

[54] DETERGENT COMPOSITIONS CONTAINING A SEQUESTANT AND OPTIONALLY A BLEACHING AGENT HAVING A REDUCED TENDENCY TO ATTACK COPPER, ZINC AND ALUMINUM

282/95

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[58] Field of Search 282/99, 89, 135, 389, DIG. 1;

[56]

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[57]

ABSTRACT

Detergent compositions are provided that are especially formulated with a sequestrant for use in hard water, and optionally, a bleaching agent, and that contain a corrosion inhibitor lessening the tendency of the composition to attack copper, zinc and aluminum.

17 Claims, No Drawings

DETERGENT COMPOSITIONS CONTAINING A SEQUESTRANT AND OPTIONALLY A BLEACHING AGENT HAVING A REDUCED TENDENCY TO ATTACK COPPER, ZINC AND ALUMINUM

In order to obtain a satisfactory detergent action in hard water, it is necessary in most detergent compositions to include a sequestrant that is capable of capturing calcium and magnesium ions present in the hard water, and reducing their concentration in the washing solution to less than 10^{-5} g./l. Pentasodium tripolyphosphate is widely used for this purpose. However, the use of phosphates in detergent compositions is no longer favored, because the phosphate content in the wash water has a considerable nutrient value, and if high phosphate waste waters find their way into fresh water streams and lakes, the growth of plant life therein is greatly accelerated, leading even to a choking up of the water courses. Since detergent formulations of the synthetic detergent type are now widely used, it is important to formulate them with non- or low-phosphate sequestrants.

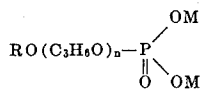
Sequestrants of the aminocarboxylic acid type, such as ethylene diamine tetraacetic acid and nitriloacetic acid, and their alkali metal and amine salts, are capable of reducing the calcium and magnesium ion concentration in hard water to the desired low level, but they strongly increase the corrosive attack of detergent solutions containing them on copper, zinc and aluminum, as well as metal alloys containing these metals. Such corrosive attack is accentuated if the detergent composition also includes bleaching agents of the peroxide type. Since copper, zinc and aluminum and their alloys are widely used in dishwashing and clothes washing machines, for example, in the protective conduits for the electric heating elements, which are of nickel-plated copper, in brass valve seats, in copper liquid thermometers, in zinc alloy pump wheels, and in zinc-plated steel outer drums, in pump casings, and the like, such corrosion presents a particularly serious problem, and must be inhibited if such sequestrants are to be used in detergent formulations.

Phosphoric acid esters of alkyl glyceryl ethers, and phosphoric acid esters of ethylene oxide adducts of fatty alcohols have been proposed as inhibitors of the corrosive effect of detergent compositions containing aminocarboxylic acid chelating agents. However, the effectiveness of these phosphoric acid esters is greatly reduced in the presence of bleaching or oxidizing agents, so that these esters are not capable of imparting a sufficient corrosion inhibiting effect to detergent formulations containing or to be used with a bleaching agent.

The salts of monocetyl and monostearyl phosphates are good metal corrosion inhibitors in detergent compositions based on nonionic and/or anionic surfactants, but these alkyl phosphates form difficultly soluble calcium and magnesium salts. Consequently, they cannot be employed in detergent formulations intended for use in hard water, unless sequestrants are also present. However, these alkyl phosphates are relatively ineffective in inhibiting the corrosive effect of aminocarboxylic acid sequestrants, such as ethylene diamine tetraacetic acid and propylene diamine tetraacetic acid.

In accordance with the invention, it has been determined that monoalkyl oxypropylene phosphoric acid esters display excellent corrosion-inhibiting properties in synthetic surfactant detergent or washing compositions containing aminocarboxylic acid sequestrants and bleaching or oxidizing agents, such as peroxides, and demonstrate this effect in both soft and hard water. The monoalkyl oxypropylene phosphoric acid esters can be used either in acid form or in salt form. If the acid form is used, the salt form may be formed in situ in the aqueous detergent or washing solution.

The monoalkyl oxypropylene phosphoric acid ester corrosion inhibitors in accordance with the invention are defined by the following general formula:



In the above formula,

R is a straight or branched chain alkyl radical having from about 15 to about 20 and preferably from 16 to 18 carbon atoms.

M is hydrogen, an alkali metal, such as sodium or potassium, ammonium or a strongly basic organic amine, such as tributylamine, monoethanolamine, diethanolamine, or triethanolamine.

n is a number representing the average number of propylene oxide ether units, and is within the range from about 1 to about 4, and preferably 1 or 2. It will be understood that when n is greater than 1, mixtures can be present, and probably will be, when propylene oxide is condensed with the alcohol. In such cases, n represents an average number, and can be any fractional number within the range from 1 to 4, for instance, 1.2, 2.5 or 3.3.

R can be, for example, pentadecyl, palmityl (cetyl), margaryl, stearyl, nonadecyl, and arachidyl.

Exemplary monoalkyl oxypropylene phosphoric acid esters are monopalmityltri(oxypropylene) phosphoric acid, monostearyldi(oxypropylene)phosphoric acid, monomargaryldi(oxypropylene)phosphoric acid, monononadecyl oxypropylene phosphoric acid, monoarachidyl oxypropylene phosphoric acid, monostearyltri(oxypropylene) phosphoric acid, monopalmityl(cetyl)tetra(oxypropylene) phosphoric acid, monopalmityl(cetyl)(oxypropylene)_{1.5} phosphoric acid, monostearyl(oxypropylene)_{2.5} phosphoric acid, and monomargaryl(oxypropylene)_{3.5} phosphoric acid, and the sodium, potassium, ammonium, tributylamine and triethanolamine salts thereof.

In addition to the monoalkyloxypropylene phosphoric acid ester, the essential ingredients of the detergent compositions of the invention are a synthetic detergent or surfactant, which can be of the anionic and/or nonionic type, and an aminocarboxylic acid chelating agent. The monoalkyloxypropylene phosphoric acid ester is intended to be used in the presence of a bleaching or oxidizing agent, such as a peroxide bleaching agent, and this is an optional ingredient, but it can be added later, when the washing solution is prepared. In addition to these components, which with the monoalkyloxypropylene phosphoric acid ester are the only essential components, there can be included as optional components builders, fillers, optical whitening agents, coloring agents, perfumes, and other conventional detergent formulation components.

As compared to detergent formulations of this type that do not contain monoalkyloxypropylene phosphoric acid esters, the detergent formulations of the invention have a reduced tendency to corrode copper, zinc and aluminum, and alloys containing such metals. In order to keep the tendency to corrode such metals at a minimum, the weight ratio of monoalkyl oxypropylene phosphoric acid ester to surfactant should be within the range from about 10:1 to about 1:10.

The detergent compositions of the invention have the following formulation, based on the solids content:

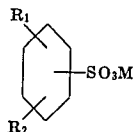
Essential ingredients	Solids %	
	Overall range	Preferred range
anionic and/or nonionic surfactant	2 to 30%	10 to 20%
Sequestrant	2 to 30%	5 to 15%
Monoalkylpropylene glycol ether phosphoric acid ester	1 to 20%	2 to 5%
Optional ingredients		
Bleaching or oxidizing agent, such as peroxide	5 to 40%	15 to 30%
Builders, soil suspending agents, and other additives	10 to 80%	20 to 60%

The essential and optional components of the detergent compositions of the invention are solids, for the most part, and consequently the detergent compositions of the invention are conveniently formulated and marketed as solids, in any particulate form, as, for instance, powders, flakes, granules, spray-dried ovoids or spheres, pellets, or other agglomerates. Preferably, the composition is in the form of particles produced by drying an aqueous mixture or slurry of the component. Spray-drying is a preferred drying method, since it produces friable light particles which dissolve rapidly and completely in water. Other drying methods include suspension-drying and drum drying, the latter procedure being particularly useful in the production of particulate detergent mixtures in flake or large particle form.

The detergent composition can also be formulated as an aqueous concentrate which forms a washing solution upon dilution with water. The concentrate has as high a composition solids content as possible, within the range from 20 to 75 percent, preferably from 30 to 60 percent by weight. The upper limit of solids content is normally determined by the solubility of the components in water or other solvent or suspending medium, such as ethyl alcohol, or methyl alcohol. However, solubility in water or other solvent can be increased in the concentrate by the addition of solubilizing agents. To some extent, the monoalkoxypropylene phosphoric acid esters display a solubilizing effect on the other ingredients. This effect can be increased by the addition of other hydrotropic substances, such as sodium xylene sulfonate and sodium toluene sulfonate. Organic solvents can be used, such as ethyl alcohol or methyl alcohol.

The synthetic detergent or surfactant employed in the compositions of the invention can be of the anionic type, of the nonionic type, or the mixed nonionic-anionic type. Mixtures of anionic and nonionic surfactants can also be employed. Among the anionic surfactants which can be employed are the alkyl aryl sulfonates, the alkyl sulfonates, the alpha-olefin sulfonates, the alkyl ether polyglycol sulfates, and the alkyl phenol ether sulfates. These are all known compounds.

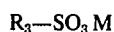
Exemplary of the alkyl aryl sulfonates are the alkyl benzene sulfonates, which have the general formula:



R_1 is a straight or branched chain alkyl radical having from about four to about 18 carbon atoms. R_2 is hydrogen or a straight or branched chain alkyl radical having from one to about 12 carbon atoms. The total of the number of carbon atoms in R_1 and R_2 is within the range from about 10 and to about 24. M is hydrogen, or an alkali metal, ammonium or organic amine cation.

Examples of suitable alkyl benzene sulfonates are sodium dodecylbenzene sulfonate, sodium polypropylene benzene sulfonate (Lewis Pat. No. 2,477,383), sodium tridecylbenzene sulfonate, sodium cetylbenzene sulfonate, potassium dodecyl toluene sulfonate, triethanolamine dodecylbenzene sulfonate, potassium dinonylbenzene sulfonate, sodium didodecylbenzene sulfonate, and ammonium polypropylene benzene sulfonate.

The alkyl sulfonates have the general formula:



R_3 is a straight or branched chain alkyl group having from about ten to about twenty carbon atoms, and M is hydrogen, or an alkali metal, ammonium or organic amine cation. Such sulfonates are obtained by sulfonating paraffinic hydrocarbons with a mixture of sulfur dioxide and oxygen using energy rich radiation. Exemplary are sodium cetyl sulfonate, potassium stearyl sulfonate, and triethanolamine myristyl sulfonate.

The alpha-olefin sulfonates have the formula:



R_4 is an alkylene (ethylenically unsaturated) radical having from about 10 to about 20 carbon atoms, and M is hydrogen, or an alkali metal, ammonium or organic amine cation. Such sulfonates are obtained by sulfonation of alpha-olefins of the general formula:



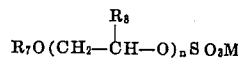
R_5 is an alkyl radical having from about nine to about 19 carbon atoms. Exemplary is the sodium salt of the alpha-olefin sulfonic acid obtained by the sulfonation of a mixture of alpha-olefins having from 14 to 18 carbon atoms.

Also useful are the alkyl sulfates, which have the formula:



R_6 is an alkyl radical having from about 10 to about 22 carbon atoms, and M is hydrogen, an alkali metal, ammonium, or an organic amine cation. Exemplary are sodium coconut oil fatty alcohols sulfate, potassium cetyl alcohol sulfate, ammonium stearyl alcohol sulfate, and triethanolamine lauryl alcohol sulfate.

The alkyl oxyalkylene sulfates have the general formula:

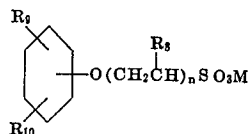


R_7 is an alkyl radical having from about 12 to about 20 carbon atoms. R_8 is hydrogen or methyl. M is hydrogen, or an alkali metal, ammonium or organic amine cation. n is an integer representing the average number of the oxyalkylene units indicated, and is within the range from 2 to 6. It will be understood that n can represent an average number, such as 2.5.

Exemplary are the sodium salt of sulfonated lauryl alcohol condensed with 3 moles of ethylene oxide, and the potassium salt of sulfonated cetyl stearyl alcohol condensed with 2 moles of propylene oxide, and then 2 moles of ethylene oxide.

These and the alkyl phenol oxyalkylene sulfates below are examples of mixed nonionic-anionic surfactants.

The alkyl phenol oxyalkylene sulfates have the general formula:

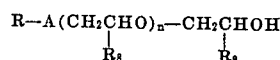


R_8 is as above. R_9 is a straight or branched alkyl radical having from four to about 16 carbon atoms, and R_{10} is hydrogen or a straight or branched alkyl radical having from one to about 14 carbon atoms, the total number of carbon atoms in R_9 and R_{10} being within the range from eight to 24. n represents the number of units enclosed by the brackets, and is a number from 1 to 6. It will be understood that n can be an average value, such as 3.5. Exemplary are sodium nonyl phenol oxyethylene sulfate (condensed with 4 moles of ethylene oxide), potassium dinonyl phenol oxyethylene sulfate (condensed with 6 mole of ethylene oxide), ammonium dibutyl phenol oxyethylene sulfate (condensed with 3 mole of ethylene oxide), and triethanolamine dodecylcresol oxyethylene sulfate (condensed with 4 moles of ethylene oxide).

The nonionic surfactants which can be employed include the polyoxyalkylene glycol monoethers, monoamines, monoamides, monocarboxylic acid esters and monothiocarboxylic acid esters.

The nonionic surfactants which can be employed include the polyoxyalkylene glycol monoethers, monoamines, monoamides, monocarboxylic acid esters and monothiocarboxylic acid esters.

The alkyl oxyalkylene ether and ester and thioether and ester derivatives have the following general formula:



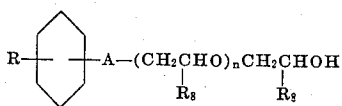
R_9 is as above, and R is a straight or branched chain saturated or unsaturated hydrocarbon group having from about

five to about 18 carbon atoms, or an aralkyl group having an aryl nucleus to which is attached a straight or branched chain saturated or unsaturated hydrocarbon group having from about eight to about 18 carbon atoms, linked through A to the aryl nucleus.

A is either oxygen, thioether, amino, amido, a carboxylic acid ester or a thiocarboxylic acid ester group. n is a number from 8 to 35, and can represent an average number, such as 10.5.

Exemplary R radicals include amyl, octyl, nonyl, decyl, tetradecyl, lauryl, myristyl, cetyl, or stearyl. Exemplary aralkyl groups include octylphenyl, nonylphenyl, decylphenyl, and stearylphenyl. These compounds are prepared by condensation of the corresponding alcohol, mercaptan, amine, oxy or thio fatty acids or esters with ethylene oxide. Exemplary are the condensation products of oleyl or lauryl alcohol, mercaptan or amine, or oleic or lauric acid, with from 8 to 17 moles of ethylene oxide, and the polyoxyethylene ester of tall oil fatty acids.

In the case where R is aralkyl, the polyoxyalkylene surfactants have the formula:

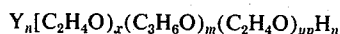


R_8 is as above. R is a straight or branched chain saturated or unsaturated hydrocarbon group having at least five carbon atoms up to about 18 carbon atoms.

A is oxygen or sulfur, and n is a number within the range from 8 to 35.

R may, for example, be a straight or branched chain amyl, octyl, nonyl, dodecyl, tetradecyl, lauryl, cetyl, myristyl or stearyl group. Exemplary are condensation products of octyl and nonyl phenol and thiophenol with from 8 to 17 moles of ethylene oxide.

Also useful are the mixed polyoxyethylene oxypropylene ethers having the formula:



These compounds are described in U.S. Pat. Nos. 2,674,619 to Lundsted, dated Apr. 6, 1954, and 2,677,700 to Jackson et al., dated May 6, 1954. They are condensates of a 1,2-alkylene oxide, such as 1,2-propylene oxide and 1,2-ethylene oxide, the ethylene oxide residues constituting from 20 to 90 percent of the resulting concentrate. Y as defined in these patents is the residue of an organic compound containing therein a single hydrogen atom capable of reacting with a 1,2-alkylene oxide, and the total of x and y is from 2 to 20. x and y may also be zero. n is a number from 1 to 25; p is a number from 1 to 5, and the average weight of the entire block polymer is from 1,000 to 4,000.

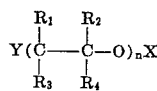
Organic compounds suitable for forming Y are compounds in which the hydrogen atoms are activated by an oxygen atom, such as in a hydroxyl group, a phenol group or a carboxyl group, or by a basic nitrogen atom, such as in an amine group and amide group, a sulfamide group, a carbamide group, and a thiocarbamide group, or by a sulfur atom, such as in a mercaptan.

Exemplary Y compounds are glycerol, ethylene glycol, propylene glycol, methanol, ethanol, isopropanol, n-butanol, 2-ethylhexanol, lauryl alcohol, cetyl alcohol, stearyl alcohol, eicosanol, oleyl alcohol, so-called OXO-alcohol mixtures, butanediol, pentaerythritol, oxalic acid, triethanolamine, aniline, resorcinol, triisopropanolamine, sucrose, ethylenediamine, diethylenetriamine, acetamide, coconut oil fatty amine, methyl mercaptan, dodecyl mercaptan, hexadecyl mercaptan, etc.

Exemplary of this type of nonionic surfactants are propylene glycol condensed with 20 moles of propylene oxide and then with 5 moles of ethylene oxide, Y being hydroxyl, $n=1$, $x+y=5$, $m=21$, and $p=1$, as well as ethylene diamine

with which have been condensed 12 moles of propylene oxide followed by 10 moles of ethylene oxide, Y being an ethylene diamine residue, $n=4$, $x=0$, $y=2.5$, $m=3$, and $p=4$.

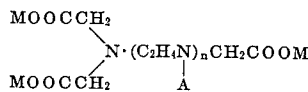
Another type of polyoxyalkylene glycol ether surfactants has the formula:



Y is an organic residue as defined above, and R_1 , R_2 , R_3 and R_4 are selected from the group consisting of hydrogen, aliphatic and aromatic radicals, at least one of these substituents not being hydrogen. n is a number greater than 6.4, as determined by hydroxyl number, and X is a water-solubilizing group, as defined in U.S. PAT. Nos. 2,674,691 and 2,677,700.

Exemplary of this type of compound are the fatty alcohol styrene oxide condensates containing 7 moles of styrene oxide, with the water-solubilizing group X being 70 moles of ethylene oxide.

The sequestrant employed in accordance with the invention to capture calcium and magnesium ions in hard water is an amino polycarboxylic acid or salt having the general formula:



A is CH_2COOM or $\text{CH}_2\text{CH}_2\text{OH}$. M is hydrogen or an alkali metal, such as sodium and potassium or ammonium, and n is a number from 0 to 5. Exemplary are nitrilotriacetic acid, ethylenediamine tetraacetic acid, the mono-, di-, tri- and tetra-sodium salts of ethylene diamine tetraacetic acid, the mono-, di- and tri-sodium salts of nitrilotriacetic acid, the mono-, di-, tri-, tetra- and penta-sodium salts of diethylenetriamine pentaacetic acid, and the mono-, di- and tri-potassium salts of hydroxyethylethylenediamine triacetic acid.

The detergent compositions of the invention may also contain or are for use with a bleaching or oxidizing agent, such as an inorganic peroxide which serves as a bleaching agent. Suitable peroxides are the perborates, persulfates, percarbonates and perpyrophosphates, in the form of their water-soluble salts, preferably their alkali metal salts. Exemplary are sodium perborate, potassium persulfate, potassium percarbonate, $\text{K}_2\text{C}_2\text{O}_6$, and sodium perpyrophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$.

As builders and fillers, there can be used tetrasodium pyrophosphate, sodium carbonate, sodium sulfate, potassium carbonate, potassium sulfate, sodium silicate, potassium silicate. Optical whitening agents, coloring agents and perfumes can also be added.

Soil-suspending agents can also be incorporated, such as sodium carboxymethyl cellulose, hydroxyethyl cellulose, and ethylhydroxy-ethyl cellulose, as well as starch, polyethylene glycols, and polyvinyl alcohol.

The following Examples in the opinion of the inventors represent preferred embodiments of their invention.

EXAMPLES 1 TO 4

A detergent composition was prepared, containing the ingredients shown in Table I.

This composition was dissolved in water of 15° of hardness (1/5 Mg-hardness, 4/5 Ca-hardness) to the solution concentration indicated.

TABLE I

Composition	% by weight	Solution Concentration
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Sequestrants		
Tetrasodium ethylenediamine tetra-acetic acid	24.2%	1.6 g/l
Pentasodium tripolyphosphate	12.1%	0.8 g/l
Bleaching agent		
Sodium perborate	24.2%	1.6 g/l
Builder		
Sodium carbonate	30.3%	2.0 g/l
Nonionic surfactant		
Condensation product of tallow fatty alcohol and 8 moles ethylene oxide	9.2%	0.6 g/l

The tendency of each solution to corrode copper metal was determined by the following test.

To 100 ml. portions of this solution there was added 0.4 g./l. of the alkylether phosphoric acid ester shown in Table II.

To each 100 ml. sample, and a control sample without the phosphoric acid ester, there was added 0.5 g. of copper powder, and the solutions boiled for 30 minutes. After removing the copper powder by filtration, the copper content of each sample was determined by means of an atom absorption photometer. The amount of copper dissolved represents the amount of copper removed by corrosion, and is thus a measure of the tendency of the detergent solution to corrode copper.

For comparison, to show the relative effectiveness of an alkyl phosphoric acid ester, (monocetyl ortho phosphate) was added to another 100 cc. sample (control B), and tested in the same way.

The data are given in Table II.

TABLE II

Example Number	Alkyl oxypropylene phosphoric acid ester ¹	Copper dissolved solution (mg./l.)
Control A	None	99
Control B	Monocetyl ortho phosphoric acid	90
1	$\begin{array}{c} \text{OH} \\ \\ \text{O}_{18}\text{H}_{33}\text{O}-\text{P} \\ \\ \text{O} \\ \\ \text{OH} \end{array}$ Mono cetyl oxypropylene phosphoric acid	43
2	$\begin{array}{c} \text{OH} \\ \\ \text{C}_{18}\text{H}_{33}-\text{O}-\text{CH}-\text{CH}_2-\text{O}-\text{P} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{O} \\ \\ \text{OH} \end{array}$ Mono cetyl di(oxypropylene) phosphoric acid	38
3	$\begin{array}{c} \text{OH} \\ \\ \text{C}_{18}\text{H}_{33}-[\text{O}-\text{CH}-\text{CH}_2-]_2-\text{O}-\text{P} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{O} \\ \\ \text{OH} \end{array}$ Mono stearyl oxypropylenephosphoric acid	49
4	$\begin{array}{c} \text{OH} \\ \\ \text{C}_{18}\text{H}_{37}-\text{O}-\text{CH}-\text{CH}_2-\text{O}-\text{P} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{O} \\ \\ \text{OH} \end{array}$ Mono stearyl-di(oxypropylene)phosphoric acid	57
	$\begin{array}{c} \text{OH} \\ \\ \text{C}_{18}\text{H}_{37}[\text{O}-\text{CH}-\text{CH}_2-]_2-\text{O}-\text{P} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{O} \\ \\ \text{OH} \end{array}$	

¹ The alkylether phosphoric acid esters were prepared by reacting the alcohol (cetyl alcohol (hexadecyl alcohol) or stearyl alcohol (heptadecyl alcohol)) with propylene oxide, and then reacting the alkyl oxypropylene alcohol with ortho phosphoric acid. The acid form was added to the solution, but the sodium salt thereof was possibly formed therein *in situ*.

The results for Control A, vis-a-vis Examples 1 to 4, in Table II show that the alkyl oxypropylene phosphoric acid esters of Examples 1 to 4 were effective in inhibiting copper corrosion by the sodium ethylenediaminetetraacetic acid and the peroxide bleaching agent. On the other hand, the alkyl phosphoric acid ester, Control B, was virtually ineffective. This demonstrates the importance of the oxypropylene group in the phosphoric acid ester, in corrosion inhibition.

EXAMPLES 5 TO 7

A detergent composition was prepared to the formulation shown in Table III. This was dissolved in water of 15° of hardness to form a solution of the concentration indicated.

TABLE III

Composition	% by weight	Solution concentration
Sequestrants		
Trisodium nitrilotriacetic acid	24.2%	1.6 g/l
Pentasodium tripolyphosphate	12.1%	0.8 g/l
Bleaching agent		
Sodium perborate	24.2%	1.6 g/l
Builder		
Sodium carbonate	30.3%	2.0 g/l
Nonionic surfactant		
Condensation product of tallow fatty alcohol and 8 moles ethylene oxide	9.2%	0.6 g/l

To 100 ml. portions of this solution, 0.4 g./l. of the alkyl oxypropylene phosphoric acid esters listed in Table IV was added. Thereafter, the amount of copper dissolved by the detergent solutions were determined, in the test described in Examples 1 to 4.

TABLE IV

Example no.	Alkyl oxypropylene phosphoric acid ester	Copper dissolved mg/l
Control C	None	46
5	Mono-cetyl oxypropylene-phosphoric acid	19
6	Mono-cetyl di(oxypropylene) phosphoric acid	15
7	Mono-stearyl di(oxypropylene)-phosphate	34

The results in Table IV show that the alkyl oxypropylene phosphates of Examples 5 to 7 are effective in inhibiting copper corrosion by nitrilotriacetic acid and peroxide bleaching agents.

EXAMPLE 8

A detergent composition was prepared to the formulation shown in Table V. The composition was dissolved in water of 5° dH to the solution concentration shown.

TABLE V

Composition	% by weight	Solution Concentration
Sequestrants		
Trisodium nitrilotriacetic acid	30.3%	1 g/l
Pentasodium tripolyphosphate	15.2%	0.5 g/l

Bleaching agent		
Sodium perborate	30.3%	1 g/l
Builders		
Sodium carbonate	7.6%	0.25 g/l
Sodium silicate	7.6%	0.25 g/l
Nonionic surfactant		
Condensation product of tallow fatty alcohol and 8 moles ethylene oxide	9.0%	0.30 g/l

To 100 ml. samples of the solution was added 0.30 g./l. of the alkyl oxypropylene phosphoric acid ester listed in Table VI. The tendency to corrode copper then was determined in the test described in Examples 1 to 4, in comparison with a control without the phosphoric acid ester.

TABLE VI

Example no.	Alkyl oxypropylene phosphoric acid	Copper dissolved (mg/l)
Control D	None	103
8	Mono-cetyl oxypropylene phosphoric acid	15

The results in Table VI show that the monocetyl oxypropylene phosphoric acid was effective in inhibiting copper corrosion.

To another 100 ml. sample of this solution was added 0.3 g./l. of mono-cetyl oxypropylene phosphoric acid. The tendency of this solution to corrode zinc metal was then determined, in comparison with a control that did not contain the phosphoric acid ester. The solution was refluxed for 30 minutes with 0.5 g. zinc powder, the undissolved powder was removed by filtration, and the zinc content of the solution was determined by means of an atom absorption photometer. The results are shown in Table VII.

TABLE VII

Example no.	Alkyl oxypropylene phosphoric acid ester	Zinc dissolved (mg/l)
Control E	None	215
8	Mono-cetyl oxypropylene-phosphoric acid	80

The results show that the cetyl oxypropylene phosphoric acid is quite effective in inhibiting zinc corrosion.

EXAMPLE 9

A detergent formulation was prepared, as shown in Table VIII. This composition was dissolved in water of 5° dH, to the solution concentration shown in the Table.

TABLE VIII

Composition	% by weight	Solution concentration
Sequestrants		
Trisodium nitrilotriacetic acid	33.3%	1 g/l
Pentasodium tripolyphosphate	16.6%	0.5 g/l
Bleaching agent		
Sodium perborate	33.3%	1 g/l
Builder		
Sodium carbonate	8.3%	0.25 g/l
Nonionic surfactant		
Condensation product of tallow fatty alcohol and 8 moles ethylene oxide	8.5%	0.30 g/l

To a 100 ml. portion of this detergent solution was added 0.3 g./l. mono-cetyl oxypropylene phosphoric acid. Then in

comparison with a control, the portion was boiled with an aluminum sheet 3 centimeters square for 30 minutes. The aluminum content of the solution was then determined, by means of an atom absorption photometer. The results are shown in Table IX.

TABLE IX

Example no.	Alkyl oxypropylene phosphoric acid	Aluminum dissolved (mg/l)
Control F	None	375
9	Mono-cetyl oxypropylene phosphoric acid	74

The results in Table IX show that the cetyl oxypropylene phosphoric acid is effective in inhibiting corrosion of aluminum metal.

The detergent compositions prepared according to the invention, as seen from the above Examples, show a very substantial decrease in the corrosion of copper, zinc and aluminum. Copper, aluminum and zinc corrosion is inhibited even when hard water is used in the preparation of the detergent solution. It, furthermore, was proved by test washing that the compositions according to the invention provide very good washing results and that, in addition, the resulting detergents are low foaming, which is important where the detergents are used in automatic washing machines.

EXAMPLES 10 TO 13

Four detergent compositions were prepared, containing the ingredients shown in Table X.

The compositions were each dissolved in water of 15° hardness (1/5 Mg-hardness, 4/5 Ca-hardness) to the solution concentration indicated.

TABLE X

Composition	Percent by weight	Solution concentration, g./l.
45 Sequestrants:		
Tetrasodium salt of ethylenediamine tetraacetic acid.....	22.9	1.6
Pentasodium tripolyphosphate.....	11.5	0.8
Bleaching agent:		
Sodium perborate.....	22.9	1.6
Builder:		
Sodium carbonate.....	28.5	2.0
Nonionic surfactant:		
Condensation product of tallow fatty alcohol and 8 moles ethylene oxide.....	8.6	0.6
Corrosion inhibitor:		
Monoalkyl oxypropylene phosphoric acid ester..	5.6	0.4
55 Mono cetyl oxy propylenephosphoric acid.....		
$C_{16}H_{33}-O-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 10
60 Mono cetyl di(oxypropylene) phosphoric acid.....		
$C_{16}H_{33}-[O-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-]_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 11
65 Mono stearyl oxypropylenephosphoric acid.....		
$C_{18}H_{37}-O-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 12
70 Mono stearyl-di(oxypropylene) phosphoric acid.....		
$C_{18}H_{37}[O-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-]_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 13

The results obtained were the same as for the corresponding alkyl oxypropylene phosphoric acid esters of Examples 1 to 4. The compositions tested were effective in inhibiting copper corrosion by the sodium ethylenediaminetetraacetic acid and the peroxide bleaching agent.

EXAMPLES 14 TO 17

Four detergent compositions were prepared, containing the ingredients shown in Table XI.

These compositions were each dissolved in water of 15° of hardness (1/5 Mg-hardness, 4/5 Ca-hardness) to the solution concentration indicated.

TABLE XI

Composition	Percent by weight	Solution concentration, g./l.
Sequestrants:		
Tetrasodium ethylenediamine tetraacetic acid...	29.6	1.6
Pentasodium tripolyphosphate.....	14.8	0.8
Builder:		
Sodium carbonate.....	37.0	2.0
Nonionic Surfactant:		
Condensation product of tallow fatty alcohol and 8 moles ethylene oxide.....	11.1	0.6
Corrosion Inhibitor:		
Monoalkyl oxypropylene phosphoric acid ester..	7.5	0.4
Mono cetyl oxy propylenephosphoric acid.....		
$\text{C}_{16}\text{H}_{33}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 14
Mono cetyl di(oxypropylene) phosphoric acid.....		
$\text{C}_{16}\text{H}_{33}-[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2]_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 15
Mono stearyl oxypropylenephosphoric acid.....		
$\text{C}_{18}\text{H}_{37}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 16
Mono stearyl-di(oxypropylene)phosphoric acid.....		
$\text{C}_{18}\text{H}_{37}[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2]_2-\text{O}-\underset{\text{O}}{\overset{\text{OH}}{\text{P}}}$		EXAMPLE 17

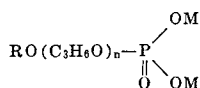
The tendency of each solution to corrode copper metal in the presence of sodium perborate was determined by the following test.

To 100 ml. portions of this solution there was added 0.6 g./l. of sodium perborate. The resulting solutions were then tested as in Examples 1 to 4.

The results showed that the alkyl oxypropylene phosphoric acid esters were effective in inhibiting copper corrosion by the sodium ethylenediaminetetraacetic acid and the peroxide bleaching agent.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A detergent composition for use in hard and soft water consisting essentially of an organic surfactant selected from the group consisting of anionic and nonionic organic surfactants, an aminocarboxylic acid or salt sequestrant in an amount to sequester calcium and magnesium ions in hard water and a mono-alkyl oxypropylene phosphoric acid ester of the formula



wherein R is an alkyl group having from 15 to 20 carbon atoms and M is selected from the group consisting of hydrogen, alkali metals, ammonium and strongly basic organic amine cations, and n is a number within the range from 1 to 4, in an amount to lessen the corrosive effect of the aminocarboxylic acid on copper, zinc and aluminum, in the presence of a bleaching or oxidizing agent.

2. A detergent composition according to claim 1, in which the weight ratio of surfactant to phosphoric acid ester is within the range from about 10:1 to about 1:10.

3. A detergent composition according to claim 1, in which the amount of surfactant is within the range from about 2 to about 30 percent by weight, the amount of the aminocarboxylic acid is within the range from about 2 to about 30 by weight, and the amount of phosphoric acid ester is within the range from about 1 to about 20 percent by weight.

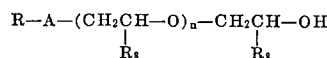
4. A detergent composition according to claim 1, consisting essentially of a bleaching or oxidizing agent in an amount within the range from about 5 to about 40 percent by weight.

5. A detergent composition according to claim 4, in which the bleaching agent is a peroxide salt.

6. A detergent composition according to claim 5, in which the bleaching agent is selected from the group consisting of the perborates, persulphates, percarbonates, and perpyrophosphates of the alkali metals.

7. A detergent composition according to claim 1, in which the anionic surfactant is selected from the group consisting of alkylaryl sulphonates, alkyl sulphonates, α -olefin sulphonates, alkyl sulphonates, alkyl oxyalkylene sulphates, and alkylphenol oxyalkylene sulphates.

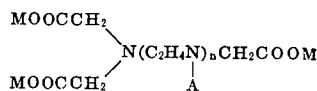
8. A detergent composition according to claim 1, in which the nonionic surfactant has the general formula



where R is selected from the group consisting of hydrocarbon groups having from 15 to 18 carbon atoms and aralkyl groups having a hydrocarbon group having from eight to 18 carbon atoms attached at the aryl nucleus and linked to A through the aryl nucleus, R₈ is selected from the group consisting of hydrogen and methyl, "A is either oxygen or sulphur, or an amino, amido, carboxylic acid ester or thiocarboxylic acid ester group", and n is a number from 8 to 35.

9. A detergent composition according to claim 1, in which the nonionic surfactant has the general formula Y_n [(C₂H₄O)_x(C₃H_{6a}^o_m(C₂H₄O)_y]_pH_n where Y is OH or a nucleating organic residue containing active hydrogen atoms, and the total of x and y is from 2 to 20, m is from 1 to 25, p is from 1 to 5 and the mean molecular weight of the entire block polymer is from 1,000 to 4,000.

10. A detergent composition according to claim 1, in which the aminocarboxylic acid or salt sequestrant has the general formula:



where A is —CH₂COOH OR —CH₂CH₂OH, M is hydrogen, or an alkali metal, ammonium or organic amine cation, and n is a number from 0 to 5.

11. A detergent composition according to claim 1, consisting essentially of one or more of builders, in an amount within the range from about 10 to about 80 percent of the total weight of the detergent composition.

12. A detergent composition according to claim 1, in which the phosphoric acid ester is monocetyloxypropylene orthophosphoric acid ester.

13. A detergent composition according to claim 1, in which the phosphoric acid ester is monocetyldi(oxypropylene) orthophosphoric acid ester.

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14. A detergent composition according to claim 1, in which the phosphoric acid ester is monostearyloxypropylene orthophosphoric acid ester.

15. A detergent composition according to claim 1, in which the phosphoric acid ester is monostearyl di(oxypropylene) orthophosphoric acid ester.

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16. A detergent composition according to claim 1 in solid particulate form.

17. A detergent composition according to claim 1, in the form of a concentrated aqueous solution having a solids content of from about 20 to about 75 percent by weight.

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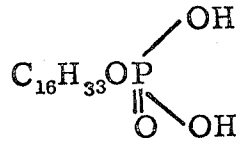
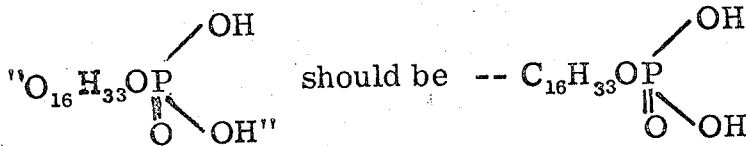
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,569 Dated April 11, 1972

Inventor(s) Martin Hellsten et al.

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

- Column 2, line 3 : "b20" should be -- 20 --
- Column 2, line 39 : "monoaklyoxypropylene" should be
-- monoalkoxypropylene --
- Column 4, line 60 : "mole" should be -- moles --
- Column 4, line 61 : "mole" should be -- moles --
- Column 5, line 41 : " $Y_n [C_2H_4O)_x (C_3H_6O)_m (C_2H_4O)_y]_p H_n$ "
should be
-- $Y_n [(C_2H_4O)_x (C_3H_6O)_m (C_2H_4O)_y]_p H_n$ --
- Column 6, line 41 : "hydroxethylethylenediamine" should be
-- hydroxyethylethylenediamine --
- Column 7, line 32 : "TABLE" should be -- Table --
- Column 7, Table II,
Formula - lines 45-
50 : $O_{16}H_{33}OP$ should be -- $C_{16}H_{33}OP$ --



Column 12, line 49 : " $x(C_3H_6)_m(C_2H_4O)_yH_n$ "
should be
-- $x(C_3H_6O)_m(C_2H_4O)_y]_pH_n$ --

Column 12, line 63 : "OR" should be -- or --

Signed and sealed this 27th day of March 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,569 Dated April 11, 1972

Inventor(s) MARTIN HELLSTEN, ET. AL.

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

Column 12, lines 44 and 46, cancel the quotation mark
(") .

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGMEYER
Acting Commissioner of Patents