DETERGENT COMPOSITION CONTAINING ORGANIC PHOSPHONATE CORROSION INHIBITORS

Roger Earl Zinnerer, Springfield Township, Hamilton County, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio
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ABSTRACT OF THE DISCLOSURE

Detergent compositions containing (1) 1—98% of water soluble amino polycarboxylate, tripolyphosphate, or polyphosphate builder, (2) less than 40% organic detergent, (3) as a corrosion inhibiting agent, 0.05—25% secondary straight chain alkyl phosphate containing 12—24 carbon atoms or straight chain alkyl benzyl phosphate wherein the alkyl chain contains 9—18 carbon atoms, and (4) up to 90% alkali metal pyrophosphates, orthophosphates, tetraborates, perborates, hexaphosphates, sesquicarbonates, and bicarbonates, the ratio of (2) to the total of (1) and (4) being from 1:2 to about 10:1.

This application is a continuation-in-part of my co-pending application Ser. No. 315,678, now abandoned, filed Oct. 11, 1963.

This invention relates to detergent compositions comprising certain detergent builders which are very corrosive towards aluminum, German silver and Zamak. Specifically, this invention relates to detergent compositions which have been inhibited against the corrosion of Zamak and, optionally, aluminum and/or German silver by the presence of certain corrosion inhibitors including specific organic phosphonate corrosion inhibitors.

Detergent builders (chelating materials) tend to corrode aluminum, German silver and Zamak when the detergens builders comprise at least with these materials in washing machines, dish pans, kitchen equipment, sinks and the like. (Zamak is a common alloy containing zinc which is particularly used in washing machine pumps. Zamak is a zinc alloy containing, e.g., 4% aluminum, 0.04% magnesium, balance zinc. Zamak #3, the most commonly used Zamak, is described on page 1169 of Metals Handbook, 8th ed., vol. I, published by the American Society for Metals.) This corrosion problem has commonly been solved with respect to aluminum and German silver by including in detergent compositions containing detergent builders, alkali metal silicates such as sodium silicate having a ratio of SiO₂:Na₂O of about 1.6 and a German silver corrosion inhibitor such as benzo-triazole. The alkali silicates are extremely efficient with respect to preventing the corrosion of aluminum and the benzo-triazole is very efficient with respect to preventing the corrosion of German silver. Furthermore, they are relatively inexpensive in effective amounts. However, the sodium silicate and benzo-triazole do not prevent these compositions from corroding Zamak and when certain very effective detergent builders and chelating agents such as sodium nitrilotriacetate are present in detergent compositions this Zamak corrosion is completely unacceptable. Therefore, it is necessary to include in such compositions a corrosion inhibitor which will prevent the corrosion of the Zamak especially when the compositions contain the more effective detergent builders such as sodium nitrilotriacetate.

Accordingly, it is an object of this invention to provide a detergent composition containing certain specified detergency builders, said detergent composition being effectively inhibited against the corrosion of Zamak and, optionally, aluminum and/or German silver by the presence of certain corrosion inhibitor compounds.

The preceding object and other objects can be achieved by providing a detergent composition comprising (1) from 1% to 98% of the composition of a detergency builder selected from the group consisting of water-insoluble amino polycarboxylates, tripolyphosphate and poly-phosphonate detergency builders and mixtures thereof; and

(2) more than about 0.05% and less than about 25% of the total detergent composition of a corrosion inhibiting compound having the formula

\[
R - \begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\]

wherein R is selected from the group consisting of (1) a straight alkyl chain with the phosphorus atom attached to secondary carbon atoms on the chain, said straight chain alkyl radical containing from about 12 to about 24 carbon atoms and (2) straight chain alkyl benzyl groups wherein the alkyl group contains from about 9 to about 18 carbon atoms and wherein Q is a water-solubilizing cation, said detergent composition being inhibited with respect to the corrosion of Zamak. "Alkyl," as used hereinafter, includes saturated and unsaturated alkyl groups.

The detergent compositions of this invention preferably consist essentially of:

(1) from about 1% to about 90% of the composition of a detergency builder selected from the group consisting of water-soluble amino polycarboxylates, tripolyphosphates, polyphosphonates and mixtures thereof;

(2) from 0% to about 15% by weight of the composition of an alkali metal silicate having a ratio of SiO₂:Na₂O of from about 1.0 to about 3.5, preferably 1.6 to 3.2, (M in the above ratio is selected from the group consisting of potassium and sodium); and

(3) more than about 0.5% and less than about 25% by weight of the total detergent composition of a corrosion inhibiting compound having the formula

\[
R - \begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\]

wherein R is selected from the group consisting of (1) a straight alkyl chain radical with the phosphorus atom attached to secondary carbon atoms on the chain, said straight chain alkyl radical containing from about 12 to about 24 carbon atoms and (2) straight chain alkyl benzyl groups wherein the alkyl group contains from about 9 to about 18 carbon atoms and wherein Q is a water-solubilizing cation, e.g., a cation selected from the group consisting of hydrogen, alkali metal, ammonium and substituted ammonium cations;

(4) from 0% to about 1%, preferably 0.02%, of a corrosion inhibiting compound for the protection of German silver;

(5) from 0% to about 40% of an organic detergent selected from the group consisting of nonionic, anionic, amphoteric, and zwitterionic detergents, and mixtures thereof;

(6) from about 0% to about 90% of other detergent builders selected from the group consisting of alkali metal pyrophosphates, orthophosphates, perborates, tetraborates, hexaphosphates, sesquicarbonates, and bicarbonates and mixtures thereof; and

(7) from 0% to about 90% water.
Typical amino polycarboxylate detergency builders include alkali metal (sodium, potassium, etc.), ammonium and substituted ammonium (substituted amonium, as used here includes mono-, di- and triethanol amonium cations) salts of the following acids: ethylenediaminetetraacetic acid, N- (2-hydroxyethyl)-ethylenediaminetriacetic acid, N-(2-hydroxyethyl)-nitrofolic acid, dihydroxyethaneacetate acid and nitrate inhibitors and silicate. The above amino polycarboxylate detergency builders are amino polycarboxylates. The trisodium salts of the above compounds are commonly used. The water soluble salts of nitritriacetic acid will hereafter be referred to as NTA, and the water-soluble salts of ethylenediaminetetraacetic acid will hereafter be referred to as EDTA.

Polyphosphonates are also valuable builders in terms of the present invention including specifically sodium and potassium salts of maleic diphosphonic acid, sodium and potassium salts of ethylene diphosphonic acid, and sodium and potassium salts of ethane-1,2-diphosphonic acid. Other examples include the water-soluble (sodium, potassium, ammonium, etc.) salts of ethane-2-carboxylic, 1,2-diphosphonic acid, hydroxymethanediphosphonic acid, carboxyldiphosphonic acid, ethane-1,2-diposphonic acid, phosphonic acid, propyne-1,2,3-triphosphonic acid, and propylene-1,2,2,3-triphosphonic acid.


Other suitable detergency builders include sodium and potassium tripolyphosphates. These detergent builder compounds normally make up from about 1% to about 90%, preferably from about 10% to about 60%, of the composition. The detergent builder compounds are preferably present in a ratio of detergent builder compounds to any detergent surfactant in the composition of from about 1:2 to about 10:1. These detergent builder compounds attack aluminum, German silver and Zamac when applied as aqueous solutions to these metals.

The silicate corrosion inhibitor defined hereinafter is the typical corrosion inhibitor which is well known to those skilled in the art. It can be present in the detergency compositions of this invention in an amount from about 1% to about 15%, preferably from about 2% to about 10%. A typical silicate corrosion inhibitor is sodium silicate having an SiO$_2$/Na$_2$O ratio of about 1.6. This silicate corrosion inhibitor prevents the corrosion of aluminum but is essentially ineffective in preventing or substantially reducing the corrosion of zinc alloys such as Zamac by, e.g., NTA regardless of the level at which the silicate corrosion inhibitor is used. The silicate corrosion inhibitor is an essential ingredient in the preparation of a general purpose detergency composition at the least cost since the phosphate corrosion inhibitor is not effective in preventing the corrosion of aluminum and German silver at levels below about 2% as specified hereinafter. The phosphate is more expensive than silicate.

The phosphate corrosion inhibitors which contain more carbon atoms will prevent the corrosion of aluminum and German silver in addition to Zamac when used at higher levels, e.g., above about 2%. However, in some cases, it would be unduly expensive to provide sufficient phosphate corrosion inhibitor for this purpose. Therefore, some silicate corrosion inhibitor is always preferred for general purpose detergents for inhibition of aluminum corrosion, although with larger amounts of higher molecular weight phosphate corrosion inhibitors, silicate is an optional ingredient insofar as aluminum corrosion is concerned.

The phosphate corrosion inhibitors which are effective at higher levels in inhibiting the corrosion of aluminum in addition to Zamac are those alkyl phosphonates and phosphonic acids wherein the alkyl group contains at least about 18 carbon atoms and alkyl benzyl phosphonic acids wherein alkyl benzyl groups contain at least about 20 carbon atoms. These last, more effective corrosion phosphate inhibitors, when used at levels above about 2%, preferably from about 2% to about 6%, inhibit the corrosion of aluminum and German silver by the effective detergency builders described hereinafter. If there are less than about 18 carbon atoms in the hydrophobic group, the inhibition film, hereinafter described, will not prevent the sequestering builders, e.g., STP, from reaching the metal surface to corrode it. If there are more than about 24 carbon atoms in the hydrophobic group, the solubility of the molecule is lessened and undesired precipitation by free calcium and magnesium ions occurs at lower and less acceptable concentrations.

Although it is not desired to be bound by theory, it is believed that the choice of the detergent builders with which the phosphate corrosion inhibitors of this invention are uniquely effective at higher levels in preventing the corrosion of aluminum is dependent upon two factors. The first factor relates to the efficiency of the detergency builder in sequestering the alkaline earth metal ions, e.g., calcium ions, present in hard water. If the free (not sequestered) calcium ion concentration in the builder solution is sufficiently large to insolubilize the corrosion inhibiting compounds by forming the calcium salt, then the corrosion inhibiting properties of the compounds are destroyed. Builders such as sodium orthophosphate apparently do not sequester the detergent builders to prevent insolubilization of the corrosion inhibiting compounds. Apparently the corrosion inhibiting compounds must be soluble to be effective. The second factor relates to the size of the detergency builder molecule. Apparently, if the builder molecule is too small (e.g., the alkali metal phosphate builder salt) then it will slip through the film of corrosion inhibitor as hereinafter more fully described. The triplyphosphate, polyphosphate, and aminopolyacrylate builders used in the composition of this invention have sufficient sequestering properties to maintain proper inhibitor solution and sufficient molecular bulk to permit proper inhibition.

Although again it is not desired to be bound by theory, it is also believed that the corrosion inhibitors of the present invention are effective with respect to the inhibition of corrosion of Zamac, aluminum, and German silver because the hydrophobic group (R) is attached to the hydrophilic group

\[ \text{(OQ)O} \]

in a "bulky" manner. This "bULKiness" is achieved in several ways. For example, a straight chain alkyl hydrophobic portion (R) of the corrosion inhibiting compound is attached to the hydrophilic group through a secondary carbon atom. Similarly, bulkiness is achieved by incorporating an aryl group such as a benzyl group into the hydrophobic group. The alkyl chains can contain a certain amount of unsaturation. Similarly, the presence of some 1-isomer is acceptable and, in fact, a random phosphate is preferred, "Random" refers to an essentially random distribution of isomers. In some instances there will be essentially no 1-isomer and in other instances there may be a slightly greater amount of 1-isomer than would be present in a completely random distribution as a result of the processes used in preparing the phosphonates.

Apparently, the most important results of this bulky
attachment is to increase the solubility of the compounds in water, especially in the form of their alkaline earth metal (e.g., calcium and magnesium) salts. The bulkier attachments, for example, where the hydrophilic group is attached near the center of straight alkyl chains are therefore preferred. If the corrosion inhibiting compound is not sufficiently reactive, then the compound will precipitate in the presence of free calcium and magnesium ions prior to forming the protective film on the metal. Corrosion inhibitors wherein the phosphonate or phosphate group is attached to a relatively unbranched (straight chain) hydrophobic group at a terminal position precipitate in the presence of free calcium and magnesium and hence cannot form a sufficiently tenacious film to prevent the sequestering builders, e.g., STP, from reaching the surface.

The phosphonate corrosion inhibitors of this invention can be prepared in several ways. For example, phosphorus trichloride, oxygen and a paraffin containing about 18 carbon atoms can be reacted together and the reaction product hydrolyzed to give the phosphonic acid.

Other methods of preparing these phosphonates are set forth in U.S. Patent 2,724,718, the references referred to therein and the concurring parent application, Ser. No. 315,678, filed Oct. 11, 1963.

Specific examples of the above compounds include: Randomly phosphonated octadecane such as the product prepared by reacting diisopropyl phosphite with a random olefin containing an average of 18 carbon atoms in the presence of a free radical initiator and thereafter pyrolyzing the phosphonate ester to give the phosphonic acid.

Other examples of phosphonate corrosion inhibitors include:
- The following compounds and the sodium, potassium, ammonium, monoethanolammonium, diethanolammonium and triethanolammonium salts thereof:
  - 10-Nondecylphosphonic acid;
  - Pentadecylbenzylphosphonic acid;
  - Allylbenzylphosphonic acid mixtures wherein the alkyl groups can be derived from (1) a mixture of propylene polymers, (2) olefins derived from cracked petroleum waxes, or (3) olefins displaced from Ziegler-type build-up reactions of ethylene, said alkyl groups ranging in size from 12 to 21 carbon atoms and averaging from about 14 to 18 carbon atoms;
  - Hexadecylbenzylphosphonic acid wherein the hexadecyl group is derived from polymerized isobutylene;
  - Alkyldiphenylphosphonic acid wherein the alkyl group is derived from a chlorinated kerosene fraction averaging from about 15 to about 18 carbon atoms;
  - 3,4-Undecenoxy-4-phosphonic acid and 5-vinyl octadecyl-4-phosphonic acid obtained by reducing the ketone obtained from the reaction between butyric acid anhydride and the allylic carbanion of 1-hexadecene to the alcohol, conversion of the alcohol to the tosyl ester, alkylation of dibutyl phosphonate anion with the ester, and hydrolysis of the resulting product;
- The hydrolyzed reaction products of phosphorus trichloride, oxygen, and a mixture of olefins containing from about 18 to about 25 carbon atoms and which can be derived from (1) cracked petroleum waxes or (2) Ziegler-type build-up reactions of ethylene (these hydrolyzed reaction products are a mixture of saturated and unsaturated phosphonic acids and saturated alkyl phosphates, some of the saturated phosphonic acids contain bound chlorine);
- The mixture of octadecylyphosphonic acids prepared by alkylating dibutyl phosphonate anion with the mixture of 2- through 9-ocatdeacyl sulfuric acids obtained by reacting 1-octadecene with excess sulfuric acid at 0°-10°C for about two to three hours and hydrolyzing the alkylated dibutyl phosphonate anion (this product is a random octadecylyphosphonic acid containing a mixture of 2-9 isomers);
- The mixture of phosphonic acids produced by first isomerizing the double bond of 1-octadecene with aluminum chloride, adding sodium hypophosphate to the resulting olefins and oxidizing the resulting phosphonates to phosphonates with nitric acid (this product is random octadecylyphosphonic acid containing a mixture of 2-9 isomers);
- The hydrolyzed reaction product of 1-octadecene, phosphorus trichloride and oxygen (these hydrolyzed reaction products are a mixture of saturated and unsaturated phosphonic acids and saturated alkyl phosphates, some of the saturated phosphonic acids contain bound chlorine);
- The hydrolyzed reaction product of 1-octadecene, phosphorus trichloride, acetic anhydride and oxygen (this hydrolyzed reaction product is a mixture of 1-9 isomers). (The last six corrosion inhibiting compounds listed above and described as reaction products are complex mixtures of what are primarily, i.e. at least 80% phosphonates wherein said phosphonate groups are attached to the hydrophobic chain through secondary carbon atoms.)

The phosphonate corrosion inhibitors of this invention are effective at preventing the corrosion of Zamak in extremely small amounts (more than 0.05% and less than 2%, preferably about 0.1%) whereas the corresponding phosphates and, especially, phosphonate esters are relatively ineffective, when used at the same levels. Also, phosphates and phosphonate esters are less effective in preventing the corrosion of aluminum when used in amounts about 2%. The mixture of silicate corrosion inhibitor and phosphonate corrosion inhibitor is more effective than the phosphonate corrosion inhibitor alone in the protection of Zamak. Similarly, the mixture of silicate corrosion inhibitor and phosphonate corrosion inhibitor are more effective than either alone in the protection of aluminum. This is particularly true with respect to die cast aluminum.

The corrosion inhibitors effective against German silver are exemplified by benzytrazole. Many other examples of effective compounds are disclosed in U.S. Patents 2,618,603, 2,618,605, 2,618,606, and 2,618,608. If substantial amounts of, e.g., alkali metal carbonate salts are present in the composition the German silver corrosion inhibitor is not required.

The corrosion inhibitors of this invention are effective in the presence of a wide variety of detergent surfactants which are optionally utilized with the detergency builders. These detergent surfactants are present in an amount from 0% to about 40%, preferably from about 10% to about 20% of the detergent composition. Examples of detergent surfactants which can be used include:
- (1) Ordinary alkali metal soaps such as the sodium and potassium salts of the higher fatty acids of naturally occurring plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease and lard, and mixtures thereof) or of synthetically produced fatty acids (e.g., rosin and those resin acids in tallow oil) and/or of naphthenic acids. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process.
- (2) Synthetic organic detergents characterized by their high solubility in water, their resistance to precipitation by the constituents of hard water and their surface active and effective detergent properties, including:
  - (a) Anionic synthetic detergents (excluding true soaps): This class of synthetic detergents can be broadly
described as the water-soluble salts, particularly the alkali metal (sodium, potassium, etc.) salts, of organic sulfuric acid reaction products having in the molecular structure an alkali metal containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by the higher alcohols produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group in a straight or branched chain contains from about 9 to about 15 carbon atoms, especially those of the types described in United States Letters Patent Nos. 2,220,099 and 2,477,385; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium salts of sulfonated α-olefins containing 8 to 22 carbon atoms, e.g., those described in U.S. patent application, Ser. No. 561,597, filed June 29, 1966; sodium coconut fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfonic acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about three moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether containing about four units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 carbon atoms; the reaction product of fatty acids esterified with isothionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methylamine in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in United States Letters Patent Nos. 2,486,921, 2,486,922 and 2,396,278.

(5) Nonionic synthetic detergents: This class of synthetic detergents may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

For example, a well known class of nonionic synthetic detergents is a product available on the market under the trade name of “Pluronic.” These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the products is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the composition product.

Other suitable nonionic synthetic detergents include:
(i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, disobutylene, octane, or octene, for example.
(ii) Those derived from the reaction of propylene oxide and ethylene diamine—products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 20% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11,000, resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight on the order of 2100 to 3000, are satisfactory.
(iii) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(c) Long chain tertiary amine oxides (nonionic detergents) corresponding to the following general formula, R₂R₃N–O– wherein R₁ contains an alkyl alkyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glycerol moiety, and R₂ and R₃ contain from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxy ethyl, or hydroxy propyl radicals. The arrow in this formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldecyl amine oxide, oleyl(2-hydroxyethyl) amine oxide, dimethylolactylamine oxide, dimethyldodecylamine oxide, dimethyloctadecylamine oxide, dodecyl methyl sulfoxide 3,69-trioxaoctadecyl 2-hydroxyethyl sulfoxide dodecyl methyl sulfoxide oleyl 3-hydroxy propyl sulfoxide.
tetradecyl methyl sulfoxide
3-methoxytridecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
3-hydroxy-4-dodec oxybutyl methyl sulfoxide

(f) Amphoteric synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., sulfate, sulfonate, sulfamate, or phosphate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-dodecylaminopropane sulfonate, dodecyl-beta-alanine, N-alkyl-taurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. 2,438,072, N-hexyl alkylic carboxylic acids such as those produced according to the teaching of U.S. 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

(g) Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

\[ \text{R}^2-Y^2-\text{CH}_2-\text{R}^4-Z^2 \]

wherein \( R^2 \) contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; \( Y \) is selected from the group consisting of nitrogen, phosphorous, and sulfur atoms; \( R \) is an alkyl or monohydroxy alkyl group containing 1 to about 3 carbon atoms; \( x \) is 1 when \( Y \) is a sulfur atom and 2 when \( Y \) is a nitrogen or phosphorous atom; \( R^4 \) is an alkylene or hydroxy alkylene of from 1 to about 4 carbon atoms and \( Z \) is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphate, and phosphinate groups.

Other examples include:

- 4-[N,N-di-(2-hydroxyethyl)-N-octadecyammonio]-butane-1-carboxylate
- 5-[3,3-dihydroxypropyl-3-hexadecyloino]-3-hydroxypropene-1-sulfonate
- 3-[N,N-dimethyl-3-hydroxypropyl-3-hexadecyloino]-3-hydroxypropene-1-sulfonate
- 4-[N,N-di-(2-hydroxyethyl)-N-(2-hydroxydecyl)-ammonio]-tetraethylene-carboxylate, 3-[3-ethylene-3-(3-hydroxy-2-hydroxypropyl)-sulfonio]-3-hydroxypropene-1-phosphate, 3-[N,N-dimethyl-3-hydroxypropyl-3-hexadecyammonio]-3-hydroxypropene-1-sulfonate, and 3-[N,N-di-(3-hydroxypropyl)-N-hexadecyammonio]-2-hydroxypropene-1-sulfonate.

Examples of compounds falling within this definition are 3-[N,N-dimethyl-3-hexadecyammonio]-propene-1-sulfonate and 3-[N,N-dimethyl-3-hexadecyammonio]-2-hydroxypropene-1-sulfonate which are especially preferred for their excellent cool water detergent characteristics.

The alkyl groups contain in said detergent surfactants can be straight or branched preferably straight and saturated or unsaturated as desired. The above list of detergent surfactants is exemplary and not limiting. Mixtures of the above detergent surfactants can be used.

The detergent compositions of this invention can be prepared in any suitable physical form such as granules (e.g., either spray dried or mechanically mixed), tablets, pastes or liquids.

The compositions can contain particulate inorganic salts which are inert to the formula to act as fillers. Examples of such salts include sodium sulfate and sodium chloride.

Other minor ingredients can also be present in the compositions of this invention. Soil suspending agents such as sodium carboxymethylcellulose, optical brighteners, dyes, germicidal agents, surfactant depressants, and susbooster, can each be added in amounts up to about 10% by weight of the composition.

The products of this invention can be used in aqueous solutions at levels of from about 0.05% to about 1% and when articles made from Zamol are contacted with these solutions there is considerably less corrosion than when similar compositions which do not contain the specific phosphonate corrosion inhibitor of this invention are used.

All parts, percentages and ratios herein are by weight unless otherwise specified.

The following examples demonstrate the desirable and unique performance of the corrosion inhibitors of this invention.

**EXAMPLE I**

A spray dried granular detergent having the following composition was prepared by mixing the individual ingredients in a conventional manner with sufficient water to form a detergent slurry and spray drying the slurry to remove excess moisture and to form detergent granules.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium straight chain alkyl benzene sulfonate having an average chain length of about 13 carbon atoms</td>
<td>35.0</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>41.4</td>
</tr>
<tr>
<td>Sodium nitritolactate</td>
<td>9.6</td>
</tr>
<tr>
<td>Sodium silicate having a SiO2:Na2O ratio of 1.6</td>
<td>10.0</td>
</tr>
<tr>
<td>Marine oil fatty acids</td>
<td>0.5</td>
</tr>
<tr>
<td>Tallow fatty acids</td>
<td>1.5</td>
</tr>
<tr>
<td>Sodium carboxymethylcellulose</td>
<td>0.33</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>11.26</td>
</tr>
<tr>
<td>Water</td>
<td>11.00</td>
</tr>
</tbody>
</table>

Miscellaneous ingredients including preservatives, optical brighteners, and pigments | 1.12 |

A similar detergent composition was prepared which contained as an additional ingredient 0.3% of random octadecylphosphonic acid prepared by adding phosphorous acid to a random mixture of octadecanes using gamma radiation as a source of radicals. The random olefins were prepared by isomerizing 1-octadecene with 10% iron pentacarbonyl at about 150° C. for approximately one hour. The added octadecylphosphonic acid replaced proportionate percentages of the ingredients in the first detergent composition.

The corrosiveness of the above two products was checked in a test using Zamol #3 test plates, which were approximately 1 inch by 4 inches by 3 inch in size. These tests plates were exposed to 140° F., solutions of the detergent composition in distilled or tap "hard" water for six hours with agitation. The corrosion products were removed by scrubbing with a brush having plastic bristles and the dried test plates were weighed to determine the weight loss due to corrosion. The results of these tests are tabulated below.

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight Loss in Milligrams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, Percent</td>
<td>Type of Water</td>
</tr>
<tr>
<td>0.2</td>
<td>Tap</td>
</tr>
<tr>
<td>0.20</td>
<td>Distilled</td>
</tr>
<tr>
<td>0.18</td>
<td>Distilled</td>
</tr>
</tbody>
</table>
EXAMPLES.—PERCENT BY WEIGHT OF THE COMPOSITION

<table>
<thead>
<tr>
<th>Component</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
<th>XII</th>
<th>XIII</th>
<th>XIV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tripolyphosphate</td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>90</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium ethane-1,4-dihydroxy-1,4-diphosphonate</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>90</td>
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</tbody>
</table>

The above compositions are useful as detergents at a level of about 0.1% in water detergents and are inhibited against the corrosion of Zamak.

EXAMPLE XV

Aluminum plates were allowed to stand in an aqueous solution containing 0.35% of a detergent composition consisting of 20% sodium tripolyphosphate, 50% sodium tripolyphosphate, 25% sodium sulfate and 5% of the below-named inhibitors. All percents here in are by weight. The aluminum plates were exposed to the aqueous detergent solution for a period of three hours at 140° F. and pH 9.5. The water was not agitated. After the three-hour period, the aluminum plates were removed with water, the corrosion products removed with cone. HNO₃, then rinsed with water and alcohol, dried and the weight was determined in milligrams per square centimeter. Results were obtained for both soft water and water containing hardness (equivalent to calcium carbonate) of 7 grams per gallon.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Wt. Loss in mg./cm.²</th>
<th>0 gr./gal.</th>
<th>7 gr./gal.</th>
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</thead>
<tbody>
<tr>
<td>(1) None.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>(2) Oleic acid.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
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<tr>
<td>(3) Oleic phosphate.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>(4) Monooctadecylamine.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>(5) Hydrolyzed reaction product of 1-octadecanol, maleic anhydride, and oxygen.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>(6) Hydrolyzed reaction product of 1-octadecanol, maleic anhydride, and oxygen.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>(7) Hydrolyzed reaction product of 1-octadecanol, maleic anhydride, and oxygen.</td>
<td>0.79</td>
<td>0.95</td>
<td>0.95</td>
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</table>

As can be seen from an inspection of the above results, the corrosion inhibitors of this invention (4, 5, 6, 7, 9) are much more effective, especially in hard water, than similar compositions which are outside the scope of this invention (2, 3, and 8). Furthermore, relative to the control (1) the corrosion inhibitors are exceptionally advantageous. These compositions are all inhibited against the corrosion of Zamak #3.

When the following detergency builders are substituted for the sodium tripolyphosphate and/or sodium nitrotriacetate in the above detergent compositions either wholly or in part so as to give, e.g., a 1:1 ratio, substantially equivalent results are obtained in that the detergent compositions containing these detergency builders are inhibited against the corrosion of Zamak #3: sodium, potassium, ammonium, monoethanol ammonium, diethanol amnonium, and triethanol amnonium salts of the following acids: ethylene diaminetetraacetic acid; N-(2-hydroxyethyl)-ethylenediaminetrimethylene triacetic acid; N-(2-hydroxyethyl)-nitrilotriacetic acid; diethylenetriaminepentaacetic acid; ethylene diphosphonic acid; ethane-1,1-diphosphonic acid; ethane-1,1,1-triphosphonic acid; ethane-2,2,2-triphosphonic acid; and propane-1,2,3-triphosphonic acid and monooctadecylamine, heptadecane, nonadecane, eicosane, and docosane homologs of the random octadecane phosphonic acids; the potassium, ammonium, monoethanol ammonium, diethanol amnonium, and triethanol ammonium salts of the foregoing phosphonic acids; the following compounds and the sodium, potassium, ammonium, and monoethanol ammonium, diethanolammonium and triethanolammonium salts thereof:

- 10-Nonadecylphosphonic acid;
- Pentadecylbenzyolphosphonic acid;
Alkylbenzylphosphonic acid mixtures wherein the alkyl groups can be derived from (1) a mixture of propylene polymers, (2) olefins derived from cracked petroleum waxes, or (3) olefins displaced from Ziegler-type build-up reactions of ethylene, said alkyl groups ranging in size from 12 to 21 carbon atoms and averaging 14, 15, 16, or 18 carbon atoms;

Hexadeccylbenzylphosphonic acid wherein the hexadecyl group is derived from polymerized isobutylenes;

Alkylbenzylphosphonic acids wherein the alkyl group is derived from a chlorinated kerosene fraction averaging 15, 16, 17, or 18 carbon atoms;

The mixture of 6-ecosenyl-4-phosphonic acid and 5-vinyl octadecyl-4-phosphonic acid obtained by reducing the ketone obtained from the reaction between butyric acid anhydride and the allylic carbamation of 1-hexadecene to the alcohol, conversion of the alcohol to the tosyl ester, alkylation of dibutyl phosphonate anion with the ester, and hydrolysis of the resulting product;

The hydrolyzed reaction products of phosphorus trichloride, oxygen, and a mixture of olefins containing 18, 19, 20, or 22 carbon atoms and which can be derived from (1) cracked petroleum waxes or (2) Ziegler-type build-up reactions of ethylene;

The mixture of octadecylphosphonic acids prepared by alkylating dibutyl phosphonate anion with the mixture of 2- through 9-octadecyl sulfonic acids obtained by reacting 1-octadecene with excess sulfonic acid at 0°–10°C for about two to three hours and hydrolyzing the alkylated dibutyl phosphonate anion;

The mixture of phosphonic acids produced by first isomerizing the double bond of 1-octadecene with aluminum chloride, adding sodium hypophosphite to the resulting olefins and oxidizing the resulting phosphinates to phosphonates with nitric acid;

The hydrolyzed reaction product of 1-octadecene, phosphorus trichloride, acetic anhydride and oxygen;

The hydrolyzed reaction product of octadecane, phosphorus trichloride and oxygen, e.g., 1:1 or 2:1 ratios. When in the above compositions the following organic detergents are substituted, either wholly or in part (e.g., a 1:1 ratio) for the said sodium alkyl benzene sulfonate having an average chain length of about 13 carbon atoms, substantially equivalent results are obtained in that the detergent composition is inhibited against the corrosion of Zamac #3:

(1) The following anionic synthetic detergents wherein the cations are sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, triethanolammonium cations. Salts of the higher fatty derived from palm oil, coconut oil, bactus oil, soybean oil, castor oil, tallow, whale oil, fish oils, grease, lard, resin acids from tall oil and/or naphthenic acids; alkyl sulfates wherein the alkyl group is derived from tallow or coconut oil; alkyl benzene sulfonates in which the alkyl groups contain 9, 11, 12, 13 or 15 carbon atoms; alkyl glycidyl ether sulfonates derived from tallow or coconut oils; coconut fatty acid monoglyceride sulfates and sulfonates; salts of sulfonic esters of the reaction product of one mole of tallow or coconut oil fatty acids and 3 or 4 moles of ethylene oxide; alkyl phenol ethylene oxide ether sulfates containing 4 or 9 ethylene oxide moieties per molecule and in which the alkyl radical contains 9, 12, 13 or 15 carbon atoms; the neutralized reaction product of coconut fatty acids with isethionic acid; coconut fatty acid amide of methyl taurine salts;

(2) The condensation product of ethylene oxide with the condensation product of propylene oxide with propylene glycol, the ethylene oxide portion of the compound being 50% of the total weight of the compound and the total molecular weight of the compound being about 1700; the condensation product of propylene oxide and ethylene diamine wherein the product contains about 65% polyethylene oxide by weight and the total molecular weight of the compound is about 6000; the condensation product of coconut oil fatty alcohol and about 15 moles of ethylene oxide per mole of coconut alcohol;

dimethyldecyl amine oxide, oleyl(2-(2-hydroxyethyl)) amine oxide, dimethyloctylamine oxide, dimethyloctadecylamine oxide, dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl) tetradecylamine oxide, 2-dodec oxyethyl dimethylamine oxide, 3-dodec oxy-2-hydroxy propyl di(3-hydroxypropyl)-amine oxide, dimethylhexadecylamine oxide, dodecyldimethylphosphonoxide, tetradecyldimethylphosphonoxide, tetradecyldimethylphenylphosphonoxide, 3,6,9-trioxaododecyldimethylphosphonoxide, cetyltrimethylphosphonoxide anion, 3-dodec oxy-2-hydroxypropyldi(2-hydroxyethyl)phosphon oxide, stearyldimethylphosphonoxide, cetylpropylphosphonoxide, oleyl diethylphosphonoxide oxide, dodec yldiethylphosphonoxide oxide, tetradecyldiethylphosphonoxide oxide, dodecylphosphonoxide oxide, dodecyl (2-hydroxyethyl) phosphon oxide, tetradecylmethyl(2-hydroxyethyl)phosphon oxide, olelyldimethylphosphonoxide, 2-hydroxydodecyldimethylphosphonoxide, octadecyl methyl sulfoxide, 3,6,9-trioxaododecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxy propyl sulf oxide, tetrahydroxy methyl sulf oxide, 3-methoxytridecyl methyl sulf oxide, 3-hydroxytridecyl methyl sulf oxide, 3-hydroxy-4-dodec oxybutyl methyl sulf oxide, sodium 3-dodecylaminopropionate, sodium 3-dodecylaminopropionate-1-sulfonate, dodecyl-beta-alanine, N-alkyltaurines;

(3) N-higher alkyl aspartic acids, wherein the alkyl group contains about 12 carbon atoms;

4-[N,N-di(2-hydroxyethyl)-N-octadecylammoniomethyl-1-carboxylate;].

5-[S-(3-hydroxypropyl)-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate; 3-[P-P-diethyl-P(3,6,9-trioxaotacosenesulfonio)-2-hydroxypropyl-1-phosphate; 3-[N,N-dipropyl-N-(3-dodec oxy-2-hydroxypropylammonio)-propyl-1-phosphonate; 3-[N,N-dimethyl-N-hexadecylammoniomethyl] propionate-1-sulfonate; 3-[N,N-dimethyl-N-hexadecylammoniomethyl]-2-hydroxypropyl-1-sulfonate; 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydecylammonio)-butane-1-carboxylate, 1-[S-ethyl-S-(3-dodec oxy-2-hydroxypropylsulfonio)-propyl-1-phosphonate; 3-[P,P-diethyl-P-(dodecylphosphonomethyl)]-propyl-1-phosphonate, 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammoniomethyl]-2-hydroxypropyl-1-sulfate; and (5) mixtures thereof in, e.g., 1:1 ratios.
When the following German silver corrosion inhibitors are substituted either wholly or in part (e.g., a 1:1 ratio) for the benzotriazole in the above detergent compositions, substantially equivalent results are obtained in that the compositions do not discolor German silver to an objectionable degree: 2-amino-benzothiazole, 3-amino-1,2,4-triazole; ethylene thiourea; 3,5-dimethyl pyrazole; adenine; and mixtures thereof (e.g., 1:1).

What is claimed is:

1. Detergent compositions consisting essentially of:

   (1) from 1% to about 98% of the composition of a detergent builder selected from the group consisting of water-soluble amino polycarboxylic acids, trikylphosphate and polyphosphonate detergent builders and mixtures thereof;

   (2) more than 0.05% and less than about 25% by weight of the total detergent composition of a corrosion inhibitor having the formula

   \[ \text{R}-\text{P}^\text{III}(\text{OQ}_2) \]

   wherein R is selected from the group consisting of

   (1) a straight alkyl chain with the phosphorus atom attached to secondary carbon atoms on the chain, said straight chain alkyl radical containing from about 24 to about 18 carbon atoms and (2) straight chain alkyl benzyl groups wherein the alkyl group contains from about 9 to about 18 carbon atoms and wherein Q is a water-solubilizing cation selected from the group consisting of hydrogen, alkali metal, ammonium, monoethanolaminium, diethanolaminium, and triethanolaminium cations;

   (3) from 0% to about 90% of other detergent builders selected from the group consisting of alkali metal pyrophosphates, orthophosphates, tetraborates, perborates, hexaphosphates, sesquicarbonates and bicarbonates and mixtures thereof; and

   (4) an organic detergent selected from the group consisting of nonionic, anionic, amphoteric and zwitterionic detergents and mixtures thereof in an amount such that the ratio of total detergent builders to organic detergent ranges from about 1:2 to about 10:1 and in an amount not greater than about 40% of the composition, said detergent composition being inhibited with respect to the corrosion of Zamak.

2. The detergent composition of claim 1 consisting essentially of:

   (1) from about 1% to about 90% of the composition of a detergent builder selected from the group consisting of water-soluble amino polycarboxylic acids, trikylphosphate and polyphosphonate detergent builders and mixtures thereof;

   (2) from 0% to about 15% by weight of the composition of an alkali metal silicate having a ratio of SiO₂/MgO of from about 1.0 to about 3.6; and

   (3) more than 0.05% and less than about 25% by weight of the total detergent composition of a corrosion inhibitor having the formula

   \[ \text{R}-\text{P}^\text{III}(\text{OQ}_2) \]

   wherein R is selected from the group consisting of

   (1) a straight alkyl chain radical with the phosphorus atom attached to secondary carbon atoms on the chain, said straight chain alkyl radical containing from about 12 to about 24 carbon atoms and (2) straight chain alkyl benzyl groups wherein the alkyl group contains from about 9 to about 18 carbon atoms; and

   (4) from 0% to about 1% of benzotriazole;

   (5) from 0% to about 90% of other detergent builders selected from the group consisting of alkali metal pyrophosphates, orthophosphates, tetraborates, perborates, hexaphosphates, sesquicarbonates and bicarbonates and mixtures thereof; and

   (6) an organic detergent in an amount such that the ratio of total detergent builders to organic detergent ranges from about 1:2 to about 10:1 and in an amount not greater than about 40% of the composition; and

   (7) from 0% to about 90% water.

3. The detergent composition of claim 2 wherein the detergent builder (1) is selected from the group consisting of the alkali metal, ammonium and substituted ammonium salts of the following acids wherein said substituted ammonium salts are selected from the group consisting of monoethanolammonium, diethanolammonium and triethanolammonium salts: ethylendiaminetetra-acetic acid; N-(2-hydroxyethyl)-ethylenediaminetriacetic acid; N-(2-hydroxyethyl)-nitrilotriacetic acid; diethylene-triaminepentacetate acid; 1,2-diaminocyclohexanetetra-acetic acid; nitrilotriacetic acid; ethylene diphosphonic acid; ethane-1-hydroxy-1,1-diphosphonic acid; ethane-1,1,2-triphosphonic acid; ethane-2-carboxy-1,1-diphosphonic acid; hydroxymethane-diphosphonic acid; carbonyldiphosphonic acid; ethane-1-hydroxy-1,1,2-triphosphonic acid; ethane-2-hydroxy-1,1,2-triphosphonic acid; propane-1,1,3,3,3-tetraphosphonic acid; propane-1,2,3,3-tetraphosphonic acid; and propane-1,2,2,3-tetraphosphonic acid and mixtures thereof.

4. The detergent composition of claim 1 wherein the corrosion (2) is an inhibitor randomly phosphonated octadecene.

5. The detergent composition of claim 2 containing as an organic detergent from about 10% to about 20% of a synthetic anionic organic detergent.

6. The detergent composition of claim 2 containing from 0.05% to about 2% of the phosphonate corrosion inhibiting compound (3) and from about 2% to about 10% of said alkali metal silicate.

7. The compositions of claim 1 wherein there is at least about 2% by weight of the total detergent composition of corrosion inhibiting compound, said phosphonate corrosion inhibiting compound being selected so that the straight chain alkyl (1) contains at least 18 carbon atoms and the straight chain alkyl benzyl (2) groups contain at least 20 carbon atoms, the composition being inhibited against the corrosion of aluminum and German silver.

8. The compositions of claim 2 wherein there is at least about 2% by weight of the total detergent composition of corrosion inhibiting compound, said corrosion inhibiting compound being selected so that the straight chain alkyl (1) contains at least 18 carbon atoms and the straight chain alkyl benzyl (2) groups contain at least 20 carbon atoms, the composition being inhibited against the corrosion of aluminum and German silver.

9. The detergent composition of claim 6 wherein the detergent builder is a mixture of water soluble triphosphonic acid, sodium and potassium tripolyphosphates.

10. The detergent composition of claim 9 wherein the detergent builder is a mixture of sodium triphosphonate sodium nitrilotriacetate in a molar ratio of from about 3:1 to about 1:3.

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LEON D. ROSDOL, Primary Examiner.

S. E. DARDEN, Examiner.