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LOW-FOAMING RINSING, WASHING AND
CLEANING COMPOSITIONSWerner Stein, Erkrath-Unterbach, and Klaus Flory,
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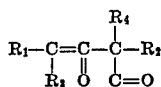
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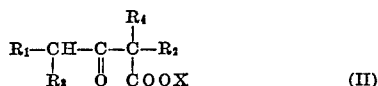
14 Claims

ABSTRACT OF THE DISCLOSURE

Low-foaming rinsing, washing and cleaning compositions comprising (a) from 90% to 99.9% by weight of at least one compound having a cleaning or complexing action, and (b) from 0.1% to 10% by weight of at least one foam-inhibiting compound of the Formula I



and its saponification product of the Formula II



wherein R_1 and R_2 represent hydrocarbon radicals with 8 to 30 carbon atoms and R_3 and R_4 represent hydrogen or hydrocarbon radicals with 1 to 30 carbon atoms, and X represents a cation.

THE PRIOR ART

It is known that non-ionic detergent substances, especially those based on polyglycol ethers, have a low-foaming power. The foam-inhibiting properties of these compounds, however, are often not sufficiently adequate to reduce the foam formation of such washing and cleaning agents which contain highly foaming tensides of the sulfate or sulfonate type. It has been, therefore, suggested to add fatty acids with more than 18 carbon atoms as foam inhibitors. The effect of these fatty acids is, however, limited to tensides of the sulfonate type and depends, in addition, upon the hardness of the water used for the preparation of the cleaning solution. The silicones widely used as foam inhibitors are less suitable for washing and cleansing agents since they may have a hydrophobizing effect on the cleaned objects and can be removed only with difficulty from the substrate.

Also in the use of tenside-free complexing polyphosphates or of tenside-free softeners containing organic complexing agents, which can be used for the removal of incrustations from textiles and washing machines, supply pipes and hot water heaters, considerable disturbances may occur through foam formation. Deposited organic impurities, such as proteins or fatty substances, lime soap residues or traces of detergents are held responsible for the foam formation.

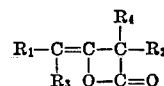
OBJECTS OF THE INVENTION

An object of the present invention is to provide washing, rinsing and cleaning agents which, compared with the known agents, have an improved anti-foaming action independent of the nature and composition of the foaming compounds as well as of the hardness of the water, have no negative effect on the cleaning action of the agents or on the usefulness of the cleaned substrate, are effective in

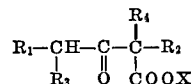
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small concentrations and overcome the disadvantages of the prior art.

Another object of the invention is to provide low-foaming rinsing, washing and cleaning compositions comprising (a) from 90% to 99.9% by weight of at least one active compound selected from the group consisting of cleaning compounds and complexing compounds, and (b) from 0.1% to 10% by weight of a foam inhibitor selected from the group consisting of (1) at least one dimer ketene of the formula



wherein R_1 and R_2 are members having 8 to 30 carbon atoms selected from the group consisting of alkyl, alkenyl, alkylcycloalkyl and alkylphenyl, and R_3 and R_4 are members selected from the group consisting of hydrogen and hydrocarbonyls having 1 to 30 carbon atoms selected from the group consisting of alkyl, alkenyl, alkylcycloalkyl and alkylphenyl, (2) at least one saponification product of said dimer ketene of the formula

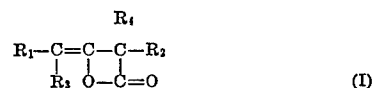


wherein R_1 , R_2 , R_3 and R_4 have the above assigned values and X represents a member selected from the group consisting of alkali metals, alkaline earth metals, ammonium and organic ammonium and its enol.

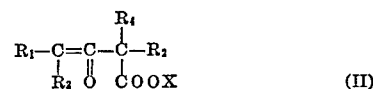
These and other objects of the present invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The invention, therefore, comprises low-foaming washing, rinsing and cleaning agents which are characterized in that they contain (a) from 90% to 99.9% of at least one compound having a cleaning or complexing action, and (b) from 0.1% to 10% by weight of at least one foam-inhibiting compound of the Formula I



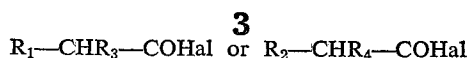
and its saponification product of the Formula II



wherein R_1 and R_2 represent hydrocarbon radicals with 8 to 30 carbon atoms and R_3 and R_4 represent hydrogen or hydrocarbon radicals with 1 to 30 carbon atoms, and X represents a cation. Preferably the cation X is from the class of alkali metals, alkaline earth metals, the ammonium and of the organic ammonium bases.

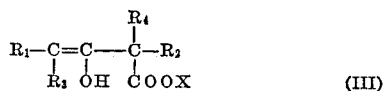
The radicals R_1 and R_2 or R_3 and R_4 can be identical or different, straight-chain or branched, saturated or unsaturated, or also cycloaliphatic or alkylaromatic. Preferably, such compounds are used in which R_1 and R_2 are straight-chain, saturated or singly unsaturated hydrocarbon radicals such as alkyls and alkenyls with 12 to 22 carbon atoms. The radicals R_3 and R_4 are hydrogen, and X is an alkali metal such as sodium or potassium.

In order to prepare the compounds, accordingly to the preceding Formulas I and II, one starts approximately from carboxylic acid chlorides or bromides of the formula



in which Hal represents chlorine or bromine. These carboxylic acid halides are derived from aliphatic, cycloaliphatic, or alkylaromatic carboxylic acids, particularly from fatty acids of natural or synthetic origin. Examples of them are lauric, myristic, palmitic, stearic, arachic, behenic, lignoceric, palmitoleic, and oleic acid, or their mixtures occurring in natural fats, such as coconut, tallow, rape oil, palm kernel, soybean oil, cottonseed oil, peanut oil, or olive oil fatty acids or their hydrogenation products. Also synthetic fatty acids and fatty acid mixtures obtainable by paraffin oxidation, ethylene polymerization, or oxosynthesis can be utilized in the form of their halides. In addition, alkylcycloalkenoic acid halides and alkylbenzoic acid halides may be employed such as dodecylcyclohexylacetyl chloride and octylphenylacetyl chloride.

From the carboxylic acid halides, ketenes are obtained in a known manner by dehydrochlorination, which ketenes dimerize spontaneously to give compounds of Formula I. The saponification products, according to Formula II, which are in equilibrium with the enol form, according to Formula III

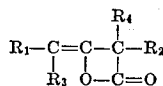


are obtained from the dimer ketenes by alkaline saponification.

The saponification of the dimer ketenes, according to Formula I, can be carried out before or during the preparation of the agents, according to the invention, or in their application. It is promoted by the use of higher temperatures and by the presence of alkaline reacting substances. Thus, for instance, on heating of an alkaline washing liquor at temperatures above 70° to 80° C., a more or less complete saponification of the dimer ketene may occur. Herein lies a particular advantage since the compounds, according to Formula I, are particularly effective in the temperature range from 50° C. to 80° C., whereas their alkaline saponification products are effective in the range from 70° C. to 100° C. Therefore, the foam-inhibiting effect of the partially saponified dimer ketenes or the mixtures of dimer ketenes and their saponification products extends over a broad temperature range. The alkali metal salts of the saponification products, according to the Formula II, are, in addition, surface active and may have a favorable influence upon the washing and cleansing power of the agents.

Also mixtures of foam inhibitors of Formula I and/or II, in which the radicals R₁ to R₄ have different constitutions or a different number of carbon atoms can be used advantageously. By this the foaming behavior can be adjusted to the respective requirements within a temperature range of from 30° C. to 100° C.

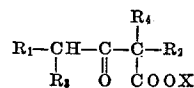
Preferably the washing, rinsing and cleaning compositions of the invention are low-foaming rinsing, washing and cleaning compositions comprising (a) from 90% to 99.9% by weight of at least one active compound selected from the group consisting of cleaning compounds and complexing compounds, and (b) from 0.1% to 10% by weight of a foam inhibitor selected from the group consisting of (1) at least one dimer ketene of the formula



wherein R₁ and R₂ are members having 8 to 30 carbon atoms selected from the group consisting of alkyl, alkenyl, alkylcycloalkyl and alkylphenyl, and R₃ and R₄ are members selected from the group consisting of hydrogen and hydrocarbonyls having 1 to 30 carbon atoms selected from the group consisting of alkyl, alkenyl, alkylcycloalkyl

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and alkylphenyl, and (2) at least one saponification product of said dimer ketene of the formula



wherein R₁, R₂, R₃ and R₄ have the above assigned values and X represents a member selected from the group consisting of alkali metals, alkaline earth metals, ammonium and organic ammonium and its enol.

The amounts of foam inhibitors to be used depend upon the amount of foaming or detergent substance present in the final composition and/or on the substrate to be cleaned as well as upon the magnitude of the desired effect. The practically important concentrations applied extend from 0.1% to 10%, preferably from 0.2% to 5% by weight, based on the solid composition. It is, of course, possible to work with still larger amounts, for instance, up to 25% by weight and more. This, however, is not required in the practice.

The foam inhibitors can be mixed with the other washing, cleansing and descaling agents in a conventional manner and can be processed together with them, for example, spray dried or granulated, or they can be converted by other known processes to solid, liquid or pasty mixtures. The foam inhibitors can also be mixed in molten or dissolved form with the other ingredients, present as powders or granules, or be sprayed or granulated on them. These other ingredients which are present in amounts from 90% to 99.9%, preferably 95% to 99.8% by weight, consist of at least one washing, bleaching, or complexing compound, such as anionic, non-ionic, amphoteric or cationic surface-active compounds, polymeric phosphates, complexing agents, as well as other non-surface-active builders, oxygen-containing bleaching agents and other ingredients customarily present in such agents.

The washing and cleansing agents can also contain anionic basic detergent substances of the sulfonate or sulfate type. Primarily alkylbenzene sulfonates, for example, dodecylbenzene sulfonate are suitable, also olefin sulfonates, such as, for example, are obtained by sulfonation of primary and secondary aliphatic monoolefins with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis, as well as alkylsulfonates obtainable from n-alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization, or by addition of bisulfite to olefins. Also suitable are α-sulfofatty acid esters, primary and secondary alkylsulfates and the sulfates of ethoxylated or propoxylated higher alcohols. Other compounds of this class which can be optionally present in the washing composition are the higher molecular weight sulfated partial ethers and partial esters of polyhydric alcohols, such as the alkali metal salts of the monoalkyl ethers or mono fatty esters of the glycerine monosulfuric acid esters, or 1,2-dihydroxy-propanesulfonic acid. Also sulfates of ethoxylated or propoxylated fatty amides and alkylphenols as well as fatty acid taurides and fatty acid isothionates are suitable.

Other appropriate anionic basic detergent ingredients are alkali metal soaps of natural or synthetic fatty acids, such as sodium soaps of coconut, palm kernel, or tallow fatty acids. As amphoteric detergent components, alkyl betaines and particularly alkyl sulfobetaines are suitable, for example, 3-(N,N-dimethyl-N-alkylammonium)-propane-1-sulfonate and 3-(N,N-dimethyl-N-alkylammonium)-2-hydroxypropane-1-sulfonate.

The anionic basic detergent ingredients can be present in the form of their alkali metal salts such as the sodium and potassium, and ammonium salt, as well as salts of organic bases, such as mono-, di- and tri-ethanolamine. Inasmuch as the named anionic and amphoteric compounds have an aliphatic hydrocarbon radical, the latter should preferably be straight-chained and should have from 8 to 22 carbon atoms. In the compounds with arali-

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phatic hydrocarbon radicals, such as alkylphenyl radicals, the preferred straight alkyl chains contain an average of from 6 to 16 carbon atoms.

As non-ionic surface-active basic detergent ingredients, primarily suitable are the polyglycoether derivatives of alcohols, fatty acids and alkylphenols which contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the hydrocarbon radical. Particularly suitable are polyoxyethyleneglycoether derivatives in which the number of oxyethylene groups is 5 to 15 and whose hydrocarbon radicals are derived from straight-chain primary alcohols with 12 to 18 carbon atoms, or from alkylphenols with a straight-chain alkyl chain of 6 to 14 carbon atoms. By the addition of 3 to 15 mols of propylene oxide to the last named polyethyleneglycoethers, or by converting them into acetals, detergents are obtained which are distinguished by a special low foaming power.

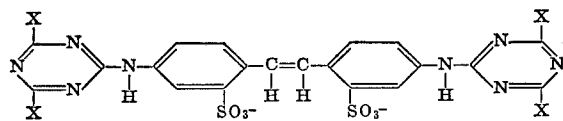
Other suitable non-ionic basic detergent ingredients are the water-soluble polyethylene oxide adducts, containing 20 to 250 ethyleneglycoether groups and 10 to 100 propyleneglycoether groups adducted to polypropylene glycol, ethylenediamine-polypropyleneglycol and alkylene-polypropyleneglycol with 1 to 10 carbon atoms in the alkylene chain. The compounds utilized usually contain 1 to 5 oxyethylene units per oxypropylene unit. Also suitable as non-ionic compounds are those of the amine oxide and sulfoxide types, which, if necessary can be ethoxylated.

Further, suitable components of the mixture include neutral salts, such as sodium sulfate and sodium chloride as well as compounds regulating the pH value, such as the bicarbonates, carbonates, borates and hydroxides of the alkali metals, such as sodium or potassium, and acids such as lactic acid and citric acid. The amount of alkaline-reacting substances including the alkali metal silicates and phosphates should be such that the pH of a liquor utilisable for mechanical dishwashing machines and descaling of textiles, service pipes, washing machines and hot water heaters, amounts to 9 to 14, and in laundry machines for coarse washing, 9 to 12, and for fine washing, 6 to 9.

By a suitable combination of different surface-active basic detergent substances and builder salts with one another, increases in activity may be obtained in many cases, for example, an improved washing powder or a reduced foaming capacity. Such improvements are possible, for example, by a combination of anionic compounds with non-ionic and/or amphoteric compounds, by a combination of different non-ionic compounds, or by mixtures of basic detergent substances of the same type which differ in regard to the number of carbon atoms or the number and position of double bonds or branching of chains in the hydrocarbon residue. Also mixtures of inorganic and organic builder salts with a synergistic action can be used or can be combined with the above-mentioned mixtures.

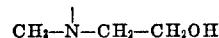
Depending on their use, the cleaning compositions of the invention may also contain oxygen-yielding or active chlorine-containing bleaching agents such as hydrogen peroxide, alkali metal perborates, alkali metal precarbonates, alkali metal perphosphates, urea perhydrate, alkali metal persulfate, alkali metal hypochlorites, chlorinated trisodium phosphate and chlorinated cyanuric acid and its alkali metal salts as well as bleaching agent activators and stabilizers such as magnesium silicate.

Further suitable components of the mixtures are optical brighteners for cellulosic fibers, for example, those of the diaminostilbene-disulfonic acid type according to the following formula



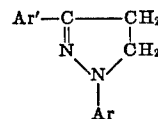
in which X and Y represent the following: —NH_2 , —NH—CH_3 , $\text{—NH—CH}_2\text{—CH}_2\text{OH}$,

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$\text{—N(CH}_2\text{—CH}_2\text{OH)}_2$, morpholino, dimethylmorpholino, $\text{—NH—C}_6\text{H}_5$, $\text{—NH—C}_6\text{H}_4\text{—SO}_3\text{H}$, —OCH_3 , —Cl , where X and Y are the same or different. Compounds in which X represents an anilino and Y a diethanolamino or morpholino group are specially suitable.

In addition, optical brighteners of the diarylpyrazoline type according to the following formula may be present:



In the formula, Ar and Ar' represent aryl residues, such as phenyl, diphenyl or naphthyl, which may carry further substituents such as hydroxy, alkoxy, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, sulfonic acid and sulfonamide groups or halogen atoms. 1,3-diarylpyrazolines are preferably used in which Ar is p-sulfonamidophenyl and Ar' is p-chlorophenyl. In addition, whiteners suitable for the brightening of other types of fibers may be present, for example, such as of the type of naphthotriazolestilbene sulfonates, ethylene-bis-benzimidazoles, ethylene-bis-benzoxazoles, thiophene-bis-benzoxazoles, dialkylaminocoumarins, and cyanoanthracenes. These brighteners or their mixtures can be present in the washing composition in amounts from 0.01% to 1.5% by weight, preferably from 0.1% to 1% by weight.

Further suitable mixture ingredients are anti-greying compounds, such as sodium celluloseglycolate, as well as the water-soluble alkali metal salts of synthetic polymers which contain free carboxylic groups. To them belong the polyesters or the polyamides of tri- and tetra-carboxylic acids and dihydric alcohols or diamines, also polymeric acrylic, methacrylic, maleic, fumaric, itaconic, citraconic and aconitic acids, as well as the mixed polymerizates of the above-named unsaturated carboxylic acids or their mixed polymerizates with olefins.

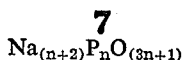
Washing agents for washing textiles may also contain restoring additives, for example, fatty acid amides of diamines or hydroxyalkyldiamines.

For a further improvement of the dirt loosening properties of the washing and cleaning compositions of the invention, they may also contain enzymes from the class of the proteases, lipases and amylases, which may be obtained from animal and vegetable origin, for example, from digestive ferments or yeasts, such as pepsin, pancreatin, trypsin, papain, catalase and diastase. Preferably, enzymic active substances are obtained from strains of bacteria or fungi, such as *Bacillus subtilis* and *Streptomyces griseus*, which substances are relatively stable towards alkalis, per-compounds and anionic detergent substances and are not appreciably inactivated even at temperatures between 45° C. and 70° C.

The washing and cleaning agents may be present in liquid, pasty or solid form, for example, pulverulent, granulated or lump form. For better solubility, liquid preparations may contain solvents miscible with water, especially ethanol and isopropanol, as well as solution aids such as the alkali metal salts of benzene-, toluene-, xylene- or ethylbenzenesulfonic acids. Skin protecting substances, such as fatty acid mono- and dialkylolamides may be added to the ring and cleaning agents intended for manual use.

The compositions of the invention may also contain dyes and perfumes, bacteriacides, restoring compounds as well as fillers such as urea.

Textile softener compositions according to the invention contain primarily alkali metal polyphosphates, such as sodium or potassium polyphosphates, for example, pentasodium triphosphate, hexasodium tetrphosphate and their mixtures with polyphosphates of the formula



where n represents a whole number from 5 to 20 and also sodium or potassium metaphosphates, such as sodium trimetaphosphate, sodium tetrametaphosphate, and sodium polymetaphosphates of the formula $(\text{NaPO}_3)_m$, where m represents a whole number from 5 to 30. The condensed phosphates may optionally be completely or partially replaced by complexing agents from the class of aminopoly-carboxylic acids, alkanediphosphonic acids, hydroxyalkanediphosphonic acids, and aminoalkanepolyphosphonic acids, or their alkali metal salts.

The above-described washing, cleansing and softening compositions may optionally contain other known foam inhibitors, such as saturated fatty acids with 20 to 24 carbon atoms or their alkali metal salts, paraffins, higher molecular weight fatty acid esters or triglycerides, or tri-alkylmelamines. Such additions may often have a synergistic effect.

The qualitative and quantitative composition of the cleansing, bleaching or complexing ingredients, apart from the foam inhibitors, is largely dependent upon the particular application of the composition and corresponds in the case of technically especially important washing and cleansing compositions to the following recipe (data in percent by weight):

- 1% to 40% of at least one compound from the class of the anionic, non-ionic and amphoteric surface-active compounds,
- 10% to 80% of at least one non-surface-active cleaning or complexing builder salt,
- 10% to 50% of a per-compound, especially sodium perborate, with or without crystalline water, as well as their mixtures with stabilizers, and activators,
- 0.1% to 20% of other auxiliary and supplementary washing agent compounds.

The surface-active compounds can consist of up to 100%, preferably from 5% to 70%, of compounds of the sulfonate and/or sulfate type, up to 100%, preferably from 5% to 40% of non-ionic compounds of the polyglycoether type and up to 100%, preferably from 10% to 50%, of soaps. The builder salts can consist of up to 100%, preferably 25% to 95%, of alkali metal triphosphates and their mixtures with alkali metal pyrophosphates, up to 100%, preferably 5% to 50%, of an alkali metal salt of a complexing compound from the class of polyphosphonic acids, nitrilotriacetic acid, ethylenediaminetetraacetic acid and their alkali metal salts, and up to 100%, preferably from 5% to 75%, of at least one compound of the class of alkali metal silicates, alkali metal carbonates and alkali metal borates.

To the additional auxiliary and supplementary washing agent compounds belong in addition to the optical brighteners, especially enzymes which can be present in an amount of up to 5%, preferably from 0.2% to 3%, and the additional anti-greying compounds which can be present in an amount of up to 5%, preferably from 0.2% to 3%.

The following specific embodiments are illustrative of the practice of the invention. They are not, however, to be deemed limitative in any respect.

EXAMPLES

A few compositions are given below which have proved especially good in practice. The invention is not restricted to the following mixtures, however, and these can be varied in many ways or be supplemented by the additional washing agent substances mentioned in the description.

The sulfate and sulfonate basic surface-active washing components and soaps are generally used as the sodium salts although other alkali metal salts may be employed. If liquid preparations are used, the anionic detergent substances may advantageously be used in the form of the mono-, di- or triethanolammonium salts.

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(1) Pulverulent, weakly foaming washing agent

- 3% to 15% of sulfonate basic surface-active washing component from the class of alkylbenzene sulfonates, olefin sulfonates and n -alkanesulfonates,
- 0.5% to 5% of alkylpolyglycoethers (C_{12} to C_{18} -alkyl) or alkylphenolpolyglycoethers (C_8 to C_{14} -alkyl), with 5 to 10 ethyleneglycolether groups,
- 0 to 5% of soap (C_{12} to C_{18}),
- 0.2% to 5% of the anti-foaming agents of the invention as well as their mixtures with saturated fatty acids or their alkali metal soaps, containing 20 to 24 carbon atoms,
- 10% to 50% of a condensed alkali metal phosphate from the class of pyro- and triphosphates,
- 0.1% to 25% of sodium ethylenediaminetetraacetate or sodium nitrilotriacetate,
- 1% to 5% of sodium silicate,
- 10% to 35% of sodium perborate tetrahydrate,
- 0 to 5% of enzymes,
- 0.05% to 1% of at least one optical brightener from the class of the diaminostilbenedisulfonic acid derivatives or the diarylpyrazole derivatives,
- 0.1% to 30% of an inorganic salt from the class of the carbonates, bicarbonates, borates, sulfates and chlorides of alkali metals.
- 0 to 4% of magnesium silicate,
- 0.5% to 3% of sodium celluloseglycollate.

(2) Mechanical dishwashing agent

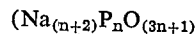
- 0.1% to 5% of compounds of the class of alkylpolyglycoether (C_{12} to C_{18} -alkyl) or alkylphenolpolyglycoether (C_8 to C_{14} -alkyl) with 5 to 30 ethyleneglycolether groups and 5 to 30 propyleneglycolether groups, and ethoxylated polypropyleneglycols,
- 0.1% to 5% of the anti-foaming agents of the invention,
- 45% to 90% of pentasodium triphosphate,
- 1% to 40% of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:1$ to $1:3$),
- 0 to 15% of potassium dichloroisocyanurate,
- 0 to 2% of other anti-foaming agents.

(3) Alkaline cleaning and bottle washing agent

- 0.1% to 5% of the anti-foaming agents of the invention,
- 0.5% to 50% of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:1$ to $1:3$),
- 0.5% to 80% of sodium hydroxide,
- 0 to 40% of trisodium phosphate,
- 0 to 40% of condensed alkali metal phosphates,
- 0 to 40% of sodium carbonate,
- 0 to 10% of hydroxyethane diphosphonate (sodium salt),
- 0 to 5% of anionic and/or non-ionic surface-active compounds.

(4) Softening agents

- 0.1% to 5% of anti-foaming agents of the invention,
- 20% to 95% of pentasodium triphosphate,
- 0 to 70% of a polyphosphate of the formula



$n=4$ to 20,

- 0 to 40% of sodium hexametaphosphate,
- 0 to 20% of sodium carbonate,
- 0 to 5% of sodium sulfate.

EXAMPLES 1 to 28

The washing agents listed in Table II were used. The numerical data is in percent by weight. The sulfonate washing ingredients and the soaps were used as sodium salts. The α -sulfo fatty esters are methyl ester of a hydrogenated tallow fatty acid, sulfonated in the α -position to the ester group. The abbreviations are:

- NTA=Sodium nitrilotriacetate
- EDTA=Sodium ethylenediaminetetraacetate
- CMC=Sodium salt of carboxymethylcellulose
- EO=Ethylene oxide groups

The difference to 100% by weight of the washing agents consisted in a mixture of the foam inhibitor and sodium sulfate, which was admixed to the washing agents as a dry powder. The composition and the percentage amount of the foam inhibitor, based on the total amount of washing agents can be found in Table I.

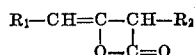
The foaming behavior was tested in a commercial, fully automated washing machine with a horizontal drum while varying the washing liquor temperature as indicated. The machine was equipped with a round sight-window through which the foam level could be observed. The following notations were used for the evaluation of the foam height:

Notation:	Maximum height of the foam level
0 -----	No foam.
1 -----	1/4 of the sight window.
2 -----	1/2 of the sight window.
3 -----	3/4 of the sight window.
4 -----	3/4 of the sight window.
5 -----	Foam visible in the filler tube.
6 -----	Foaming over.

The washing machine was loaded with 3 kgm. of clean laundry. The concentration of the washing agent was 5 gm./liter. The weight ratio of textiles to washing liquor was 1:15. The hardness of the water was expressed in German degree of hardness (1° dH corresponds to 1 mgm. CaO in 100 ml. water). The foam behavior is reported in Table III.

In the absence of a foam inhibitor, foaming over of the washing liquor occurred in all temperature ranges.

As foaming inhibitors, the dimer ketenes of the formula



obtained by dehydrochlorination of fatty acid chlorides were used or their saponification products in the form of the sodium salts. The fatty acids used for the preparation of the fatty acid chlorides or the dimer ketenes and the number of carbon atoms of the radicals R_1 and R_2 are summarized in Table I.

TABLE I

Sign	Starting material	Formula	R_1 and R_2 , No. of carbon atoms
S ₁ -----	Myristic acid.....	I	C ₁₂ .
S ₂ -----	Palmitic acid.....	I	C ₁₄ .
S ₃ -----	Stearic acid.....	I	C ₁₆ .
S ₄ -----	Arachic acid.....	I	C ₁₈ .
S ₅ -----	Behenic acid.....	I	C ₂₀ .
S ₆ -----	Tallow fatty acid.....	I	C ₁₈₋₁₈ -mixture.
S ₇ -----	Hydrogenated rape oil fatty acid.....	I	C ₁₈₋₂₂ -mixture.
S ₈ -----	Mixture of hydrogenated tallow fatty acid and behenic acid in weight ratio 1:1.	I	C ₁₈₋₂₂ -mixture.
S ₉ -----	Compound S ₂ , saponified.....	II	C ₁₆ .
S ₁₀ -----	Compound S ₅ , saponified.....	II	C ₂₀ .

TABLE II

[Amounts are in percent by weight]

	E	F	G	H	J	K	L	M
n-Dodecylbenzene sulfonate.....	7.5	9.0	-----	-----	5.0	5.0	-----	-----
α -olefin sulfonate (C ₁₂₋₁₈).....	-----	-----	7.0	-----	3.0	-----	-----	-----
n-Alkane sulfonate (C ₁₂₋₁₇).....	-----	-----	-----	8.0	-----	3.0	-----	-----
α -sulfo fatty acid ester.....	-----	-----	-----	-----	-----	8.0	9.5	-----
Alkylpolyglycoether (9 EO).....	2.5	2.5	-----	2.0	3.5	-----	2.0	3.5
Nonylphenolpolyglycoether (9 EO).....	-----	-----	3.0	-----	-----	3.0	-----	-----
Soap C ₁₂ -C ₁₈	4.0	-----	3.0	4.0	1.0	2.0	3.0	-----
Soap C ₁₂ -C ₂₀	-----	-----	-----	-----	0.5	-----	-----	-----
Pentasodium triphosphate.....	40.0	25.0	40.0	40.0	40.0	40.0	40.0	40.0
Tetrasodium pyrophosphate.....	5.0	-----	5.0	5.0	5.0	5.0	5.0	5.0
Sodium silicate (Na ₂ O:SiO ₂ =1:3.3).....	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Magnesium.....	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Sodium carbonate.....	-----	10.0	-----	-----	-----	-----	-----	-----
Sodium perborate.....	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
NTA.....	-----	12.0	-----	-----	-----	-----	-----	-----
EDTA.....	0.5	-----	0.5	0.5	0.5	0.5	0.5	0.5
CMC.....	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Enzyme concentrate.....	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Optical brighteners, dyes, perfumes.....	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Difference to 100%.....	7.0	8.0	8.0	7.0	8.0	8.0	7.0	8.0

TABLE III

Ex.	Wash. agent	Foam inhibitor	Hardness, °dH	Foam notation				
				30°	50°	70°	90°	95°
5	1-----	E	1% S ₁ -----	3	3	1	0	2
	2-----	E	1% S ₂ -----	3	3	1	0	0
	3-----	E	1% S ₃ -----	3	3	1	0	1
	4-----	E	0.5% S ₃ -----	3	4	2	1	1
	5-----	E	0.5% S ₄ -----	3	3	2	1	1
10	6-----	E	0.5% S ₅ -----	3	3	1	0	0
	7-----	E	1% S ₆ -----	3	1	2	1	2
	8-----	E	1% S ₇ -----	3	3	0	0	0
	9-----	E	1% S ₈ -----	3	3	3	0	0
	10-----	E	1% S ₁₀ -----	3	3	3	0	0
15	11-----	E	1% S ₉ -----	16	3	1	0	1
	12-----	F	1% S ₃ -----	3	4	4	2	4
	13-----	F	1% S ₅ -----	3	5	3	0	1
	14-----	F	1% S ₆ -----	3	5	4	2	2
	15-----	F	1% S ₁₀ -----	3	5	4	1	0
20	16-----	F	1% S ₈ -----	3	5	3	0	1
	17-----	F	-----do-----	6	4	2	0	1
	18-----	F	-----do-----	9	3	2	0	1
	19-----	G	1% S ₇ -----	16	3	1	0	1
	20-----	H	-----do-----	16	3	2	0	0
25	21-----	J	-----do-----	16	4	2	0	0
	22-----	K	-----do-----	16	3	1	0	1
	23-----	L	1% S ₅ -----	3	2	1	0	0
	24-----	L	1% S ₇ -----	3	2	1	0	0
	25-----	M	1% S ₄ -----	3	3	5	1	1
30	26-----	M	1% S ₇ -----	3	4	3	0	0
	27-----	M	1% S ₈ -----	3	1	1	0	0
	28-----	E	Mixture 0.4% S ₃ , 0.4% S ₉ .	3	3	2	0	0
	29-----							
	30-----							

EXAMPLES 29 TO 33

In the following Table IV, examples for softening and descaling agents are given. The foaming inhibitors were admixed in solid form to the granular polyphosphate mixtures with the aid of an efficient pressure mixer. The agents are suitable for prewashing or descaling of textiles, as adducts to washing and dishwashing liquors in the use of hard water, and for the removal of lime sediments in washing machines and hot water heaters. Foaming of the treating solutions, whose concentrations varied from 0.5 to 5 gm./liter, was not observed.

TABLE IV

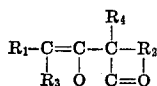
[Amounts are in percent by weight]

Ingredient	Examples				
	29	30	31	32	33
Compound S ₇ -----	0.3	0.5	0.3	0.8	0.5
Na ₂ (n+2)P ₂ O ₇ (3n+4):					
With n=3.....	95.0	40.0	7.5	35.0	35.0
With n=4 to 9.....	4.7	55.0	9.0	15.0	15.0
With n=10 to 20.....	-----	4.5	65.0	-----	-----
Sodium hexametaphosphate.....	-----	-----	-----	-----	30.5
NTA.....	-----	-----	-----	10.0	-----
Sodium silicate (Na ₂ O:SiO ₂ =1:3.3).....	-----	-----	-----	10.0	-----
Sodium carbonate.....	-----	2.2	-----	-----	15.0
Sodium sulfate.....	-----	16.0	29.2	4.0	-----

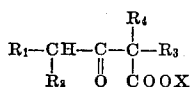
The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art may be employed without departing from the spirit of the invention.

We claim:

1. Low-foaming rinsing, washing and cleaning compositions consisting essentially of (A) from 90% to 99.9% by weight of active compounds selected from the group consisting of cleaning compounds and complexing compounds, said active compounds being from 0 to 40% of at least one surface-active compound selected from the group consisting of anionic, non-ionic and amphoteric surface-active compounds from 10% to 100% of at least one builder component selected from the group consisting of non-surface-active cleaning builder salts and complexing builder salts, and from 0 to 50% of an active-oxygen per compound, and (B) from 0.1% to 10% by weight of a foam inhibitor selected from the group consisting of (1) at least one dimer ketene of the formula



wherein R_1 and R_2 are members having 8 to 30 carbon atoms selected from the group consisting of alkyl, alkenyl, alkylcycloalkyl and alkylphenyl, and R_3 and R_4 are members selected from the group consisting of hydrogen and hydrocarbonyls having 1 to 30 carbon atoms selected from the group consisting of alkyl, alkenyl, alkylcycloalkyl and alkylphenyl, and (2) at least one saponification product of said dimer ketene of the formula



wherein R_1 , R_2 , R_3 and R_4 have the above-assigned values and X represents a member selected from the group consisting of alkali metals and ammonium and its enol.

2. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein said foam inhibitor is said dimer ketene.

3. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein said foam inhibitor is said saponification product of said dimer ketene and its enol.

4. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein said foam inhibitor is a mixture of said dimer ketene and said saponification product of said dimer ketene and its enol.

5. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein R_1 and R_2 represent members selected from the group consisting of alkyl having from 12 to 22 carbon atoms and alkenyl having from 12 to 22 carbon atoms, R_3 and R_4 are hydrogen and X is a cation selected from the group consisting of sodium and potassium.

6. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein said foam inhibitor is present in an amount of from 0.2% to 5% by weight.

7. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein said ingredient A contains from 1% to 40% by weight of said ingredient A of at least one surface-active compound selected from the group consisting of anionic, non-ionic and amphoteric surface-active compounds, from 10% to 80% by weight of said ingredient A of builder compounds selected from the

group consisting of non-surface-active cleaning builder salts and complexing builder salts, and from 10% to 50% by weight of said ingredient A of an active-oxygen per compound.

8. The low-foaming rinsing, washing and cleaning compositions of claim 7 wherein said at least one surface-active compound consists of from 25% to 70% by weight of surface-active sulfonates and sulfates, from 5% to 40% of non-ionic polyglycoethers and from 10% to 50% of soap.

9. The low-foaming rinsing, washing and cleaning compositions of claim 7 wherein said builder compounds consist of from 25% to 95% of alkali metal triphosphates and their mixtures with alkali metal pyrophosphates, from 5% to 50% of an alkali metal salt of a complexing compound selected from the group consisting of polyphosphonic acids, nitrotriactic acid and ethylenediaminetetraacetic acid, and from 5% to 75% of at least one compound selected from the group consisting of alkali metal silicates, alkali metal carbonates and alkali metal borates.

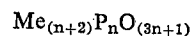
10. The low-foaming rinsing, washing and cleaning compositions of claim 7 having a further content of from 0.2% to 3% by weight of said ingredient A of enzymes selected from the group consisting of proteases, lipases and amylases.

11. The low-foaming rinsing, washing and cleaning compositions of claim 7 having a further content of from 0.2% to 3% by weight of said ingredient A of greying inhibitors.

12. The low-foaming rinsing, washing and cleaning compositions of claim 7 having a further content of from 0.01% to 1.5% by weight of said ingredient A of optical brighteners.

13. The low-foaming rinsing, washing and cleaning compositions of claim 7 having a further content of from 0 to 5% by weight of said ingredient A of foam inhibitors selected from the group consisting of saturated fatty acids having 20 to 24 carbon atoms and their alkali metal salts, paraffins, triglycerides of fatty acids and trialkylmelamines.

14. The low-foaming rinsing, washing and cleaning compositions of claim 1 wherein said ingredient A consists of cleaning and complexing compounds selected from the group consisting of polyphosphates of the formula



and metaphosphates of the formula



wherein Me represents a metal ion selected from the group consisting of sodium and potassium, n represents an integer from 3 to 20 and m represents an integer from 5 to 30, sodium nitrilotriacetate, potassium nitrilotriacetate, sodium ethylenediaminetetraacetate and potassium ethylenediaminetetraacetate.

References Cited

UNITED STATES PATENTS

3,173,899	3/1965	Clark	260—343.9
3,282,963	11/1966	Nations	260—343.9
3,524,877	8/1970	Haage et al.	260—526 R

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252—Dig. 12, 99, 132, 135, 358; 260—343.9, 526