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[54] WASHING, RINSING AND CLEANSING
AGENT COMPOSITIONS CONTAINING
FURAN-MALEIC ANHYDRIDE
COPOLYMER SEQUESTERING AGENTS

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[57] ABSTRACT

Washing, rinsing and cleansing agent compositions containing from 5 to 95 percent by weight of the usual ingredients and from 95 to 5 percent by weight of copolymer-carboxylate sequestering agents capable of sequestering alkaline earth metal ions prepared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymer-carboxylate sequestering agents being present as water-soluble salts capable of complex formation with alkaline earth metal ions. The invention also resides in the process of sequestering alkaline earth metal ions using aqueous solutions of the washing, rinsing and cleansing agent compositions.

16 Claims, No Drawings

WASHING, RINSING AND CLEANSING AGENT COMPOSITIONS CONTAINING FURAN-MALEIC ANHYDRIDE COPOLYMER SEQUESTERING AGENTS

THE PRIOR ART

The effect of the known washing, rinsing and cleansing agent compositions is based to a substantial part on the presence of inorganic or organic sequestering agents for alkaline earth metal ions. These sequestering agents support the effect of other non-sequestering inorganic or organic cleaning substances. To such sequestering agents belong, for example, sodium tripolyphosphate or various organic sequestering agents of the type of the phosphonates or of the aminopolycarboxylic acids. The use of these sequestering agents in washing, rinsing and cleansing agents has been criticized publicly in connection with questions of ecology. The still strongly controversial opinion has been expressed thereby, that the nourishing of the waters and the excessive growth of algae, connected with it, is derived largely from the phosphorus or nitrogen containing compounds that come through such washing and cleansing agent compositions into the waters. Therefore, a demand has been made for washing, rinsing and cleansing agent compositions that contain ingredients innocuous in regard to waste water biology.

OBJECTS OF THE INVENTION

An object of the invention is to replace the known inorganic or organic sequestering agents, containing phosphorus and/or nitrogen, wholly or partly, by sequestering agents that do not contain such chemical elements and possess beyond that a good washing and cleansing power.

A further object of the present invention is the development of washing, rinsing and cleansing compositions consisting essentially of (a) from 5 to 95 percent by weight of at least one compound having a cleaning action selected from the group consisting of (1) anionic surface-active compounds, non-ionic surface-active compounds, amphoteric surface active compounds, and mixtures thereof, (2) organic builder salts and inorganic builder salts, and (3) mixtures of (1) and (2), and (b) from 95 to 5 percent by weight of at least one copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions prepared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymer-carboxylate sequestering agents being present as water-soluble salts capable of complex formation with alkaline earth metal ions.

A yet further object of the present invention is the development in the process of washing, rinsing and cleansing solid materials which comprises contacting solid materials having soil thereon with an aqueous solution containing from 0.5 to 80 gms/liter of a cleansing agent consisting of from 5 to 95 percent of at least one compound having a cleaning action and from 95 to 5 percent of a sequestering agent capable of sequestering alkaline earth metal ions, for a time sufficient to disperse and dissolve said soil in said aqueous solution and removing said cleansed solid materials, the improvement consisting of utilizing, as said sequestering agent, at least one copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions pre-

pared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymer-carboxylate sequestering agents being present as water soluble salt capable of complex formation with alkaline earth metal ions.

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

DESCRIPTION OF THE INVENTION

This invention relates to washing, rinsing or cleansing agents, containing sequestering agents for alkaline earth metal ions, being present as solids, pastes, dispersions or solutions, of the following composition, based on the products free of water and/or solvents:

5 to 95 percent by weight of polymers prepared from approximately equal molar amounts of maleic acid and furan having a molecular weight of about 300 to 20,000, preferably 500 to 5,000, said polymers being present preferably in the form of their water-soluble salts capable of sequestering or of complex formation with alkaline earth metal ions, and

95 to 5 percent by weight of other customary ingredients of washing, rinsing and cleansing agents, particularly of organic or inorganic compounds having a cleaning action.

Preferably, the compositions of the invention are washing, rinsing and cleansing compositions consisting essentially of (a) from 5 to 95 percent by weight of at least one compound having a cleaning action selected from the group consisting of (1) anionic surface-active compounds, non-ionic surface-active compounds, amphoteric surface-active compounds, and mixtures thereof, (2) organic builder salts and inorganic builder salts, and (3) mixtures of (1) and (2), and (b) from 95 to 5 percent by weight of at least one copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions prepared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymercarboxylate sequestering agents being present as water-soluble salts capable of complex formation with alkaline earth metal ions. The copolymer-carboxylate may also be employed in their free acid form; however, since the copolymer as polymerized contains acid anhydride groups, it is preferable to convert the same to the water-soluble salts capable of sequestering alkaline earth metal ions.

In addition to the copolymer-carboxylate sequestering agents, the washing, rinsing and cleansing compositions of the invention contain at least one substance with a cleaning action. This consists of an inorganic or organic builder salt or a surface-active basic detergent substance or a combination of these. The agents usually contain several such substances having a cleaning action, the types of which depend on the ultimate use of the agents.

When the agents, according to the invention, are solids, they are mostly present as fine to grainy powders, as agglomerates or granulates. Such agents can be practically anhydrous; but they can also contain water of crystallization or water of hydration. The agents of the invention may, however, also be utilized in the form of pastes, dispersions or solutions. In these forms, they contain smaller or larger amounts of liquid solvents, such as water or organic water-soluble solvents in which the other ingredients are dissolved partly or

completely. For certain cleaning purposes, for example, solutions can be used that contain up to 1 percent by weight, preferably up to 4 percent by weight, of the solid agent. The solutions, dispersions or pastes may also be substantially more concentrated, so that the amounts of the solvent constitutes up to 30 percent by weight, preferably up to 50 percent by weight. Into the solutions, dispersions or pastes also hydrotropic substances may be incorporated.

The present invention, therefore, also includes in the process of washing, rinsing and cleansing solid materials which comprises contacting solid materials having soil thereon with an aqueous solution containing from 0.5 to 80 gms/liter of a cleansing agent consisting of from 5 to 95 percent of at least one compound having a cleaning action and from 95 to 5 percent of a sequestering agent capable of sequestering alkaline earth metal ions, for a time sufficient to disperse and dissolve said soil in said aqueous solution and removing said cleansed solid materials, the improvement consisting of utilizing, as said sequestering agent, at least one copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions prepared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymer-carboxylate sequestering agents being present as water-soluble salts capable of complex formation with alkaline earth metal ions.

The polymers of the above definition that can be used according to the invention, particularly their salts, hereafter called "copolymers," are described in the "Journal of Macromolecular Science-Chemistry," Vol. A 4(1), pages 52 to 54. The products can be obtained by copolymerization of about equimolar amounts of furan and maleic acid anhydride or by polymerization of the Diels-Alder adduct of furan and maleic acid anhydride, for example, by reaction in a benzene solution with azobisisobutyronitrile as a catalyst. The polymers thus obtained are converted into their salts by saponification with inorganic or organic bases.

These copolymer compounds are preferably utilized as the sodium salts. They can also be present as other alkali metal salts such as potassium salts or as ammonium salts, as well as water-soluble salts of organic bases, particularly of the alkyl amines or alkylolamines with at most 6 carbon atoms in the molecule, for instance, as salts of di- or trimethylamine, mono-, di- or triethylamine, mono-, di- or triethanolamine, mono- or dihydroxypropylamine, etc.

Copolymer-Sodium Salt

230 gm of a polymer produced by polymerization of 1,2,3,6-tetrahydro-3,6-epoxy-phthalic acid anhydride with an average molecular weight of about 4000, were suspended in an eight-fold amount of water and stirred at 70°C for a length of time (about 1 hour) until a clear solution was obtained. Then the solution was adjusted to a pH of 8 to 9 with a 20 percent aqueous solution of sodium hydroxide, filtered, and the filtrate was evaporated to dryness. The preparation obtained after drying had a Hampshire Test Value of 610.

Copolymer-Ammonium Salt

A suspension of 200 gm of a product obtained by copolymerization of equimolar amounts of maleic acid anhydride and furan, with an average molecular weight of 2500 was stirred in 1.8 liters of water at 70°C until a clear solution was obtained. The solution was adjusted to a pH of 8 to 9 with concentrated aqueous am-

moniz, and ammonia, ammonium salt was precipitated by the addition of ethanol. The ammonium salt thus obtained had a Hampshire Test Value of 500.

The Hampshire Test Value is a measure for the calcium carbonate-binding power. An exact description of the method of determination is found in the "Hampshire NTA Technical Bulletin," appendix p.A2 (June 1960) by Hampshire Chemical Corp.

The washing, rinsing or cleansing agent compositions of the invention may be applied in numerous fields of technical nature as well as of the home for the most varied cleaning problems. Examples for such fields of application are the cleaning of instruments, apparatus pipe lines and vessels of wood, plastics, metal, ceramics, glass, etc. in the industry or in commercial plants, the cleaning of furniture, walls, floors, of objects of ceramics, glass, metal, wood, plastics, the cleaning of polished or lacquered surfaces in the home, etc. A particularly important application field is the washing and bleaching of textiles of any kind, as well as the automatic cleaning of dishes in industry, in commercial plants and in the home. In all these cleaning problems the above-defined copolymer-carboxylates are distinguished by a good sequestering power for alkaline earth metal ions and by a good cleansing and washing power.

The composition of the products of the invention can be very different, according to their application field. For the industrial cleaning of the surfaces of solid materials, with the exception of textiles, for instance the products of the following composition are suitable:

- 5 to 30 percent by weight of the copolymer-carboxylates
- 10 to 30 percent by weight of alkali metal silicates
- 10 to 40 percent by weight of caustic alkalis
- 0 to 10 percent by weight of surface-active compounds.

These agents may besides contain alkaline- or neutral-reacting salts, corrosion inhibitors, disinfectants, other sequestering agents, particularly for heavy metals, and other customary ingredients of such agents. As cleaning agents for the production sector of the metal industry, for instance, products of the following composition are suitable:

- 10 to 30 percent by weight of the copolymer-carboxylates
- 10 to 30 percent by weight of alkali metal silicates
- 10 to 40 percent by weight of caustic alkalis
- 0 to 10 percent by weight of tensides.

As cleaners for the food industry, compounds of the following composition are suitable:

- 5 to 30 percent by weight of the copolymer-carboxylates
- 10 to 20 percent by weight of alkali metal silicates
- 40 to 80 percent by weight of caustic alkalis
- 0 to 5 percent by weight of tensides

As cleaning agents for the automatic dishwashing in commercial and home dishwashing machines the preparations of the following composition are usable:

- 5 to 90 percent by weight of the copolymer-carboxylates
- 95 to 5 percent by weight of water-soluble alkali metal silicates
- 0 to 20 percent by weight of alkali metal hydroxides or alkali metal carbonates
- 0 to 10 percent by weight of low-foaming nonionic tensides 0 to 25 percent by weight of other custom-

ary ingredients of dishwashing agents, such as active-chlorine compounds, enzymes, sequestering agents for heavy metals, dyes and perfumes.

While the preparations containing caustic alkalis are used mostly in the industry or commercial plants, and for machine dishwashing, the preparations used for these purposes in the home or for the soaking, washing and bleaching of textiles in the industry, in commercial laundries or in the home, contain no caustic alkalis, and their 1 percent aqueous solutions have a pH-value of a maximum of 11.5.

The soaking, prewashing, fine-washing, washing and bleaching agent compositions, according to the invention, containing copolymer-carboxylates, can be used with textiles derived from the most varied fibers of natural or synthetic origin. To them belong, for instance, cotton, viscose or linen as well as textiles, that contain highly processed cotton or synthetic fibers, such as polyamide, polyester, polyacrylonitrile, polyurethane, polyvinyl chloride or polyvinylidene chloride fibers. The washing agent compositions of the invention can also be used for laundering of textiles, designated as "easy care," occasionally also as "no-iron," of synthetic fiber-cotton-mixed fabrics.

The composition of these agents, possessing in a 1 percent aqueous solution a pH-value of at most 11.5, is within the range of the following recipe:

0 to 80 percent, preferably 5 to 40 percent by weight, of a tenside component, consisting of anionic and/or amphoteric and/or nonionic tensides

5 to 95 percent, preferably 10 to 80 percent by weight, of the copolymer-carboxylates, serving as builders

95 percent to 0, preferably 90 to 20 percent by weight, of other inorganic and/or organic builders as well as optionally of a bleaching agent

0 to 30 percent, preferably 1 to 25 percent by weight, of other customary ingredients of washing and cleansing agents.

To the other customary washing and cleansing agent ingredients belong, for example, foam stabilizers, nontenside foam inhibitors, brighteners, antimicrobials, enzymes, dyes and perfumes. The bleaching component consists of bleaching-active, active chlorine or active oxygen compounds and optionally of activators and/or stabilizers for them.

With the use of the above-defined copolymer-carboxylates which contain no phosphorus or nitrogen and which are non-toxic to fish, the up-to-now used or suggested in the literature, phosphorus and/or nitrogen containing sequestering builders can be partly or completely replaced.

If the condensed phosphates, such as sodium tripolyphosphate as well as organic sequestering agents, containing phosphorus and/or nitrogen, are replaced in the present commercial agents, for instance, one-half by the copolymer-carboxylates and optionally by other conventional builders, free of P and/or N, this leads in the application in the conventional washing and cleansing liquors, already to a considerable reduction of the P and/or N concentration in the waste waters.

The sequestering power of the copolymer-carboxylates is particularly pronounced with respect to the alkaline earth metals, so that they can support and enhance the washing and cleansing processes. On the other hand, their sequestering power for heavy metals is, likewise as in other known sequestering builders,

only slight. It is, therefore, recommended to add to the agents, according to the invention, such sequestering agents for heavy metals in slight amounts of, for instance, from 0.1 to 5 percent, preferably 0.1 to 2 percent by weight. As sequestering agents for heavy metals, particularly for copper, for instance, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid or aminotriethylidene-diphosphonic acid or their salts are suitable.

In the washing agent compositions, according to the invention, to which particularly belong the pre-, fine- and boiling-washing agents, the tenside component contains preferably at least 50 percent by weight of anionic tensides. Under anionic tensides, substantially surface-active sulfates and/or sulfonates and/or soaps are to be understood. The amount of builders, including the copolymer-carboxylates, constitutes preferably from 0.5- to 7-fold, and particularly from 1- to 5-fold of the total tenside component. If the invention preparations contain more than 40 percent by weight of the tenside component, they are mostly used for commercial purposes, for instance in laundries and in the textile industry, where they are rarely applied alone, more frequently in combination with other conventional additives.

The composition of powdery preparations, according to the invention, used particularly as washing or cleansing agents, is generally in the range of the following recipe:

5 to 50 percent, preferably 8 to 40 percent by weight of a tenside component, consisting substantially of anionic and/or amphoteric and/or nonionic tensides as well as, optionally, of one or more of the following substances:

0 to 10 percent, preferably 0.5 to 8 percent by weight of the tenside component, of foam stabilizers,

0 to 10 percent, preferably 0.5 to 8 percent by weight of the tenside component, of nontenside foam inhibitors,

95 to 5 percent, preferably 92 to 10 percent by weight of the copolymer-carboxylates.

0 to 90 percent, preferably 5 to 82 percent by weight of inorganic and/or other organic builders as well as optionally of bleaching components and

0 to 30 percent, preferably 1 to 15 percent weight of other washing agent ingredients, such as soil-suspending agents, textile softeners, anti-microbial agents, enzymes, optical brighteners, dyes and perfumes, water.

The tenside component consists preferably at least to 50 percent by weight of anionic tensides from the group of the alkylbenzenesulfonates, alkanesulfonates, fatty-acid ester sulfonates, olefinsulfonates, fatty alcohol or fatty alcoholglycoether sulfates and of the soaps. Foam-suppressing washing agents, according to the preceding formula, suitable for use in drum-washing machines, contain either a combination of tensides of the sulfonate and/or sulfate type and soap in the quantitative ratio of from 30:1 to 1:5, preferably from 20:1 to 1:2 and/or a non-tenside foam inhibitor. The foam suppression is particularly pronounced, if the soap portion contains at least 5 percent and preferably at least 10 percent by weight of soaps from saturated fatty acids with 20 to 24, preferably 20 to 22 carbon atoms.

The bleaching component amounts mostly to 5 to 40 percent, preferably 7 to 35 percent by weight of the total washing agent.

The powdery washing, rinsing and cleansing agent compositions can be produced by various known methods. Thus, for example, the single ingredients, present as more or less fine powders or as granulates, can be mixed with each other. According to the presently technically preferred production method for washing and cleansing agents, an aqueous mixture of those ingredients which are insensitive to water and heat, is dried in a known manner, for instance, on hot surfaces or in a hot airstream. To the powder obtained, further ingredients, which by such a processing could lose their effect completely or partly, are admixed. To them belong, for example, foam inhibitors, bleaching agents, enzymes, anti-microbial agents, dyes and perfumes, etc. In addition, it is optionally of advantage, particularly for the protective incorporation of smaller amounts of substances, to convert them by admixing them with a part of the builders to a dry, powdery pre-product, which is then admixed in a conventional way to the washing and cleansing powder.

In the following, the ingredients contained in the washing, rinsing and cleansing agent compositions according to the invention, as arranged by substance classes, are described more particularly.

The tensides contain in the molecular at least one hydrophobic residue of mostly eight to 26, preferably 10 to 22 and especially 12 to 18 carbon atoms, and least one anionic, nonionic 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 groups or through intermediate members, such as through benzene rings, carboxylic-acid ester links, carbonamide links or sulfonic-acid amide links as well as through ether- or ester-like residues of polyhydric alcohols.

Soaps, which are derived from natural or synthetic fatty acids, possibly also from resin acids or naphthenic acids, are utilizable as anionic detergent substances, especially if these acids have iodine values of not more than 30 and preferably less than 10. Among the synthetic anionic tensides, the sulfonates and sulfates possess particularly practical importance.

The sulfonates include, for example, alkylbenzenesulfonates with preferably straight-chain C_{9-15} , especially C_{10-14} alkyl residues, alkanesulfonates, obtainable from preferably saturated aliphatic C_{8-18} , especially C_{12-18} hydrocarbons by sulfochlorination or sulfoxidation, mixtures of alkenesulfonates, hydroxyalkanesulfonates and alkanedisulfonates, known under the name of "olefinsulfonates," which are formed by acidic or alkaline hydrolysis of the sulfonation products which first result from terminal or non-terminal C_{8-18} and preferably C_{12-18} olefins by sulfonation with sulfur trioxide. The sulfonates, utilizable according to the invention, include also salts, preferably alkali metal salts of α -sulfo fatty acids and salts of esters of these acids with mono or polyhydric alcohols with one to four, and preferably one to two carbon atoms.

Further useful sulfonates are salts of fatty acid esters of hydroxyethanesulfonic acid or of dihydroxypropanesulfonic acid, the salts of the fatty alcohol esters of lower aliphatic or aromatic sulfomono- or dicarboxylic acids, containing one to eight carbon atoms, the alkyl-

glycerylether sulfonates and the salts of the amide-like condensation products of fatty acids or sulfonic acids with aminoethanesulfonic acid.

Tensides of the sulfate type include fatty alcohol sulfates, especially those derived from coconut fatty alcohols, tallow fatty alcohols or from oleyl alcohol, also sulfatized 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 with 0.5 to 20, preferably one to eight, and particularly two to four ethylene and/or propyleneglycol residues in the molecule.

As anionic tensides of the carboxylate type, for example, the fatty acid esters or fatty alcohol ethers of hydroxycarboxylic acids, are suitable as well as the amide-like condensation products of fatty acids or sulfonic acids with aminocarboxylic acids, such as glycocoll, sarcosine or with protein hydrolysates.

The anionic tensides are mostly present as salts of the alkali metals, particularly of sodium, as well as the ammonium salts and salts of lower alkylamines or lower alkylolamines.

The nonionic tensides, for the sake of simplicity called hereafter "Nonionics," include the polyethyleneglycol ethers, obtained by addition of from four to 100, preferably six to 40 and especially eight to 20 mols of ethylene oxide to fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty acid amides or sulfonic acid amides, as well as the still water-soluble adducts of propylene oxide or butylene oxide to the above. Furthermore, products known by the trade name "Pluronics" or "Tetronics" belong to the Nonionics. These products are obtained from water-insoluble polypropyleneglycols or from water-insoluble propoxylated lower aliphatic alcohols with one to eight, preferably three to six carbon atoms, or from water-insoluble propoxylated lower alkylenediamines, by ethoxylation until water-soluble. Finally, the partly water-soluble reaction products of the above-named aliphatic alcohols with propylene oxide, known as "Ucon-Fluid" can also be used as Nonionics.

Further useful Nonionics are fatty acid alkylolamides of sulfonic acid alkylolamides, derived, for example, from mono- or diethanolamine, from dihydroxypropyl amine or other polyhydroxyalkyl amines, such as the glycamines. Also the oxides of higher tertiary amines with a hydrophobic alkyl residue and two shorter alkyl and/or alkylol residues, with up to four carbon atoms each, can be considered as Nonionics.

Amphoteric tensides contain in the molecule both acidic groups, such as carboxyl, sulfonic acid, sulfuric acid half esters, phosphonic acid and phosphoric acid partial ester groups, and also basic groups, such as primary, secondary, tertiary and quaternary ammonium groups. Amphoteric compounds with quaternary ammonium groups belong to the type of the betaines. Carboxy, sulfate and sulfonate betaines have a particularly practical interest because of their good compatibility with other tensides.

The foaming powder of the tenside can be increased or reduced by combination of suitable tenside types, as well as changed by additions of non-tenside organic substances.

Suitable foam stabilizers, particularly in tensides of the sulfonate or sulfate type, are surface-active carboxy or sulfobetaines, as well as the above-named non-ionics of the alkylolamide type. Moreover, fatty alcohols or

higher terminal diols have been suggested for this purpose.

A reduced foaming power, that is desirable for the use in washing machines, is often attained by combination of different tenside types, such as of sulfates and/or sulfonates and/or of nonionics, on the one hand, with soaps, on the other hand. In soaps, the foam inhibition increases with the degree of saturation and the number of carbons in the fatty acid residue. Soaps derived from saturated C_{20-24} fatty acids have been proven good as foam inhibitors.

The non-tenside foam inhibitors included N-alkylated aminotriazines, optionally containing chlorine, which are obtained by the reaction of 1 mol of cyanuric acid chloride with 2 to 3 mols of a mono- and/or dialkylamine with six to 20, preferably eight to 18 carbon atoms in the alkyl radicals. Similarly effective are propoxylated and/or butoxylated aminotriazines, such as, products that are obtained by the addition of from 5 to 10 mols of propylene oxide to 1 mol of melamine and further addition of from 10 to 50 mols of butylene oxide to this propylene-oxide derivative.

Other non-tenside foam inhibitors are water-insoluble organic compounds, such as paraffins or halogenated paraffins with melting points below 100°C , aliphatic C_{18} to C_{40} ketones as well as aliphatic carboxylic acid esters which contain in the acid or alcohol residue, optionally also in both of these residues, at least 18 carbon atoms (such as triglyceride or fatty acid/fatty alcohol esters). These compounds can be used for the inhibition of foam, above all in combinations of tensides of the sulfate and/or sulfonate type with soaps.

As particularly low-foaming nonionics which can be used both alone, and also in combination with anionic, amphoteric and nonionic tensides and to reduce the foaming power of better foaming tensides, addition products of propylene oxide to the above-described surface-active polyethyleneglycol ethers are suitable as well as the also above-described "Pluronic," "Tetric" and "Ucon-Fluid" types.

All weakly acidic, neutral and alkaline reacting organic or organic salts, particularly inorganic or organic sequestering agents, are suitable as builders.

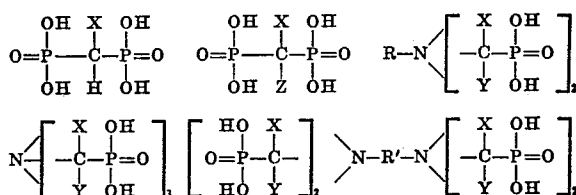
Weakly acidic, neutral or alkaline reacting salts usable according to the invention are, for example, the bicarbonates, carbonates, borates or silicates of the alkali metals, also mono-, di- or trialkali metal orthophosphates, di- or tetraalkali metal pyrophosphates, alkali metal metaphosphates known as sequestering agents, alkali metal sulfates as well as the alkali metal salts of organic non-surface-active sulfonic acids, carboxylic acids and sulfocarboxylic acids, containing from one to eight carbon atoms. To them belong, for instance, the water-soluble salts of benzene-, toluene- or xylene-sulfonic acid, water-soluble salts of sulfoacetic acid, sulfobenzoic acid or salts of sulfodicarboxylic acids as well as the salts of the acetic acid, lactic acid, citric acid and tartaric acid.

Further usable as builders are the water-soluble salts, such as the alkali metal salts, of higher-molecular weight polycarboxylic acids, particularly polymerizates of maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, methylenemalononic acid and citraconic acid. Also mixed polymerizates of these acids with each other, or with other polymerizable substances, such as, ethylene, propylene, acrylic acid, methacrylic acid, crotonic acid, 3-butenecarboxylic acid,

3-methyl-3-butenecarboxylic acid as well as with vinyl-methyl ether, vinyl acetate, isobutylene, acrylamide and styrene, are usable.

Also suitable as sequestering builders are the alkaline reacting polyphosphates, particularly tripolyphosphate.

The organic sequestering agents include, for example, nitrilotriacetic acid, ethylenediaminetetraacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid, polyalkylene-polyamine-N-polycarboxylic acids and other known organic sequestering agents. Also combinations of different sequestering agents may be used. The other known sequestering agents include also di- and polyphosphonic acids of the following constitutions:



wherein R represents alkyl and R' represents alkylene residues with one to eight, preferably one to four carbon atoms; X and Y represent hydrogen atoms or alkyl radicals with one to four carbon atoms and Z represents the groups -OH, -NH₂ or -NXR. For a practical use, the following compounds are considered above all: methylenediphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, 1-aminoethane-amino-tri-(methylenephosphonic acid), -diphosphonic acid, amino-tri-(methylelephosphonic methylamino- or ethylamino-di-(methylenephosphonic acid), and ethylenediaminetetra-(methylenephosphonic acid). All these sequestering agents may be present as free acids, or preferably as their alkali metal salts.

The higher molecular weight polycarboxylic acids that are suitable as sequestering builders also include the practically uncross-linked polyhydroxycarboxylic acids and polyaldehydecaboxylic acids containing primarily C—C bonds in the principal chain, which are composed substantially of ethylene units with one carboxyl-, formyl-, hydroxymethyl- or hydroxyl group each. The polyhydroxycarboxylic acids have a ratio of carboxyl groups to hydroxyl groups of 1.1 to 1.5, preferably two to nine, and a degree of polymerization of preferably three to 600 units. They can be produced, for example, by copolymerization of acrolein and acrylic acid in the presence of hydrogen peroxide and subsequent Cannizzaro reaction.

The polyaldehydecaboxylic acids have a ratio of carboxyl to formyl groups of at least one, and a degree of polymerization of preferably three to 100 units, optionally the polymers have terminal hydroxyl groups. They can be produced, for example, by oxidative-polymerization of acrolein with hydrogen peroxide.

Soil-suspending agents which keep the dirt, loosened from the fiber, suspended in the liquor, and thus preventing graying, can also be utilized in the washing agents and washing auxiliaries of the invention. For this, water-soluble colloids, mostly organic in nature, are suitable, such as the water-soluble salts of polymeric carboxylic acids, glue, gelatins, salts of ethercarboxylic acids or ethersulfonic acids of starch or cellu-

lose or salts of acidic sulfuric acid esters of cellulose or starch. Also water-soluble polyamides, containing acidic groups, are suitable for this purpose. Furthermore, soluble starch preparations and starch products other than the above-named, such as degraded starch, aldehyde starches, etc. may be used. Also polyvinylpyrrolidone is usable.

The ingredients of the washing agents and washing auxiliaries of the invention, particularly the builders are mostly so selected, that the preparations react neutral to distinctly alkaline in aqueous solution. Preferably, the pH-value of a 1 percent solution of the preparation mostly lies in the range from seven to a maximum of 11.5. Fine-washing agents have mostly a neutral to weakly alkaline reaction (pH-value = 7 to 9.5), while soaking, pre-washing and boiling-washing agents are more strongly alkaline (pH-value = 9.5 to 11.5, preferably 10 to 11).

Among the compounds serving as bleaching agents, releasing H_2O_2 in water, sodium perborate tetrahydrate ($NaBO_2 \cdot H_2O_2 \cdot 3 H_2O$) and the monohydrate ($NaBO_2 \cdot H_2O_2$) have particularly practical importance. But also other H_2O_2 releasing borates are usable, such as perborax $Na_2B_4O_7 \cdot 4H_2O$. These compounds may partly or completely be replaced by other carriers of active oxygen, particularly by peroxyhydrates, such as percarbonates, ($Na_2CO_3 \cdot 1.5H_2O_2$), perpyrophosphates, citrate perhydrate, percarbamide or melamine- H_2O_2 compounds as well as by H_2O_2 releasing peracidic salts, such as caroates ($KHSO_5$), perbenzoates or perphthalates.

It is recommended to incorporate conventional water-soluble and/or water-insoluble stabilizers for percompounds in amounts from 0.25 percent to 10 percent by weight. Water-insoluble percompound stabilizers, which amount to, for example, from 1 to 8 percent, preferably 2 to 7 percent of the weight of the whole preparation, are, for example, the magnesium silicates, mostly obtained by precipitation from aqueous solutions, $MgO : SiO_2 = 4:1$ to $1:4$, preferably $2:1$ to $1:2$ and particularly $1:1$. In their place, other alkaline earth metal, cadmium or tin silicates of a corresponding composition are usable. Also water containing oxides of tin are suitable as stabilizers. Water-soluble stabilizers which may be present together with the water-insoluble ones, are the organic sequestering agents whose quantity may amount to 0.25 to 5 percent, preferably 0.5 to 2.5 percent of the weight of the whole preparation.

The active chlorine compounds, serving as bleaching agents, may be inorganic or organic.

The inorganic active-chlorine compounds include alkali metal hypochlorites, which can be used particularly in the form of their mixed salts or addition compounds to orthophosphates or to condensed phosphates, such as to pyro and polyphosphates or to alkali metal silicates. If the washing and cleansing agents of the invention contain monopersulfates and chlorides, in aqueous solution active chlorine is formed.

As organic active-chlorine compounds, particularly the N-chlorinated compounds are of interest, in which one or two chlorine atoms are bound to one nitrogen atom, while the third valence of the nitrogen atoms is bonded to an electrophilic, particularly to a CO- or SO_2 - group. These compounds include dichloro- and trichlorocyanuric acid or their salts, chlorinated alkylguanides or alkylbiguanides, chlorinated hydantoins and chlorinated melamines.

Certain N-acyl-O-acyl compounds, forming with the H_2O_2 organic peracids, as well as carbonic acid or pyrocarbonic acid esters, whose activation value for the percompounds (= titer) is at least three, preferably at least 4.5, serve as activators for the percompounds, releasing H_2O_2 in water. This activation value is determined in the following manner.

Solutions that contain 0.615 gm/liter of $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$ (4 m mol/liter) and 2.5 gm/liter of $Na_2P_2O_7 \cdot 10 H_2O$ are treated, after heating to $60^\circ C$, with 4 m mol/liter of activator and kept for 5 minutes at this temperature 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 the addition of 0.35 gm of potassium iodide, with 0.1N sodium thiosulfate solution with starch as indicator. The amount of thiosulfate solution used in ml is the activation value (= titer). At a 100 percent activation of the peroxide used, it would amount to 8.0 ml.

Of the types of activators described below, particularly those compounds are suitable which have a melting point of at least $70^\circ C$, preferably at least $100^\circ C$, and especially at least $150^\circ C$. Furthermore, the equivalent weight of these compounds (under equivalent weight is here understood the quotient from the molecular weight and the number of acyl residues, or carbonic acid or pyrocarbonic acid residues in the molecule) should be at most 170, preferably at most 130 and especially at most 110.

The activators, usable according to the invention, include:

- the N-diacylated and N,N'-tetraacylated amines, such as N,N,N',N'-tetraacetyl-methylenediamine, N,N,N',N'-tetraacetyl-ethylenediamine, N,N-diacetylaniline and N,N-diacetyl-p-toluidine or 1,3-diacylated hydantoins, such as the compounds 1,3-diacetyl-5,5-dimethylhydantoin and 1,3-dipropionyl-hydantoin;
- the N-alkyl-N-sulfonyl-carbonamides, for example, the compounds N-methyl-N-mesyl-acetamide, N-methyl-N-mesyl-benzamide, N-methyl-N-mesyl-p-nitrobenzamide and N-methyl-N-mesyl-p-methoxybenzamide;
- The N-acylated cyclic hydrazides, acylated triazoles or urazoles, such as the monoacetylmaleic acid hydrazide;
- the O,N,N,-tri-substituted hydroxyl amines, such as O-benzoyl-N,N-succinylhydroxylamine, O-acetyl-N,N-succinylhydroxylamine, O-p-methoxybenzoyl-N,N-succinylhydroxylamine, O-p-nitrobenzoyl-N,N-succinylhydroxylamine and O,N,N-triacetylhydroxylamine;
- the N,N-diacyl-sulfonylamides, such as N,N'-dimethyl-N,N'-diacetyl-sulfonylamide and N,N'-diethyl-N,N'-dipropionyl-sulfonylamide;
- the triacylcyanurates, such as triacetylcyanurate anurate and tribenzoylcyanurate;
- the carboxylic acid anhydrides, such as benzoic acid anhydride, m-chlorobenzoic acid anhydride, phthalic acid anhydride, 4-chlorophthalic acid anhydride;
- the sugar esters, such as glucosepentaacetate;
- The 1,3-diacyl-4,5-diacyloxy-imidazolidines, such as the compounds 1,3-diformyl-4,5-diacetoxyimidazolidine, 1,3-diacetyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-dipropionyloxy imidazolidine;

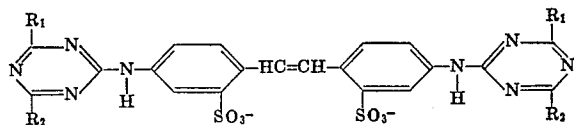
- j. the acylated glycoluril compounds, such as tetraacetylglcoluril and tetrapropionylglycoluril;
 k. the diacylated 2,5-diketopiperazines, such as 1,4-diacetyl-2,5-diketo-piperazine, 1,4-dipropionyl-2,5-diketo-piperazine, 1,4-dipropionyl-3,6-dimethyl-2,5-diketo-piperazine;
 l. the acylation products of propylenediurea or 2,2-dimethylpropylenediurea (2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), particularly tetraacetylpropylenediurea, tetrapropionyl-propylenediurea or their dimethyl derivatives;
 m. the carbonic acid esters, for example, the sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxycarbonyloxy)-benzenesulfonic acid.
 Of particularly practical interest are the activator types named under (j), (k) and (l).

In the activation of the percompounds by the names N-acyl- and O-acyl compounds, carboxylic acids, such as acetic acid, propionic acid, benzoic acid, are liberated, and it is recommended to add corresponding amounts of alkalis to neutralize these carboxylic acids. In effective activators, an activation is visible already in using amounts of 0.05 mols of activator per gm-atom of active oxygen. Preferably 0.1 to 1 mol of activator are used. The amount may, however, be raised up to 2 mols of activator per gm-atom of active oxygen if desired.

The optical brighteners which can be utilized in the compositions are mostly, if not exclusively, derivatives of aminostilbenesulfonic acid, or of diaminostilbenedisulfonic acid, of diarylpyrazolines, of carbostyryl, of 1,2-di-(2-benzoxazolyl)-ethylene or 1,2-di-(2-benzimidazolyl)-ethylene, of benzoxazolyl-thiophene and of the coumarins.

Examples of brighteners from the class of the diaminostilbenedisulfonic acid derivatives are compounds, according to formula I:

I:

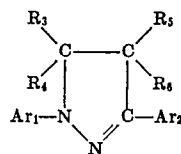


In the formula, R_1 and R_2 represent alkoxy, amino, or residues of aliphatic, aromatic or heterocyclic, primary or secondary amines as well as residues of aminosulfonic acids, where the aliphatic residues present in the above groups, contain preferably one to four and particularly two to four carbon atoms, while the heterocyclic ring systems are mostly five to six membered rings. As aromatic amines the residues of the aniline, of the anthranilic acid or the anilinesulfonic acid are preferred. Brighteners, derived from the diaminostilbenedisulfonic acid, are mostly used as cotton brighteners. The following products, derived from formula I, are commercially available, where R_1 represents the residue $-\text{NHC}_6\text{H}_5$ and R_2 may represent the following residues: $-\text{NH}_2$, $-\text{NHCH}_3$, $\text{NHCH}_2\text{CH}_2\text{OH}$, $-\text{NHCH}_2\text{CH}_2\text{OCH}_3$, $-\text{NHCH}_2\text{CH}_2\text{OCH}_3$, $-\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$, $-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, morpholino-, $-\text{NHC}_6\text{H}_5$, $-\text{NHC}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{OCH}_3$. Some of these brighteners are, in regard to their fiber affinity, regarded as transitional types to the polyamide brighteners, such as the brightener with $R_2 = -\text{NHC}_6\text{H}_5$. The compound 4,4'-bis-(4-phenyl-1,2,3-triazole-2-yl)-2,2'-stilbenedisulfonic acid belongs also to the cotton

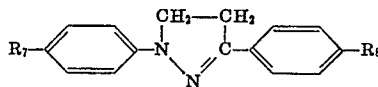
brighteners of the diaminostilbenedisulfonic acid type.

Diarylpyrazolines of the formulae II and III belong to the polyamide brighteners.

II:



III:



In the formula II R_3 and R_5 represent hydrogen, alkyl and aryl, optionally substituted by carboxyl, carbonamide or carboxylic acid ester groups, R_4 and R_6 represent hydrogen or lower alkyl, Ar 1 and Ar 2 represent aryl radicals, such as phenyl, diphenyl or naphthyl, which may carry further substituents, such as hydroxy, alkoxy, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, carboxylic acid esters, sulfonic acid, sulfonamide and sulfone groups or halogen atoms. Commercially available brighteners of this type are derived from the formula III, where the radical R_7 may represent the groups Cl , $-\text{SO}_2\text{NH}_2$, $-\text{SO}_2\text{CH}=\text{CH}_2$, and $-\text{COOCH}_2\text{CH}_2\text{OCH}_3$, while R_8 mostly represents a chlorine atom. Also the 9-cyanoanthracene belongs to the polyamide brighteners.

The polyamide brighteners further include aliphatically or aromatically substituted aminocoumarins, such as 4-methyl-7-dimethylamino-coumarin or 4-methyl-7-diethylaminocoumarin. Further usable as polyamide brighteners are the compounds 1-(2-benzimidazolyl)-2-(1-hydroxyethyl)-2-benzimidazolyl-ethylene and 1-ethyl-3-phenyl-7-diethyl-amino-carbostyryl. Suitable as brighteners for polyester and polyamide fibers are the compounds 2,5-di-(2-benzoxazolyl)-thiophene, 2-(2-benzoxazolyl)-naphtho[2,3-b]-thiophene, and 1,2-di-(5-methyl-2-benzoxazolyl)-ethylene.

If the brighteners together with other ingredients of the invention products are present as aqueous solution or paste, and are to be transformed to solids by heat drying, it is recommended to incorporate organic sequestering agents in amounts of at least 0.1 percent, preferably 0.2 percent to 1 percent by weight of the solid products in order to stabilize the brighteners.

The enzyme preparations to be used are mostly a mixture of enzymes with different effects, such as proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases. Of particular interest are the enzymes, obtained from bacteria strains or from fungi, such as *Bacillus subtilis* or *Streptomyces griseus*, particularly proteases and amylases, which are relatively stable towards alkalis, percompounds, and anionic tensides and are still effective at temperatures up to 70°C.

Enzyme preparations are marketed by the manufacturers mostly as aqueous solutions of the active substances or as powders, granulates or as cold-sprayed products. They frequently contain sodium sulfate, sodium chloride, alkali metal ortho-, pyro- and polyphosphates, particularly tripolyphosphate, as fillers. Dust-free preparations are particularly valued. These are ob-

tained in a known manner by incorporating of oily or pasty Nonionics or by granulation with the aid of melts of water-of-crystallization-containing salts in their own water-of-crystallization.

Enzymes may be incorporated which are specific for certain types of soil, for example, proteases or amylases or lipases. Preferably, combinations of enzymes with different effects are used, particularly combinations of proteases and amylases.

The following examples are illustrative of the practice of the invention without being deemed limitative in any manner.

EXAMPLES

The following examples describe compositions of some washing agents, washing auxiliaries, rinsing and cleaning agents, according to the invention. The percentage amounts of the ingredients were, unless stated otherwise, calculated on anhydrous agent compositions, with the exception of the ingredients borax and perborate, wherein the content of water-of-crystallization is stated. However, the agents, prepared by heat-drying of an aqueous mixture, contain generally 5 to 20 percent by weight of water in the form of water-of-crystallization or of hydration. If the agents contain borax or perborate, they are admixed to the heat-dried powder. Synthetic tensides of the sulfate or sulfonate type contain generally as impurities slight amounts of sodium sulfate, insignificant for the formulation. The presence of this sodium sulfate is marked in the Na₂SO₄-lines of the table of the examples with a x.

The salt-like ingredients, contained in the agents of the examples, such as salt-like tensides, other organic salts, as well as inorganic salts, are present as the sodium salts, unless expressly stated as otherwise. The notations or abbreviations used have the following meanings:

"ABS" — the salt of an alkylbenzenesulfonic acid with 10 to 15, preferably 11 to 13 carbon atoms, in the alkyl chain, obtained by condensation of straight-chain terminal olefins with benzene and sulfonation of the thus-formed alkylbenzene,

"Alkanesulfonate" — a sulfonate obtained from paraffins with 12 to 16 carbon atoms by sulfoxidation,

"Fs-estersulfonate" — a sulfonate obtained from the methyl ester of a hardened tallow fatty acid, by sulfonation with SO₃,

"Olefinsulfonate" — a sulfonate obtained from olefin mixtures with 12 to 18 carbon atoms by sulfonation with SO₃ and hydrolysis of the sulfonation product with aqueous sodium hydroxides. The olefinsulfonate consists substantially of alkenesulfonate and hydroxyalkanesulfonate, and contains, however, also a slight amount of disulfonates,

"CA-sulfate" or "TA-sulfate" — the salts of sulfated, substantially saturated fatty alcohols, prepared by reduction of coconut fatty acid or tallow fatty acid respectively,

"CA-EO-sulfate" or "TA-EO-sulfate" or "OA-EO-sulfate" — the sulfated addition products of 2 mols of ethylene oxide to 1 mol of coconut fatty alcohol or of 3 mols of ethylene oxide to 1 mol of tallow fatty alcohol or of 2 mols of ethylene oxide to 1 mol of oleyl alcohol respectively,

"Soap" — the salts derived from fatty acid mixtures

of an iodine number of at most seven, whose composition was within the following range: 0 to 20 percent by weight of C₁₂, 0 to 15 percent by weight of C₁₄, 5 percent to 40 percent by weight of C₁₆, 5 percent to 70 percent by weight of C₁₈, 0 to 20 percent by weight of C₂₀, 0 to 80 percent by weight of C₂₂, whereby the foam inhibiting effect of this soap increases with rising average carbon number,

"OA + 5 EO," "OA + 10 EO" and "CA + 20 EO" — the addition products of ethylene oxide (EO) to technical oleyl alcohol (OA) or coconut alcohol (CA), whereby the numbers signify the molar amount of ethylene oxide, added to 1 mol of alcohol,

"CA + 9 EO + 12 PO" — a Nonionic, obtained by reaction of 1 mol of "CA + 9 EO" with 12 mols of propylene oxide,

"NTA," "EDTA" or "HEDP" — salts of nitrilotriacetic acid, ethylenediaminetetraacetic acid or hydroxy-ethanediphosphonic acid,

"Perborate" — a product of the approximate composition NaBO₂·H₂O₂·3 H₂O, containing about 10 percent of active oxygen,

"CMC" — the salt of carboxymethylcellulose.

"Copolymer" — a polymer having a molecular weight of about 4,000, obtained by polymerization of 1,2,3,6-tetra-hydro-3,6-epoxy-phthalic acid anhydride, followed by hydrolysis and conversion to the disodium salt.

"Copolymer Mixture" — In Table I, an admixture of the above "copolymer" with other builder salts for which the details are given before Table I.

The agents, whose composition is described in the Examples 1 to 7, are preferably intended for the following application purposes:

Example 1: Cleaning agent for the metal industry

Example 2: Cleaning agent for the food industry (both prepared by mixing of the powdery ingredients)

Example 3: Foam-inhibited boiling washing agent

Example 4: Strongly foaming product, also usable as fine washing agent

Example 5: Soaking agent (all prepared by heat-spraying)

Example 6: Soaking agent (prepared by spraying of the Nonionic onto the mixture of the powdery ingredients)

Example 7: Cleaning agent, also usable in the home, for non-textile materials (heat-dried).

In the agents, according to the Examples 1, 2 and 5 to 7, the quantitative data for the copolymer-carboxylate refer to the technically pure product ("Copolymer"). In the agents, according to the Examples 3 and 4, the quantitative data for the "copolymer mixture" refer both to the technically pure "copolymer" and also to the mixture of equal parts of weight of this "copolymer" with the following builders:

a. a salt, obtainable in a known way from polymerized acrolein by treatment with alkali metal hydroxides, according to Cannizzaro, optionally in the presence of formaldehyde, of a polyhydroxypoly-carboxylic acid of the average degree of polymerization of 40 and a molar ratio COOH : OH = 7.3

b. Na₂SiO₂

c. Sodium citrate

d. Na₅P₃O₁₀

TABLE I

Ingredient	% by weight of ingredient in agent according to example					
	1	2	3	4	5	7
ABS	5.0	2.0	7.8	20.0	4.0	20.0
CA-EO-Sulfate						3.0
Soap			3.5			
OA + 10 EO			2.6			4.0
"Copolymer mixture"	30.0	25.0	42.5	40.0	33.0	60.0
Na ₃ P ₃ O ₁₀						10.0
EDTA			0.3			
HEDP					0.3	
Perborate			26.2	30.0		
NaOH	30.0	48.0				
Na ₂ O:3.3 SiO ₂	20.0	15.0	3.8		3.0	6.0
Na ₂ CO ₃					40.0	
Na ₂ B ₄ O ₇ ·10 H ₂ O						5.0
Na ₂ SO ₄	15.0	10.0	12.1	10.0	15.0	62.0
MgSiO ₃					5.0	
CMC			1.2			1.2

The agents, described in examples 8 to 20, prepared, except for Example 11, by spray drying, are preferably intended for the following application purposes:

Example 8: Soaking or pre-washing agent

Examples 9 to 11 and 13 to 17: All-purpose washing agents, particularly bleaching, boiling washing agents

Examples 12 and 18: Colored goods washing agent

Examples 19 and 20: Fine-washing agents

The boiling washing agents, on the one hand, and the colored goods or fine-washing agents, on the other hand, differ, as not shown in the following formulations, by the presence or absence of cotton and/or polyamide and/or polyester brighteners.

As foam inhibitor, a mixture of about 45 percent of

a di-(alkylamino)-monochlorotriazine and about 55 percent of a N,N',N''-trialkylmelamine was used. In all these triazine derivatives the alkyl residues were present as mixtures of homologs with eight to 18 carbon atoms. With a similar success also the monochlorotriazine derivative or the trialkylmelamine can be used. If the described products contained synthetic sulfates or sulfonates together with soap, the other non-tenside foam inhibitors named in the specification, could be utilized, such as paraffin oil or paraffin. In the preparation of the products, the foam inhibitor used was dissolved in a suitable organic solvent or sprayed in the molten state, with the aid of a nozzle, onto the moving powdery preparation.

TABLE II

Ingredient	% by wt. of ingredient in agent accord to example					
	8	9	10	11	12	13
ABS		10.8	13.2			
Olefin sulfonate	6.1				14.3	
Soap		2.4			11.2	15.2
OA +5 EO					6.2	2.2
OA + 10 EO		9.6	7.2			4.3
CA + 20 EO				13.6		
CA + 9 EO + 12 PO	3.7			9.3		
Foam Inhibitor	0.4		0.6		1.0	
Copolymer	73.7	28.7	40.7	32.0	49.6	38.0
Na ₃ P ₃ O ₁₀		20.3				
NTA				9.9		
EDTA	1.8			0.9	3.7	2.2
HEDP			0.7	0.9		
Perborate		19.1	22.8	19.8		21.8
Na ₂ O:3.3 SiO ₂		5.4	4.8	5.6		
Na ₂ P ₂ O ₇				6.2		
Na ₂ CO ₃	11.1		7.2		12.4	13.0
Na ₂ SO ₄	+	+	+	+	+	
MgSiO ₃	1.2	1.9	1.2			2.2
CMC	2.0	1.8	1.6	1.8	1.6	1.1

TABLE III

Ingredient	% by wt. of ingredient in agent accord to example					
	14	15	16	17	18	20
ABS	9.4		7.0			
Alkanesulfonate		8.0				
Fs-estersulfonate				9.4		18.5
Olefin sulfonate						3.9
CA-Sulfate	1.8	3.4	1.2		1.7	
TA-Sulfate	0.6			3.5	1.7	
CA-EO-Sulfate	2.2				2.8	9.2
TA-EO-Sulfate					8.6	
OA-EO-Sulfate					6.7	
Soap	6.4	11.4	6.8	10.8	7.9	4.7
OA + 5 EO		3.1			7.9	
OA + 10 EO			2.7	4.9		
Foam Inhibitor			0.6			9.9
Copolymer	32.1	35.7	40.0	30.5	36.8	35.5
Na ₃ P ₃ O ₁₀						40.6
NTA	11.1					13.5
EDTA	0.3	0.4	0.5	0.5	1.2	
Perborate	26.6	30.8	27.0	30.4	24.5	
Na ₂ O:3.3 SiO ₂	5.5	4.9	6.0	4.9	4.3	4.2
Na ₂ CO ₃			5.0			

TABLE III - Continued

Ingredient	% by wt. of ingredient in agent accord to example						
	14	15	16	17	18	19	20
MgSiO ₃	2.2			3.5			
CMC	1.8	2.3	1.2	1.6	1.8	1.5	2.1
Na ₂ SO ₄			2.0		6.1	41.2	11.1
H ₂ O	Remainder						

Examples 21 and 22: Pre-washing agents which also make possible at temperatures up to 60°C an extensive, although not complete disinfection.

Example 21	Example 22	
13.7	10.0	% by weight of ABS, alkanesulfonate or olefinsulfonate
7.0	5.0	% by weight of soap
0.5	0.5	% by weight of foam inhibitor
60.0	20.0	% by weight of copolymer
0.0	24.5	% by weight of Na ₂ CO ₃
4.0	9.0	% by weight of NaOH (for neutralization of the phenols)
13.8	30.0	% by weight of o-phenylphenol, pentachlorophenol or their mixtures
1.0	1.0	% by weight of Na ₂ SO ₄

Example 23: Antimicrobial, bleaching after-rinsing agent for washed laundry, which simultaneously dissolves fiber incrustations, particularly lime-containing fiber incrustations

- 30.0 percent by weight of perborate
- 30.0 percent by weight of copolymer
- 15.0 percent by weight of Na₂CO₃
- 2.6 percent by weight of 2-hydroxy-2', 4,4'-trichlorodiphenylether
- 8.0 percent by weight of MgSiO₃
- 14.4 percent by weight of Na₂SO₄

Example 24: Dishwashing agent for industrial and household dishwashing machines:

- 55.0 percent by weight of copolymer
- 42.0 percent by weight of sodium metasilicate of the composition Na₂O : 2.75 SiO₂
- 1.0 percent by weight of OA + 5 EO
- 2.0 percent by weight of potassium dichlorisocyanurate

Example 25: A disinfecting surface-cleaning agent:

- A 25 percent solution of a mixture of
- 40.0 percent by weight of ABS
- 48.0 percent by weight of copolymer
- 12.0 percent by weight of 2-hydroxy-2',4,4'-trichloro-diphenylether in a mixture of 0.2 percent of perfume oil, 10 percent of isopropanol and 89.8 percent of water.

The washing agents, rinsing agents and cleaning agents described in the examples have a good washing and cleaning power, which is equal or even superior to the corresponding preparations on the basis of tripolyphosphate. Because of the excellent sequestering power of the copolymer carboxylates for alkaline earth metal ions, the excellent properties of the preparations according to the invention appear primarily when washing and cleaning in hard water. The copolymer carboxylates that can be used according to the invention are in addition practically non-hygroscopic, which is of great importance for the storability and pouring behavior of the powdery preparations.

If, in these preparations, the disodium salt of the

polymer, obtained by polymerization of the furan-maleic acid anhydride adduct is replaced by the salt of a product with a molecular weight of about 3,000 obtained by direct copolymerization of maleic anhydride and furan in a molar ratio of 1:1, similar results are obtained.

If the perborate-containing agents, particularly those to be utilized below 80°C (after-rinsing agents), are compounded with activators for percompounds, for example, with tetraacetylglycoluril, tetraacetylmethylene-diamine or tetraacetylenehydrazine, a good bleaching effect is obtained also at temperatures of from 20° to 70°C.

The preceding examples 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. Washing, rinsing and cleansing compositions consisting essentially of (a) from 5 percent to 95 percent by weight of at least one compound having a cleaning action selected from the group consisting of (1) anionic surface-active compounds, non-ionic surface-active compounds, amphoteric surface-active compounds, and mixtures thereof, (2) organic builder salts and inorganic builder salts, and (3) mixtures of (1) and (2), and (b) from 95 to 5 percent by weight of at least one copolymercarboxylate sequestering agent capable of sequestering alkaline earth metal ions prepared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymer-carboxylate sequestering agents being present as water-soluble salts capable of complex formation with alkaline earth metal ions.

2. The washing, rinsing and cleansing compositions of claim 1 wherein said copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions is selected from the group consisting of a saponified polymer of 1,2,3,6-tetrahydro-3,6-epoxyphthalic acid anhydride in the free acid form having a molecular weight of from 500 to 5000, a saponified copolymer of substantially equal molar amounts of furan and maleic acid anhydride in the free acid form having a molecular weight of from 500 to 5000, their alkali metal salts, their ammonium salts, their lower alkylamine salts and their lower alkylolamine salts.

3. The washing, rinsing and cleansing composition of claim 1 wherein said copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions is the sodium salt of a polymer of 1,2,3,6-tetrahydro-3,6-epoxy-phthalic acid having an average molecular weight of from 500 to 5,000.

4. The washing, rinsing and cleansing composition of claim 1 wherein said copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions is the ammonium salt of a copolymer of equal

molar amounts of furan and maleic acid anhydride saponified with aqueous ammonia and having an average molecular weight of from 500 to 5,000.

5. The washing, rinsing and cleansing composition of claim 1 containing from 10 to 30 percent by weight of alkali metal silicates, from 10 to 80 percent by weight of caustic alkalis, from 0 to 10 percent by weight of nonionic tensides and from 5 to 30 percent by weight of said copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions, for use in the industrial cleaning of solid material other than textiles.

6. The washing, rinsing and cleansing composition of claim 1 containing from 5 to 40 percent by weight of tensides selected from the group consisting of anionic surface-active compounds, nonionic surface-active compounds and amphoteric surface-active compounds, from 20 to 90 percent by weight of builders selected from the group consisting of organic builder salts and inorganic builder salts and from 10 to 80 percent by weight of said copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions, said compositions having a pH in a 1 percent aqueous solution of from 7 to 11.5.

7. The composition of claim 6 wherein said tenside component includes from 0.5 to 10 percent by weight of the tenside component of foam stabilizers and from 0.5 to 10 percent by weight of the tenside component, of non-tenside foam inhibitors.

8. The composition of claim 6 wherein said builder component includes from 5 to 40 percent by weight of the composition of a bleaching component selected from the group consisting of percompounds, their mixtures with bleach activators and stabilizers, and active-chlorine compounds.

9. The composition of claim 6 including a further content of from 0.1 to 5 percent of soil-suspending agents, from 0 to 5 percent by weight of enzymes selected from the group consisting of proteases, lipases and amylases, and from 0 to 1 percent by weight of an optical brightener.

10. The washing, rinsing and cleansing composition of claim 1 wherein said at least one compound having a cleaning action is selected from the group consisting of alkali metal silicates, and mixtures thereof with alkali metal hydroxides and alkali metal carbonates, wherein said composition in aqueous solution has a pH of between 8 to 12 for use in automatic dishwashing machines.

11. The composition of claim 10 having a further content of from 0.5 to 10 percent by weight of nonionic surface-active compounds, from 0 to 20 percent by weight of active-chlorine compounds, from 0 to 5 per-

cent by weight of enzymes selected from the group consisting of proteases, lipases and amylases, and from 0 to 1 percent by weight of sequestering agents capable of sequestering heavy metals.

12. The composition of claim 11 wherein said active-chlorine compounds are present in an amount of from 1 to 5 percent and are sodium or potassium dichloroisocyanurate.

13. In the process of washing, rinsing and cleansing solid materials which comprises contacting solid materials having soil thereon with an aqueous solution containing from 0.5 to 80 gm/liter of a cleansing agent consisting of from 5 to 95 percent of at least one compound having a cleaning action and from 95 to 5 percent of a sequestering agent capable of sequestering alkaline earth metal ions, for a time sufficient to disperse and dissolve said soil in said aqueous solution and removing said cleansed solid materials, the improvement consisting of utilizing, as said sequestering agent, at least one copolymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions prepared from approximately equal molar amounts of maleic acid and furan, and having a molecular weight of from about 300 to 20,000, said copolymer-carboxylate sequestering agents being present as water-soluble salts capable of complex formation with alkaline earth metal ions.

14. The method of claim 13 wherein said co-polymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions is selected from the group consisting of a saponified polymer of 1,2,3,6-tetrahydro-3,6-epoxy-phthalic acid anhydride in the free acid form having a molecular weight of from 500 to 5,000, a saponified copolymer of substantially equal molar amounts of furan and maleic acid anhydride in the free acid form having a molecular weight of from 500 to 5,000, their alkali metal salts, their ammonium salts, their lower alkylamine salts and their lower alkyl-olamine salts.

15. The method of claim 13 wherein said co-polymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions is the sodium salt of a polymer of 1,2,3,6-tetrahydro-3,6-epoxy-phthalic acid having an average molecular weight of from 500 to 5,000.

16. The method of claim 13 wherein said co-polymer-carboxylate sequestering agent capable of sequestering alkaline earth metal ions is the ammonium salt of a copolymer of equal molar amounts of furan and maleic acid anhydride saponified with aqueous ammonia and having an average molecular weight of from 500 to 5,000.

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