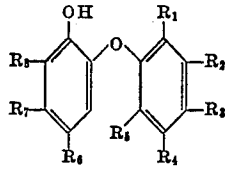
ABSTRACT OF THE DISCLOSURE

A synergistic bleaching textile treating composition with an antimicrobial action comprising (a) an optionally substituted 2-hydroxydiphenylether, (b) a per-compound yielding H_2O_2 in water, and (c) an activator for active oxygen. The composition can be utilized alone in aqueous solution or in combination with other customary components of textile treating compositions. The bleaching and antimicrobial action of the compositions is effective at temperatures down to room temperature.

In the treatment of textiles with aqueous solutions of textile treatment compositions containing per-compounds the destruction of micro-organisms which are on the textiles or in the treatment baths can only take place with certainty at temperatures at which the per-compounds can develop their bleaching action. In the usual bleaching washing compositions on the market this range of temperature lies approximately from 70° to 100° C. In such cases the germs are killed both by elevated temperature and by the chemical action of the active oxygen. In order to attain a corresponding action at temperatures which are not high enough for an activation of the per-compounds, it has already been proposed to add to washing compositions antimicrobial organic substances which however often only have a microbiostatic action.

An object of the present invention is the obtention of a synergistic bleaching textile treating composition with an antimicrobial action which is effective at temperatures below 70° C. to room temperature.

Another object of the present invention is the development of a synergistic bleaching textile treating composition with an antimicrobial action which is effective at temperatures below 70° C. to room temperature consisting essentially of (a) from 0.05% to 25% by weight of a 2-hydroxydiphenyl ether of the formula



wherein R_1 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and hydroxy; R_2 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and cyano, R_3 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, carbomethoxy and carboxyl; R_4, R_5 and R_7 are members selected from the group consisting of hydrogen, fluorine, chlorine and bromine, R_6 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, cyano, carbomethoxy and carboxyl; and R_8 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and tert. butyl; (b) from 25% to 80% by weight of a per-compound yielding H_2O_2 in water; and (c) from 5% to 60% by weight of an activator for active oxygen selected from the group consisting of N-acyl and O-acyl compounds having 2 to 9 carbon atoms in the acyl residue, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Per-Acid Formation Test, wherein from 0.05 to 2 mols of activator are present per gram-atom of active oxygen of said per-compound.

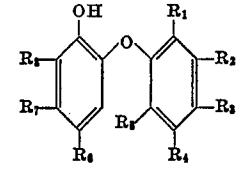
Another object of the invention is the development of textile treating compositions comprising from 5% to 90% by weight of the above synergistic bleaching textile treating composition with an antimicrobial action and from 10% to 95% by weight of customary textile treating ingredients for bleaching, presoaking, washing and cleansing compositions and concentrates.

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

The textile treatment compositions containing per-compounds have now been discovered according to the invention which are marked by an improved antimicrobial action compared with the previously described compositions. The composition of the products according to the invention is as follows:

(1) 5% to 100%, preferably 10% to 90%, by weight of an antimicrobial component, consisting essentially of

(a) 0.05% to 25%, preferably 0.1% to 10%, by weight of a possibly substituted 2-hydroxydiphenyl ether of the general formula



in which R_1 to R_8 represent hydrogen, fluorine, chlorine, or bromine and R_1 may also represent hydroxyl, R_2 and R_6 may also represent a cyano, R_3 and R_6 may also represent a carbomethoxy or carboxyl and R_8 may also represent a tertiary butyl,

(b) 25% to 80%, preferably 30% to 70%, by weight of a per-compound yielding H_2O_2 in water,

(c) 5% to 60%, preferably 20% to 50%, by weight of an activator for active oxygen which is an N-acyl or O-acyl compound with 2 to 9 carbon atoms in the acyl or a carbonic acid ester or pyrocarbonic acid ester, the activating action of which, determined by the Per-Acid Formation Test, described hereinafter, is at least 3, preferably 4.5 while 0.05 to 2, preferably 0.1 to 1, and especially 0.2 to 0.75 mol of activator are present per gram-atom of active oxygen in the textile treatment compositions, and

(2) 95% to 0, preferably 90% to 10%, by weight of other customary components of such textile treatment compositions.

The usual components of such textile treatment compositions include neutral-reacting fillers, especially neutral-reacting inorganic salts, surface-active compounds, the usual builders, especially alkaline-reacting salts without complex-forming ability, neutral- or alkaline-reacting inorganic or organic complex-forming substances, soil suspending agents, brighteners, enzymes, odorous substances or perfumes and water, which is preferably present as water of hydration or crystallization.

The products according to the invention may be used in the textile industry, in industrial laundries and in the home and marketed as antimicrobial additives for washing and bleaching baths, soaking or pre-washing compositions, and as fine washing or complete washing compositions, their

compositions being adapted to the particular purpose of use.

Suitable antimicrobial additives for the textile industry and for industrial laundries are, for example, the antimicrobial components of the above formulation without any further additives. However, the antimicrobial component is frequently admixed with amounts of neutral, preferably alkaline-reacting, builders such that the antimicrobial component constitutes more than 50% by weight of the mixture and the builders constitute from 10% to 45% by weight of the mixture. Such products can also be used as bleaching antimicrobial rinsing agents for washed laundry.

In contrast to this, the actual washing assistants and washing compositions used principally in the home, especially the steeping, prewashing, fine washing and complete washing compositions, contain not more than 50% by weight preferably not more than 45% by weight of the antimicrobial component.

The composition of the soaking compositions generally lies within the following formulation:

0 to 5% by weight of surface-active compounds,
10% to 50% by weight, preferably 10% to 45%, of the antimicrobial component according to the above definition, and

the remainder being neutral or preferably alkaline-reacting builders.

The composition of prewashing, fine washing and complete washing compositions generally lies within the following formulation:

5% to 40% by weight of surface-active compounds,
10% to 50% by weight, preferably 10% to 45%, of the above-described antimicrobial component,
5% to 80% by weight of neutral or preferably alkaline-reacting builders,
0 to 20% by weight of other customary constituents of washing compositions.

The amount of builders, preferably of the alkaline-reacting builders, is usually at least as great and preferably greater than the amount of surface-active compounds.

Representatives of each of the types of surface-active compound described below may be present as the surface-active compounds. In the actual washing compositions, i.e., in the pre-, fine- and complete-washing compositions, combinations of different surface-active compounds are usually employed which may also contain non-surface-active additives serving to control the foaming. The composition of the surface-active component of this kind of formulation generally lies within the following formulation:

0 to 100%, preferably 25% to 65%, by weight of surface-active compounds of the sulfonate and/or sulfate type with preferably 8 to 18 carbon atoms in the hydrophobic residue,
0 to 100%, preferably 5% to 40%, by weight of non-ionic surface-active compounds,
0 to 100%, preferably 10% to 50%, by weight of soap,
0 to 6%, preferably 0.5% to 3%, by weight of foam stabilizers,
0 to 8%, preferably 0.5% to 5%, by weight of foam inhibitors,

The washing compositions are frequently intended for use in washing machines, where the washing baths produced therefrom should only develop small quantities of foam. In such cases, the surface-active component has, for example, the following composition:

8% to 95%, preferably 25% to 75%, by weight of surface-active compounds of the sulfonate and/or sulfate type with preferably 8 to 18 carbon atoms in the hydrophobic residue,
0 to 80%, preferably 10% to 50%, by weight of soap; if soap is present the relative proportion (sulfonate +sulfate) to soap lies in the range of from 10:1 to 1:10, preferably 5:1 to 1:2;
0 to 35% by weight of non-ionic surface-active compounds,
0 to 6%, preferably 0.5% to 3%, by weight of foam stabilizers,
0 to 8%, preferably 0.5% to 5%, by weight of non-surface-active foam inhibitors,

the foaming power of the surface-active component being reduced either by simultaneous presence of surface-active compounds of the sulfonate and/or sulfate type and foam-inhibiting soap and/or by presence of the non-surface-active foam inhibitors.

The other customary constituents of washing compositions are the substances present mostly in smaller amounts of, for example, not more than 3% by weight in each case, such as organic complex-forming substances (which, of course, as organic builders, may also be present in larger amounts), dirt carriers or soil suspending agents, brighteners, enzymes, dyes and odorant substances. The other customary constituents also include textile softeners, which usually constitute 2% to 15%, preferably 7% to 13%, by weight of the total washing composition.

The textile treatment compositions according to the invention can be used, quite generally, for bleaching, especially for soaking, prewashing, washing and after-rinsing of textiles made from a great variety of natural or synthetic fibers, for example, wool, cotton, regenerated cellulose or linen, as well as for the so-called "easy care" textiles, which consist wholly or partly of highly finished cotton or of synthetic chemical fibers, for example, polyamide, polyester, polyacrylonitrile, polyurethane, polyvinyl chloride or polyvinylidene chloride fibers. Therefore, the textile treatment compositions according to the invention may also contain brighteners for the said fibrous materials or combinations of such brighteners. Since the antimicrobial component has both good bleaching and antimicrobial properties at low washing temperatures, it is preferred for use in soaking and cold water washing treatments.

We have surprisingly found that the constituents of the above-described antimicrobial component have a synergistic action, that is, both the number of surviving germs still remaining on the textiles after the treatment with the textile treatment compositions according to the invention is greatly reduced, in the most favorable case is reduced to zero, and also, those which may remain, are prevented from multiplying. This is of particular practical interest, whether it is to keep the bacterial contamination better under control after a disinfecting washing process or to stop or reduce the formation of objectionable odors during the wearing of textiles as a result of the decomposition of sweat by bacteria.

This action is present to a far less extent in the case of a simple combination of the antimicrobial substances to be used according to the invention with per-compounds in the absence of activators. Moreover, compared with others, the antimicrobial substances used according to the invention occupy a special position in that their synergistic action with per-compounds and activators is pronounced.

Of the antimicrobial substances of the above-indicated formula, the chlorine- and/or bromine-substituted compounds are most suitable. The 2',4,4'-trichloro-2-hydroxydiphenylether is of special practical importance, but the following compounds may also be used in its place:

2,2'-dihydroxydiphenylether
2,2'-dihydroxy-dichlorodiphenylether
2,2'-dihydroxy-5,5'-dibromodiphenylether
2,2'-dihydroxy-3,3',5,5'-tetrabromodiphenylether
2-hydroxy-3-tert.-butyl-5-carboxy-2',4',6'-trichlorodiphenylether

2-hydroxy-3-tert.-butyl-5-carboxy-2',4',5'-trichlorodiphenylether
2-hydroxy-3-tert.-butyl-5,4'-dicarboxy-2',6-dibromodiphenylether
2-hydroxy-3-tert.-butyl-5-cyano-2',4',5'-trichlorodiphenylether
2-hydroxy-3-tert.-butyl-5-cyano-2',4',6'-trichlorodiphenylether
2-hydroxy-3-tert.-butyl-5-carboxy-2',3',4',5',6'-pentachlorodiphenylether, and
2-hydroxy-3-tert.-butyl-5-carbomethoxy-2',4',5'-trichlorodiphenylether.

2',4,4'-trichloro-2-hydroxydiphenylether is preferred and soaking, prewashing, fine washing and complete washing compositions preferably contains from 0.05% to 10%, especially 0.075% to 5%, by weight of this antimicrobial substance. The other 2-hydroxydiphenylethers may be used in the same or in larger amounts, depending on their activity.

Of the preferably inorganic, per-compounds yielding H_2O_2 in aqueous solution, sodium perborate tetrahydrate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$) is of special practical importance. Partly or completely dehydrated perborates, i.e., up to $NaBO_2 \cdot H_2O_2$, may be used in its place. Borate such as $NaBO_2 \cdot H_2O_2$, described in German Pat. 901,287 and U.S. Pat. 2,491,789, in which the ratio $Na_2O:B_2O_3$ is less than 0.5:1 and preferably lies in the region of 0.4 to 0.15:1, while the ratio H_2O_2:Na lies in the region of 0.5 to 4:1 are also useful. All these perborates may be wholly or partly replaced by other inorganic per-compounds, especially by peroxyhydrates, such as the peroxyhydrates of ortho-, pyro- or polyphosphates, especially of the tripolyphosphates, as well as the carbonates.

It is advisable to incorporate in the compositions from 0.25% to 10% by weight of the usual water-soluble and/or water-insoluble stabilizers for the stabilization of the per-compounds. Suitable water-insoluble per-compound stabilizers which, for example, constitute 1% to 8%, preferably 2% to 7%, of the weight of the total preparation, are the magnesium silicates ($MgO:SiO_2$=4:1 to 1:4, preferably 2:1 to 1:2 and especially 1:1), mostly obtained by precipitation from aqueous solutions. Other alkaline earth metal, cadmium or tin silicates of corresponding composition are utilizable in their place.

Per-acid formation test

The activation value (=titre) for the activators is determined in the following way:

Solutions which contain 0.615 gm./liter of

$$NaBO_2 \cdot H_2O_2 \cdot 3H_2O$$

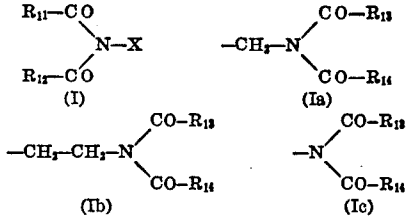
(4 mMol/liter) and 25 gm./liter of $Na_4P_2O_7 \cdot 10H_2O$, are heated to 60° C., and then are mixed with 4 mMol/liter of activator and maintained at the said temperature for 5 minutes with stirring. Then 100 ml. of this liquid is added to a mixture of 250 gm. of ice and 15 ml. of glacial acetic acid and titrated immediately after addition of 0.35 gm. of potassium iodide with 0.1 N sodium thiosulfate solution, using starch as indicator. Under the given experimental conditions, for a 100% activation of the peroxide used, 8.0 ml. of thiosulfate solution are consumed, the titre is 8.0. This maximum value is of course seldom attained. Good activators have a titre of at least 4.5, preferably of at least 6. Useful results are often obtained with activators having a titre of at least 3.0.

Activators of the N-acyl or O-acyl compounds type contain an acyl residue R—CO—, in which R represents optionally substituted hydrocarbon residues with 1 to 8 carbon atoms. If the residues R are aliphatic, they preferably have 1 to 3 carbon atoms, and if they are aromatic, they may contain up to 8 carbon atoms. Consequently, the residue R is preferably one of the following: lower alkyl, such as methyl, ethyl, n-propyl or isopropyl; phenyl; alkylphenyl such as toluyl or xylyl residues. Suitable substituents are C_{1-3} alkoxy groups, halogen atoms, nitro or nitrile groups; when R is an aromatic residue it may be chloro- and/or nitro-substituted, especially m-chloro or m- or p-nitro-substituted. Such substituents are, for example, chloroalkyl having 1 to 3 carbon atoms, m-chlorophenyl, p-nitrophenyl, and p-methoxyphenyl.

Of the activators described below, compounds with a melting point of at least 70° C., preferably at least 100° C. and especially at least 150° C., are specially suitable. Further the equivalent weight of these compounds should be not more than 170, preferably not more than 130 and especially not more than 110 (the equivalent weight is here the quotient of the molecular weight and the number of R—CO— residues present in the molecule where the compound is N-acylated or O-acylated).

The types of compound mentioned under (a) to (1) are useful activators according to the invention. In the formulae the numbered residues R have the meaning given for R above unless specifically otherwise indicated. If several residues R are present in a molecule, they may be the same or different.

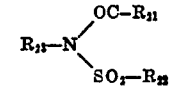
(a) N-diacylated amines of the Formula I, in which X represents a residue R or one of the residues Ia, Ib, or Ic.



(I) (Ia) (Ib) (Ic)

From this class of compounds, N,N,N',N'-tetraacetylmethylenediamine (melting point 92°–95° C.), N,N,N',N'-tetraacetylethylenediamine, N,N-diacetylaniline and N,N-diacetyl-p-toluidine are named as examples.

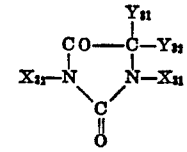
(b) N-alkyl-N-sulfonyl-carbonamides of Formula II, in which R_{23} preferably signifies a C_{1-3} alkyl residue.



(II)

Activators of this type are, for example, N-methyl-N-mesylacetamide (melting point 73°–79° C.), N-methyl-N-mesyl-benzamide (M.P. 116°–118.5° C.), N-methyl-N-mesyl-p-nitrobenzamide (M.P. 159°–160° C.) and N-methyl-N-mesyl-p-methoxybenzamide (M.P. 117°–117.5° C.).

(c) N-acylhydantoins of Formula III, in which at least one of the residues X_{31} and X_{32} represent an R—CO— residue, while the other may also represent a residue R or a carboxymethyl or a lower alkoxycarbonylmethyl residue; Y_{31} and Y_{32} represent hydrogen or alkyl residues with 1 or 2 carbon atoms.



(III)

Suitable compounds are, for example, 1,3-diacetyl-5,5-dimethylhydantoin, 1,3-dipropionylhydantoin (M.P. 104.5° to 106° C.) and 3-benzoylhydantoin-1-acetic acid ethyl ester.

(d) Cyclic N-acylhydrazides of Formula IV, in which the two nitrogen atoms are part of a 5- or 6-membered hetero-ring from the group of maleic acid hydrazide, phthalic acid hydrazide, triazole or urazole.

(IV)

A suitable compound is, for example, mono-acetyl-maleic acid hydrazide.

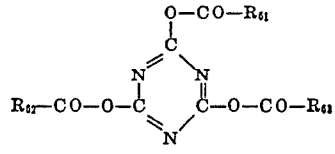
(e) Carbonic acid esters of Formula V, in which X_{51} represents an electron-attracting residue, preferably selected from the group p-carboxyphenyl, p-sulfophenyl or alkoxycarbonyl:

$$X_{51}—O—CO—O—R_{52} \qquad (V)$$

For example, p-ethoxycarbonyloxy-benzoic acid (M.P. 175° C.) is utilizable.

(f) Pyrocarbonic acid esters of C_1 to C_4 alkanols as, for example, pyrocarbonic acid diethyl ester.

(g) Triacyl-cyanurates of Formula VI

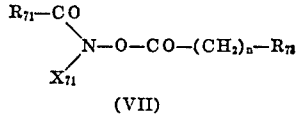


(VI)

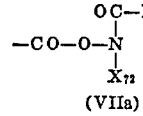
For example, triacetyl- or tribenzoyl-cyanurate.

(h) Optionally substituted anhydrides of benzoic or phthalic acids, especially benzoic anhydride itself or m-chlorobenzoic anhydride (M.P. 95° C.).

(i) O,N,N-trisubstituted hydroxylamines of Formula VII, in which R_{73} represents a residue R, preferably a methyl or ethyl residue, an optionally substituted aryl residue or the Group VII*a*, while X_{71} and X_{72} represent one of the residues R—CO—, R—SO_2— or one of the above-described aromatic residue, or each can be linked with the corresponding residue R_{71} or R_{72} to give a succinyl or phthalyl residue and *n* signifies a whole number from 0 to 2.



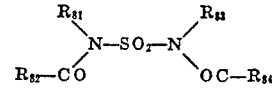
(VII)



(VIIa)

Activators of this type are, for example, O-benzoyl-N,N-succinyl-hydroxylamine (M.P. 137–139° C.), O-acetyl-N,N-succinyl-hydroxylamine (M.P. 132–134° C.). O-p-methoxybenzoyl - N,N - succinyl-hydroxylamine (M.P. 142°–145° C.). O-p-nitrobenzoyl-N,N-succinyl-hydroxylamine (M.P. 212°–215° C.) and O,N,N-triacetyl-hydroxylamine.

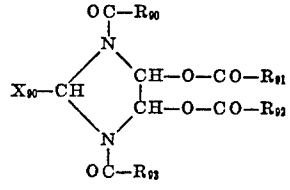
(j) N,N'-diacyl-sulfurylamides of Formula VIII, in which R_{81} and R_{83} preferably represent C_{1-4} alkyl residues or aryl residues such as phenyl, while R_{82} and R_{84} preferably represent C_{1-5} alkyl residues, especially C_{1-3} alkyl residues.



(VIII)

N,N'-dimethyl-N,N'-diacetyl-sulfurylamide (M.P. 58° to 60° C.) and N,N'-diethyl-N,N'-dipropionyl-sulfurylamide (M.P. 95°–97° C.) may be mentioned as examples.

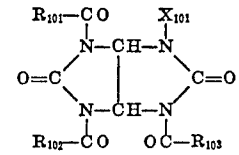
(k) 1,3-diacyl-4,5-diacyloxy-imidazolidines of Formula IX, in which X_{90} represents hydrogen or R, and R_{90} and R_{93} represent hydrogen or R.



(IX)

To these belong: 1,3-diformyl-4,5-diacetoxy-imidazolidine (M.P. 160°–165.5° C.), 1,3-diacetyl-4,5-diacetoxy-imidazolidine (M.P. 139–140.5° C.), 1,3-diacetyl-4,5-dipropionyloxy-imidazolidine (M.P. 85°–87° C.).

(l) Acylated glycolurils of the General Formula X, in which X_{101} represents the residue R or R—CO.



(X)

Tetraacylated glycolurils and especially tetraacetylglycoluril (M.P. 233–240° C.) are preferably used. In addition, the following acylated glycolurils are suitable:

di-(chloracetyl)-diacetyl-glycoluril (M.P. 267–269° C.),
tetrapropionyl-glycoluril (M.P. 144°–146° C.),
1-methyl-3,4,6-triacetylglycoluril (M.P. 179°–180° C.),
diacetyldipropionylglycoluril (M.P. 144–146° C.) and
diacetyl-dibenzoyl-glycoluril (M.P. 244°–249° C.).

The acylated glycolurils are not only of special practical importance on account of their excellent properties as activators, but owing to their high melting point they are very suitable for the preparation of pulverulent products which are stable on storage.

It is often sufficient to activate only a part of the active oxygen present. For this, additions of activator of at least 0.05, preferably of at least 0.1 mol of activator per gram-atom of active oxygen are sufficient. If the greatest possible activation of the active oxygen is required, the addition of activator can be increased up to 2 mols, preferably up to 1 mol. However, it is preferred to work with 0.2 to 0.75 mol of activator per gram-atom of active oxygen. These amounts can, of course, be varied according to the activity of the particular activator used.

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

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

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

Of the synthetic anionic surface-active compounds, the sulfonates and sulfates possess special practical importance.

The sulfonates include, for example, the alkylaryl sulfonates, especially alkylbenzene sulfonates, which are obtained from preferably straight-chain aliphatic hydrocarbons having 9 to 15, especially 10 to 14 carbon atoms, by chlorinating and alkylating benzene or from corresponding terminal or non-terminal olefins by alkylation of benzene and sulfonation of the alkylbenzenes obtained. Further, aliphatic sulfonates are of interest, such as are obtainable, for example, from preferably saturated hydrocarbons containing 8 to 18 and preferably 12 to 18 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. As aliphatic sulfonates, mixtures containing alkene sulfonates, hydroxyalkane sulfonates and disulfonates are useful, which are obtained from terminal or non-terminal C_{8-18} and preferably

C_{12-18} olefins by sulfonation with sulfur trioxide and acid or alkaline hydrolysis of the sulfonation products. In the aliphatic sulfonates thus prepared, the sulfonate group is frequently found attached to a secondary carbon atom; however, sulfonates with a terminal sulfonate group obtained by reaction of terminal olefins with bisulfite can also be used.

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

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

As tensides of the sulfate type are fatty alcohol sulfates, especially those prepared from coconut fat alcohols, tallow fat alcohols or oleyl alcohol. Useful sulfonation products of the sulfate type are also obtainable from terminal or non-terminal C_{8-18} olefins. Sulfated fatty acid alkylolamides or fatty acid monoglycerides, and sulfated alkoxylation products of alkylphenols (C_{8-15} alkyl), fatty alcohols, fatty acid amides or fatty acid alkylolamides, which may contain in the molecule 0.5 to 20, preferably 1 to 8 and especially 2 to 4 ethylene and/or propylene glycol residues, also belong to this group of surface-active compounds.

Suitable anionic surface-active compounds of the carboxylate type are the fatty acid esters or fatty alcohol ethers of hydroxycarboxylic acids, and the amide-like condensation products of fatty acids or sulfonic acids with aminocarboxylic acids, for example, with glycocoll, sarcosin or protein hydrolysates.

The non-ionic surface-active compounds, here called "non-ionics," for the sake of simplicity, include products which owe their solubility in water to the presence of polyether chains, amineoxide, sulfoxide or phosphineoxide groups, alkylolamide groups and very generally, to an accumulation of hydroxyl groups.

The products obtainable by addition of ethylene oxide and/or glycide to fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty acid 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 residue, particularly ethylene glycol ether residues. Moreover, propylene or butylene glycol ether residues or polyether chains may be present in or at the ends of these polyether residues.

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

The non-ionics also include fatty acid or sulfonic acid alkylolamides which are derived, for example, from mono- or di-ethanolamine, dihydroxypropylamine or other polyhydroxyalkylamines, for example the glycamines. They can be replaced by amides from higher primary or secondary alkylamines and polyhydroxycarboxylic acids.

The surface-active amineoxides include, for example, the products 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.

Amphoteric surface-active compounds contain in the molecule both acidic and basic hydrophilic groups. Carboxyl, sulfonic acid, sulfuric acid half ester, phosphonic acid and phosphoric acid partial ester groups are the acid groups. Basic groups include primary, secondary, tertiary and quaternary ammonium groups. Amphoteric compounds with quaternary ammonium groups belong to the betaine type.

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

The foaming power of the surface-active compounds can be increased or reduced by combination of suitable types of surface-active compounds, just as it can be changed by additions of non-surface-active organic substances.

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

Products with a reduced foaming power are primarily intended for use in washing and dishwashing machines, where sometimes a limited repression of foam is sufficient while in other cases a stronger foam repression may be desired. Products which foam in the middle range of temperature up to about 65° C., but at higher temperatures (70° to 100° C.) develop less and less foam are of special practical importance.

A reduced foaming power is frequently obtained with combinations of different types of surface-active compounds, especially with combinations of synthetic anionic surface-active compounds, particularly 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 the components (1) and (2) or (1), (2) and (3), the foaming power can be affected by the particular soap used. The inhibition of foam is smaller with soaps from preferably saturated fatty acids with 12 to 18 carbon atoms, while a greater inhibition of foaming, particularly in the higher temperature range, is obtained by soaps from saturated fatty acid mixtures having 20 to 26, preferably 20 to 22 carbon atoms, used in an amount of from 5 to 10% by weight of the total soap fraction present in the combination of surface-active compounds.

The foaming power of the surface-active compounds can also be reduced, by the addition of known, non-surface-active foam inhibitors. These include optionally chlorine-containing N-alkylated aminotriazines, which are obtained by reacting 1 mol of cyanuric chloride with 2 to 3 mols of a mono- and/or di-alkylamine having 6 to 20, preferably 8 to 18 carbon atoms in the alkyl residue. Aminotriazine or melamine derivatives which contain propylene glycol or butylene glycol ether chains, in an amount of 10 to 100 of such glycol residues per 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. The reaction products from 1 mol of melamine with at least 20 mol of propylene oxide or at least 10 mol of butylene oxide are preferred. Products 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 have proved particularly effective.

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

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

When foam stabilizers are combined with foam inhibitors dependent upon temperature, good foaming products are obtained at lower temperatures which, as the temperature approaches the boiling temperature, foam less and less.

Suitable weakly-foaming non-ionics, which can be used both alone and in combination with anionic, amphoteric and non-ionic surface-active compounds and which reduce the foaming power of more strongly foaming surface-active compounds, are products of addition of propylene oxide to the above-described surface-active polyethylene glycol ethers as well as the also above-described Pluronic, Tetronic and Ucon-Fluid types.

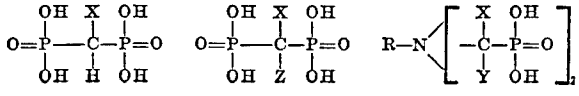
Suitable builders are weakly acid, neutral and alkaline reacting inorganic or organic salts, especially inorganic or organic complex-foaming substances.

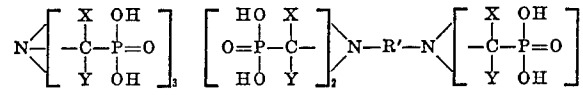
Useful, weakly acid, neutral or alkaline reacting salts according to the invention are, for example, the alkali metal bicarbonates, carbonates, borates or silicates, mono-, di- or tri-alkali metal orthophosphates, di- or tetra-alkali metal pyrophosphates, alkali metal metaphosphates known as complex-forming substances, alkali metal sulfates and the alkali metal salts of organic, non-surface-active sulfonic acids, carboxylic acids and sulfocarboxylic acids containing 1 to 8 carbon atoms. These include, for example, water-soluble salts of benzene-, toluene- or xylene-sulfonic acid, water-soluble salts of sulfoacetic acid, sulfobenzoic acid or salts of sulfodicarboxylic acids and the salts of acetic acid, lactic acid, citric acid and tartaric acid.

Further, the water-soluble salts of higher molecular weight polycarboxylic acids are utilizable as builders, especially polymerizates of maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, methylenemalonic acid and citraconic acid. Co-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-butenecarboxylic acid and with vinyl methyl ether, vinyl acetate, isobutylene, acrylamide and styrene, are utilizable.

Suitable complex-forming builders are also the weakly acid reacting metaphosphates and the alkaline reacting polyphosphates, especially tripolyphosphate, in the form of their alkali metal salts. They may be wholly or partly replaced by organic complex forming substances.

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





in which R represents alkyl and R' alkylene radicals with 1 to 8, preferably 1 to 4 carbon atoms, X and Y represent hydrogen or alkyl radicals with 1 to 4 carbon atoms and Z represents —OH, —NH_2 or NXR. For a practical application above all the following compounds are considered:

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

as well as ethylenediamine-tetra-(methylenephosphonic acid). All these complexing compounds may be present as free acids or preferably as the alkali metal salts.

Further, soil suspending agents or greying inhibitors may be contained in the preparations according to the invention, which hold the dirt loosened from the fiber suspended in the bath and thus prevent greying. Water-soluble colloids of mostly organic nature are suitable for this purpose, for example, the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ether-carboxylic acids or ether-sulfonic acids of starch or cellulose or salts of acid sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also suitable for this purpose. Furthermore, soluble starch preparations and starch products other than those mentioned above can be used, for example, degraded starch, and aldehyde starches. Polyvinylpyrrolidone is also useful.

The constituents of the antimicrobial textile treatment compositions according to the invention, especially washing compositions and washing assistants of this kind, and particularly the builder substances, are usually chosen so that the preparations have a neutral to distinctly alkaline reaction, so that the pH value of a 1% solution of the preparations mostly lie in the region from 7 to 12. Fine washing compositions usually have a neutral to weakly alkaline reaction (pH value 7 to 9.5), while soaking, prewashing and boiling washing compositions are adjusted to be more strongly alkaline (pH value 9.5 to 12, preferably 10 to 11.5). The action of the activators is combined with a certain consumption of alkali. Therefore, the builder substances present should be in an amount sufficient to prevent the pH value from falling below the given minimum values during the whole period of treatment.

The enzymes to be used are mostly a mixture of different enzymic substances. They are called proteases, amylases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases, depending upon their action. The enzymic substances obtained from strains of bacteria or fungi such as *Bacillus subtilis* and *Streptomyces griseus* are of particular interest, especially proteases or amylases. Preparations obtained from *Bacillus subtilis* have the advantage compared with others that they are relatively stable towards alkali, per-compounds and anionic detergent substances and are still active at temperatures up to 70° C.

Enzyme preparations are usually marketed by the manufacturers as aqueous solutions of the active substances or with the addition of diluents, as powders. Suitable diluents are sodium sulfate, sodium chloride, alkali metal ortho-, pyro- or polyphosphates, especially tripolyphosphate. Frequently moist enzyme preparations are mixed with calcined salts, which then bind water or crystallization present and the enzymic substance, possibly with agglomeration of the particles to larger particles.

When the enzymic substances are present as dry powders, liquid, paste-like and possibly also solid, non-

ionic, preferably surface-active, organic compounds, especially the above-described non-ionics, can be used at the usual room temperatures to bind the enzymes to the powders of the washing compositions or washing assistants. For this purpose a mixture of the respective product and the enzymic substance is preferably sprayed with the above-mentioned non-ionic substances, or the enzyme preparations is dispersed in the said non-ionic substance and this dispersion is united with the other constituents of the product. When these other constituents are solids, the dispersion of the enzymic substances in the non-ionic component can also be sprayed on the other solid constituents.

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

These data on enzyme activities result from the activities of those enzyme preparations which at the present time seem to be suitable from the econimic standpoint for use in the washing composition field. From the chemical-technical standpoint the enzyme activities of the preparations can be increased as desired, so that the activities in the case of proteases and amylases may be raised, for example, up to five times, and in the case of lipases, for example, up to ten times, the highest values given above. If, therefore, in the future preparations with such high activities should be available which also economically appear appropriate for the use in the application fields, named at the beginning, products with respective higher enzyme activities can be prepared.

With reference to the determination of the enzyme activities, the following literature references are given;

Determination of the activity of proteases according to Löhlein-Volhard: A. Kunzel, "Chemical Tanning Pocketbook," 6th ed., Dresden and Leipzig, 1955;

Determination of the activity of amylases: J. Wohlgemuth, "Biochemische Zeitschrift," vol. 9, (1908), pp. 1–9; R. M. Sandstedt et al., "Cereal Chemistry," vol. 16 (1939), pp. 712–723;

Determination of the activity of lipases: R. Willstätter et al., "Hoppe-Seylert's Zeitschrift für Physiologiche Chemie," vol. 125 (1923), pp. 110–117; R Boissonas, "Helvetica Chimica Acta," vol. 31 (1948), pp. 1571–1576.

The following examples illustrate the practice of the invention without being limitative in any respect.

EXAMPLES

The salt-like constituents contained in the following, such as salt-like surface-active compounds, other organic salts as well as inorganic salts, are present as the sodium salts, unless otherwise stated. The expressions and abbreviations used have the following meanings:

"ABS" is the 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 alkylbezene thus formed.

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

"Fs-ester sulfonate" is a sulfonate obtained from the methyl ester of a hardened tallow fatty acid by sulfonation with SO_3.

"Olefin sulfonate" is a sulfonate obtained from mixtures of olefins with 12 to 18 carbon atoms by sulfonating with SO_3 and hydrolyzing the sulfonation product with an alkaline liquor, which sulfonate consists substantially of alkenesulfonate and hydroxyalkanesulfonate, but contains in addition small quantities of disulfonates.

Each olefin sulfonate-containing preparation was prepared by use of two different types of olefin sulfonate; one was prepared from a mixture of straight-chain terminal olefins and the other from a mixture of non-terminal olefins.

"KA-sulfate" and "TA-sulfate" are the salts of sulfated substantially saturated fatty alcohols, prepared by reduction of coconut fatty acid and tallow fatty acid, respectively.

"KA-EO-sulfate," "TA-EO-sulfate" and "OA-EO-sulfate" are the sulfated products of addition of 2 mols of ethylene oxide to 1 mol of coconut fatty alcohol, of 3 mols of ethylene oxide to 1 mol of tallow fatty alcohol and of 2 mols of ethylene oxide to 1 mol of oleyl alcohol, respectively.

"OA+5 EO," "OA+10 EO" and "NP+9.5 EO" are the products of addition of ethylene oxide (EO) to technical oleyl alcohol (OA) and nonylphenol (NP), respectively, the numbers representing the molar quantity of ethylene oxide added on to 1 mol of starting material.

"Fs-monoethanolamide" and "Fs-diethanolamide" are the corresponding amides of the C_{12-14} fraction from coconut fatty acid.

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

"NTA," "EDTA" and "HEDP" are the salts of nitrilotriacetic acid, ethylenediaminetetraacetic acid and hydroxyethanediphosphonic acid, respectively.

"CMC" is the salt of carboxymethylcellulose.

The composition of the fatty acid mixture from which the soap B was prepared, and the composition of fatty acid mixtures the soaps from which may be used instead of soap B, are seen from the following Table I.

TABLE I

	Percent weight of fatty acid constituent in the soap of—			
	B	C	D	G
Number of carbon atoms in the fatty acid:				
C_{10}	2	2	4	1
C_{12}	19	21	16	6
C_{14}	8	6	10	5
C_{16}	4	16	25	28
C_{18}	22	33	45	60
C_{20}	8	4	----	----
C_{22}	37	18	----	----
Iodine value of the fatty acid mixture	4	8	6	4

If the soap B in the formulations given below is replaced by the same quantity of the soaps C, D or G, washing compositions are obtained in which the foaming is somewhat less strongly inhibited.

Together with these soaps or in place of them, non-surface-active foam inhibitors can be used, for example, a mixture of about 45% of a di(alkylamino)-monochlorotriazine and about 55% of a N,N',N''-trialkylmelamine. In all these triazine derivatives the alkyl residues may be present as mixtures of homologs with 8 to 18 carbon atoms. The monochlorotriazine derivative or trialkylmelamine can also be used with a simliar result. Provided the described washing compositions contain synthetic sulfates or sulfonates together with soap, the other non-surface-active foam inhibitors mentioned in the description can be used, as for example, paraffin oil or paraffin. It is advisable to incorporate the non-surface-active foam inhibtior used separately in the washing composition, for example, dissolved in a suitable organic solvent or sprayed in the molten state on the moving powder by means of a nozzle.

The activators used were:

"TAGU" Tetraacetylglycoluril
"DADH" 1,3-diacetyl-5,5-dimethylhydantoin
"TAMD" N,N,N',N'-tetraacetyl-methylenediamine.

The following substances were used from the class of antimicrobial substances of the hydroxydiphenylether type according to the invention:

(I) 2,4,4'-trichloro-2-hydroxydiphenylether
(II) 2-hydroxy-3-tert.-butyl-5-carboxy-2',4',5'-trichlorodiphenylether
(III) 2-hydroxy-3-tert.-butyl-5-carbomethoxy-2',4',5'-trichlorodiphenylether
(IV) 2,2'-dihydroxy-diphenylether
(V) 2,2'-dihydroxy-3,3',5,5'-tetrabromodiphenylether.

In some experiments the three antimicrobial substances mentioned below were used for comparison purposes.

"TBBS" Mixture of 3,4',5-tribromo- and 4',5-dibromosalicylanilide
"BHTM" Bis-(2-hydroxy-3,5,6-trichlorophenyl)-methane
"TCC" 3,4,4'-trichlorocarbanilide.

The product according to Example 1 was prepared by mixing the individual constituents. In the case of the products according to Examples 2 to 8, a powder obtained by hot spray drying which contained no perborate, no activator, no antimicrobial substance and no enzymes, was admixed with the last mentioned substances.

In the large scale commercial production of such washing compositions it is advisable to use a coated activator and to incorporate the antimicrobial substance in the form of a premixture, which is obtained as a dry, more or less fine-grained granulate by spraying an aqueous suspension of the antimicrobial substance in the aqueous solution of an anionic surface-active compound on to a calcined salt, as for example, Na_2SO_4, $Na_4P_2O_7$ or $Na_5P_3O_{10}$.

The technical effect attained according to the invention can be demonstrated in the following way.

Using the products according to the invention, treatment baths of the concentrations given below are prepared at temperatures of 20° and 40° C. Sterile textile samples of cotton and woolen material, 1 x 1 cm. in size, were moved about in these treatment baths for 30 minutes at the given temperatures, then thoroughly rinsed twice with sterile water and subsequently dried at 50° C.

For the test on the microbiostatic properties the materials so treated were placed on Merck-Standard-I-agar inoculated with the test germs used in each case. After remaining for 30 minutes at this first place of contact, the textile sample was removed from the first place of contact and again placed on the surface of the agar broth for a second place of contact at a distance from the first place of contact. After 24 hours incubation at 37° C. it was evaluated.

On the agar broth, surfaces with a distinct inhibiting action of different nature and size showed at the two contact places, which served for the evaluation of the inhibiting action. At the first contact place the inhibiting action was decisive at the contact surface; a corona occurring in some cases at the first contact place outside the actual contact surface was included in the evaluation, since the evaluation point number was increased according to the given point scheme depending on the occurrence of a partial or complete inhibition.

At the second place of contact the evaluation depended exclusively on the size of the corona showing inhibition.

A point system served for the evaluation of the inhibiting action, the points given having the following meaning:

First place of contact:	Points
Uninhibted growth	0
Slightly checked growth	1
Distinctly checked growth	2
Distinctly checked growth with partial checking around the contact place	3
No growth	4
No growth with partial checking around the contact place	5
No growth with checking effect around the contact place	6
Second place of contact:	
No inhibited corona	0
Breadth of corona up to 3 mm.	1
Breadth of corona >3 to 6 mm.	2
Breadth of corona >6 to 9 mm.	3
Breadth of corona >9 to 12 mm.	4
Breadth of corona >12 to 15 mm.	5
Breadth of corona >15 mm.	6

All experiments were carried out as duplicate determinations. The results are seen from the tables associated with the following examples. The evaluation numbers are the sums of the point evaluations for the first and for the second place of contact. The sums of the point evaluations for the individual determinations are denoted by E, and the sume of the point evaluations of all individual determinations of a preparation are denoted by S.

Examples 1a–c

Products which are utilizable in the textile industry or in the industrial laundry as antimicrobial and bleaching additives for textile treatment baths as well as additionally in the home as antimicrobial and bleaching afterrinsing compositions for washed laundry were prepared with the following general composition:

30.00% by weight perborate
30.00% by weight activator
0.25 and 0.50% by weight antimicrobial substance I
30.00% by weight $Na_5P_3O_{10}$
8.50 and 8.75% by weight Na_2SO_4
1.00% by weight $MgSiO_3$

The antimicrobial properties of aqueous solutions of three products of this general composition, which contained as activators: a—TAGU, b—DADH, c—TAMD were tested by the above-described test method on pieces of cotton or wool material compared with those of similarly composed products which contained no activator and/or no antimicrobial substance, and in which these substances had been replaced by corresponding weights of Na_2SO_4. The concentration used in all cases was 4 gm./liter. The results thereby obtained are seen from the following Tables II and IIa.

Tables for Example 1a: Test results on use of a product according to Example 1a as well as corresponding products not containing TAGU and/or antimicrobial substance. Since duplicate tests were performed the highest valuation in points for E would be 12 and for S it would be 24.

TABLE II

	Evaluation numbers for test germ *Escherichia coli* at—											
	20° C.						40° C.					
	Without TAGU			With TAGU			Without TAGU			With TAGU		
	E	E	S	E	E	S	E	E	S	E	E	S
Percent weight of antimicrobial substance I	Cotton			Cotton			Cotton			Cotton		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	1	1	2	8	8	16	2	2	4	5	5	10
0.50	6	6	12	8	8	16	5	5	10	6	5	11
	Wool			Wool			Wool			Wool		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	2	1	3	3	3	6	8	8	16	8	6	14
0.50	4	4	8	6	6	12	9	8	17	9	9	18

TABLE IIa

Percent weight of antimicrobial substance I	Evaluation numbers for test germ *Staphylococcusaureus* at—											
	20° C.						40° C.					
	Without TAGU			With TAGU			Without TAGU			With TAGU		
	E	E	S	E	E	S	E	E	S	E	E	S
	Cotton			Cotton			Cotton			Cotton		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	2	2	4	9	10	19	3	2	5	10	10	20
0.50	4	3	7	9	10	19	4	9	13	10	10	20
	Wool			Wool			Wool			Wool		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	2	7	9	8	9	17	3	7	10	10	9	19
0.50	4	8	12	9	9	18	8	8	16	11	10	21

Examples 2a–c

Foam inhibited complete washing compositions, which may also be used at correspondingly lower temperatures as fine washing compositions or colored washing compositions, were prepared having the following general composition:

Percent by weight:

9.0	ABS.
0.5	OA+10EO.
3.2	KA+20EO.
2.2	Soap B.
4.0	$NA_2O \cdot 3.3SiO_2$.
42.0	$Na_5P_3O_{10}$.
15.0	Perborate.
15.0	Activator.
Percent by weight:	
1.3	CMC.
1.0	$MgSiO_3$.
0.25 and 0.5	Antimicrobial substance I.
0.7	Brightener.
5.85 and 5.6	Na_2SO_4 ($+H_2O$).

The antimicrobial activity of such washing compositions containing as activators, a: TAGU, b: DADH and c: TAMD, was compared, in the same way as in the case of the composition according to Example 1, with two washing compositions which contained no activator and/or no antimicrobial substance. The results are seen from the following Tables III and IIIa. Tables for Example 2a:

TABLE III

Percent weight of antimicrobial substance I	Evaluation numbers for test germ *Escherichia coli* at—											
	20° C.						40° C.					
	Without TAGU			With TAGU			Without TAGU			With TAGU		
	E	E	S	E	E	S	E	E	S	E	E	S
	Cotton			Cotton			Cotton			Cotton		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	0	0	0	2	3	5	1	1	2	3	2	5
0.50	2	3	5	3	3	6	3	3	6	6	4	10
	Wool			Wool			Wool			Wool		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	1	1	2	3	3	6	3	2	5	6	6	12
0.50	3	2	5	6	4	10	6	4	10	8	8	16

TABLE IIIa

Percent weight of antimicrobial substance I	Evaluation numbers for test germ *Staphylococcus aureus* at—											
	20° C.						40° C.					
	Without TAGU			With TAGU			Without TAGU			With TAGU		
	E	E	S	E	E	S	E	E	S	E	E	S
	Cotton			Cotton			Cotton			Cotton		
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	1	1	2	4	4	8	3	1	4	4	3	7
0.50	7	4	11	4	7	11	4	3	7	4	9	13
	Wool			Wool			Wool			Wool		
0.00	0	0	0	0	0	0	0	0	0	0	0	8
0.25	3	2	5	4	4	8	5	4	9	8	8	10
0.50	3	3	6	8	8	16	8	8	16	9	9	16

The same effect was found with the textile treatment compositions according to Examples 1b and 1c as with the washing compositions according to Examples 2b and 2c (activators DADH and TAMD respectively), although to a somewhat smaller extent.

Similar synergistic effects are also shown when the antimicrobial substance I in the textile treatment compositions according to Examples 1a–c are replaced by 2.5% or 5% by weight of the antimicrobial substance V, and by 2.0% or 3.5% by weight of said substance in the washing compositions according to Examples 2a–c. The antimicrobial substances II to IV are suitably used in amounts of 4 to 8% by weight.

For comparative purposes, products were also prepared which differed from those of Examples 1a–c and 2a–c only by the incorporated antimicrobial substances. In the products for comparison the antimicrobial substances were TBBS, BHTM and TCC, respectively. On testing these products for comparison in the way described above, a synergistic effect between per-compound, activator and antimicrobial substance would not be found. The evaluation figures were also substantially lower. Under the most favorable conditions evaluation figures of 5 at most were found.

Examples 3 to 8 give the formulations for washing compositions with the following applications:

Example 3—Prewashing composition
Example 4—Complete washing composition
Example 5—Special washing composition for delicate textiles
Example 6—Cold washing composition
Example 7—Fine washing composition
Example 8—Washing composition for industrial laundries.

TABLE IV

Constituents of the preparation	Percent weight of constituents in the preparation according to Example—					
	3	4	5	6	7	8
ABS				15.0	19.0	7.0
Olefinsulfonate			7.0			
KA-sulfate				5.0		
TA-EO-sulfate					3.5	
Soap B		3.5	2.5			
OA+5 EO	1.5					5.0
OA+10 EO	4.5		3.0			7.0
NP+9.5 EO		2.5				
Fs-monoethanolamide				2.5		
Fs-diethanolamide					1.5	
Na_2CO_3						6.0
$Na_2O \cdot 3.3\ SiO_2$	5.0	3.5	4.0		3.5	
$Na_4P_2O_7$				20.0		
$Na_5P_3O_{10}$	55.0	32.0	43.0		32.0	
$Na_2SO_4(+H_2O)$						32.0
Perborate	10.0	21.0	21.0	10.0	8.0	18.0
TAGU	5.0	15.0	2.5	10.0	2.0	16.0
Antimicrobial substance I	0.2	0.15	0.50	0.60	1.0	1.50
$MgSiO_3$		2.0				
EDTA	0.3	0.15	0.6			2.0
CMC	1.7	1.0	2.0	1.8	1.5	2.7
Brightener	0.18	0.30	0.40	0.28		
Enzymes	0.7	0.4				
Residue	15.92	10.50	13.50	34.82	28.00	2.80

The residue is primarily Na_2SO_4 with some water.

The activator TAGU used in the washing compositions according to Examples 3 to 8 may be replaced by other activators, especially by DADH or TAMD and the antimicrobial substance used therein may be replaced by other antimicrobial substances.

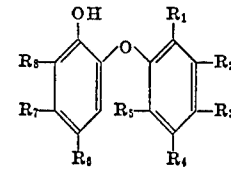
If the washing compositions are primarily intended for use at higher temperatures (washing compositions according to Examples 2, 4 and 8) the ABS may be partly replaced by TA-sulfate. If on the other hand the washing compositions are primarily intended for use at lower temperatures (Examples 6 and 7), a part of the ABS may be replaced by Fs-estersulfonate, OA- or KA-EO sulfate. In all washing compositions the synthetic detergent substances ABS or olefin sulfonate present may be wholly or partly replaced by alkanesulfonate. These changes in the surface-active component may obviously also alter the foaming power of the washing composition. This alteration of the foaming power, however, can be compensated by changing the quantity or type of the soap or by use of special foam inhibitors.

Known cotton brighteners, polyamide brighteners or polyester brighteners or optional combinations of these brighteners may be used. Suitable enzymes are preferably proteases from *Bacillus subtilis*. Amylasses may also be incorporated in their place or together with them.

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

We claim:

1. A synergistic bleaching textile treating composition with an antimicrobial action which is effective at temperatures below 70° C. to room temperature consisting essentially of (a) from 0.05% to 25% by weight of a 2-hydroxydiphenyl-ether of the formula:



wherein R_1 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and hydroxy; R_2 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and cyano; R_3 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, carbomethoxy and carboxyl; R_4, F_5 and R_7 are members selected from the group consisting of hydrogen, fluorine, chlorine and bromine; R_6 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, cyano, carbomethoxy and carboxylic; and R_8 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and tert. butyl; (b) from 25% to 80% by weight of a water-soluble inorganic per-compound yielding H_2O_2 in water; and (c) from 5% to 60% by weight of an activator for active oxygen selected from the group consisting of N-acyl and O-acyl compounds having acyls of carboxylic acids having 2 to 9 carbon atoms, carbonic acid esters and pyrocarbonic acid esters, said activator having an activating action of at least 3 in the Per-Acid Formation Test, wherein from 0.05 to 2 mols of activator are present per gram-atom of active oxygen of said per-compound.

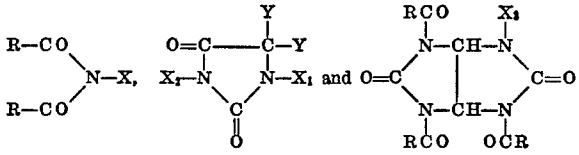
2. The textile treating composition of claim **1** wherein said component (a) is in an amount of from 0.1% to 10% by weight, said component (b) is present in an amount of from 30% to 70% by weight, said component (c) is present in an amount of from 20% to 50% by weight and has an activating action of at least 4.5 in the Per-Acid Formation Test, and wherein from 0.1 to 1 mol of activator are present per gram-atom of active oxygen of said per-compound.

3. The textile treating composition of claim **1** wherein said component (a) is 2',4,4'-trichloro-2-hydroxydiphenylether and is present in an amount of from 0.075% to 5% by weight.

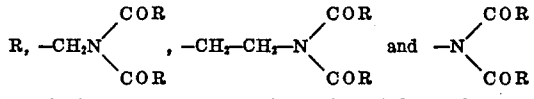
4. The textile treating composition of claim **1** wherein said inorganic per-compound is a sodium perborate.

5. The textile treating composition of claim **1** having a further content of from 1% to 8% by weight of a water-insoluble per-compound stabilizer.

6. The textile treating composition of claim 1 wherein said activator for active oxygen of component (c) is an N-acyl compound of the formulae:



wherein R represents a member selected from the group consisting of alkyl having 1 to 3 carbon atoms, chloroalkyl having 1 to 3 carbon atoms, phenyl, chlorophenyl, nitrophenyl, alkoxyphenyl having 1 to 2 carbon atoms in the alkoxy group and alkylphenyl having 7 to 8 carbon atoms, X represents a member selected from the group consisting of



X_1 and X_2 represent a member selected from the group consisting of RCO—, and R and lower alkoxycarbonylmethyl wherein at least one of X_1 and X_2 is RCO, Y represents a member selected from the group consisting of hydrogen and alkyl having 1 to 2 carbon atoms, and X_3 represents a member selected from the group consisting of R and RCO.

7. The textile treating composition of claim 1 wherein said activator for active oxygen is tetracetylglycoluril.

8. A bleaching antimicrobial rinsing agent consisting essentially of from 55% to 90% by weight of the textile treating composition of claim 1 and from 10% to 45% by weight of alkaline-reacting inorganic builders.

9. A bleaching antimicrobial soaking agent consisting essentially of from 10% to 45% by weight of the textile treating composition of claim 1, from 0.5% to 5% by weight of surface-active compounds selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds and amphoteric surface-active compounds, and from 50% to 89.5% of alkaline-reacting inorganic builders.

10. A bleaching antimicrobial washing agent consisting essentially of from 10% to 50% by weight of the textile treating composition of claim 1, from 5% to 40% by weight of surface-active compounds selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds, and amphoteric surface-active compounds, from 10% to 85% by weight of alkaline-reacting inorganic builders, and from 0 to 20% by weight of at least one other customary component of washing agents selected from the group consisting of organic complex-forming compounds, soil suspending agents, optical brighteners, enzymes, dyes, odorant compounds, non-surface-active foam inhibitors, foam stabilizers and water.

11. The textile treating composition of claim 2 wherein from 0.2 to 0.75 mol of activator are present per gram-atom of active oxygen of said per-compound.

12. The composition of claim 10 wherein said surface-active compound component has the following formulation:

0 to 100% by weight of surface-active compounds of the sulfonate and/or sulfate type with 8 to 18 carbon atoms in the hydrophobic residue
0 to 100% by weight of non-ionic surface-active compounds
0 to 100% by weight of soap
0 to 6% by weight of foam stabilizer and
0 to 8% by weight of foam inhibitor.

13. A composition as claimed in claim 10 in which the surface-active component has the following composition:

8% to 95% by weight of surface-active compounds of the sulfonate and/or sulfate type with 8 to 18 carbon atoms in the hydrophobic residue

0 to 80% by weight of soap provided that if soap is present, the proportion of (sulfonate+sulfate) to soap lies in the range from 10:1 to 1:10,
0 to 35% by weight of non-ionic surface-active compounds
0 to 6% by weight of foam stabilizers
0 to 8% by weight of non-surface-active foam inhibitors,

while the foaming power of the surface-active component is reduced either by simultaneous presence of surface-active compounds of the sulfonate and/or sulfate type and foam-inhibiting soap and/or by presence of the non-surface-active foam inhibitors.

14. A composition as claimed in claim 12 in which the surface-active component contains 25 to 65% by weight of surface-active compounds of the sulfonate and/or sulfate type.

15. A composition as claimed in claim 12 in which the surface-active component contains 5 to 40% by weight of non-ionic surface-active compounds.

16. A composition as claimed in claim 12 in which the surface-active component contains 10 to 50% by weight of soap.

17. A composition as claimed in claim 12 in which the surface-active component contains 0.5 to 3% by weight of foam stabilizer.

18. A composition as claimed in claim 12 in which the surface-active component contains 0.5 to 5% by weight of foam inhibitor.

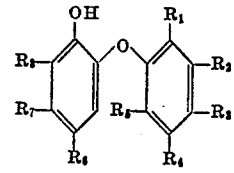
19. A composition as claimed in claim 13 in which the surface-active component contains 25 to 75% by weight of surface-active compounds of the sulfonate and/or sulfate type.

20. A composition as claimed in claim 13 in which the surface-active component contains from 10% to 50% by weight of soap and the proportion of (sulfonate+sulfate) to soap is from 5:1 to 1:2.

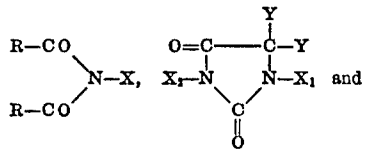
21. A composition as claimed in claim 13 in which the surface-active component contains 0.5 to 3% by weight of foam stabilizer.

22. A composition as claimed in claim 13 in which the surface-active component contains 0.5 to 5% by weight of foam inhibitor.

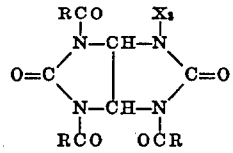
23. A synergistic bleaching textile treating composition with an antimicrobial action which is effective at temperatures below 70° C. to room temperature consisting essentially of (a) from 0.05% to 25% by weight of a 2-hydroxydiphenyl-ether of the formula:



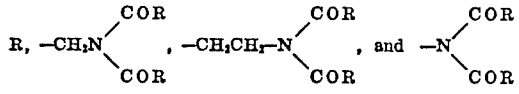
wherein R_1 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and hydroxy; R_2 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and cyano; R_3 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, carbomethoxy and carboxyl; R_4, R_5 and R_7 are members selected from the group consisting of hydrogen, fluorine, chlorine and bromine; R_6 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, cyano, carbomethoxy and carboxyl; and R_8 is a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine and tert. butyl; (b) from 25% to 80% by weight of a sodium perborate; and (c) from 5% to 60% by weight of an activator for active oxygen selected from N-acyl compounds of the formulae.



and



wherein R represents a member selected from the group consisting of alkyl having 1 to 3 carbon atoms, chloroalkyl having 1 to 3 carbon atoms, phenyl, chlorophenyl, nitrophenyl, alkoxyphenyl having 1 to 2 carbon atoms in the alkoxy group and alkylphenyl having 7 to 8 carbon atoms, X represents a member selected from the group consisting of



X_1 and X_2 represent a member selected from the group consisting of RCO—, and R and lower alkoxycarbonylmethyl wherein at least one of X_1 and X_2 is RCO, Y represents a member selected from the group consisting of hydrogen and alkyl having 1 to 2 carbon atoms, and X_3 represents a member selected from the group consisting of R and RCO, said activator having an activating action of at least 3 in the Per-Acid Formation Test, wherein from 0.05 to 2 mols of activator are present per gram-atom of active oxygen of said per-compound.

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MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—99, 106; 260—613; 424—340, 341