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NONTARNISHING DETERGENT COMPOSITIONS CONTAINING A HYDROXYLAMINE SALT AND AN ALKALI METAL SILICATE

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This invention relates to detergent compositions containing tarnish inhibitors and more particularly to polyphosphate compositions containing a hydroxylamine salt and an alkali metal silicate as synergistic tarnish inhibitors.

Compositions containing polyphosphates are now widely used for detergent and other purposes. Aqueous solutions of polyphosphates tend, when at certain pH values to tarnish copper, and nickel and copper alloys such as German silver (a nickel-zinc-copper alloy) to a variety of shades from yellow to bluish-black, especially if the solutions are at elevated temperatures and are allowed to remain in contact with a metal for several minutes. Since German silver is frequently used for household articles commonly washed in polyphosphate-built detergent compositions, it is evident that this is a serious problem.

The tarnishing effect of polyphosphate compositions upon these metals and alloys may be readily tested by the following procedure. An amount of the polyphosphate composition is dissolved in somewhat less than one quart of water at a temperature under 170° F. to provide 2.25 grams of polyphosphate per quart of solution. A tarnish inhibitor may then be added thereto in the form of a solution. More water is then added thereto to give a total volume of one quart and the pH adjusted when necessary to about 10. 300 mls. of the solution is placed in a beaker and the temperature adjusted to 160° F. to 170° F. A strip of metal, such as German silver, six inches by one inch, which has been cleaned with a metal polish and rinsed and dried is partially immersed in the solution and allowed to remain for ½ hour at 160° F. to 170° F. The metal strip is then removed, rinsed and dried with a cloth. The strip is visually examined for tarnish and the effectiveness of any tarnish inhibitor graded as follows:

Grade No.	Degree of Tarnish
0	No tarnish.
1	Interface stain only.
2	Barely noticeable tarnish.
3	Slight tarnish.
4	Moderate tarnish.
5	Considerable (heavy) tarnish.
6	Severe, as when inhibitor is absent.

This test procedure has been used throughout the examples described herein.

An attempt was made to solve the problem of tarnishing by polyphosphate compositions by including therein a hydroxylamine salt, such as hydroxylamine hydrochloride, as a tarnish inhibitor. The hydroxylamine hydrochloride was ineffective as a tarnish inhibitor at various concentrations as can be readily seen from the following six examples.

Examples 1, 2 and 3

Three 2.25 gram portions of pentasodium tripolyphosphate were dissolved separately in each of three portions of somewhat less than one quart of distilled water at a temperature under 170° F., hydroxylamine hydrochloride was added respectively at three concentrations, i. e., 0.11%, 0.22% and 0.88%, based on total weight of the composition, and the three solutions were then diluted to one quart. A strip of German silver metal was placed in each of the three solutions for ½ hour at 160° F. to 170° F. The tarnish upon the German silver metal strips had a grading of 6, that is severe tarnish, in all three tests.

Examples 4, 5 and 6

Another polyphosphate, tetrasodium pyrophosphate, was tested in the same manner as the pentasodium tripolyphosphate in Examples 1, 2 and 3 at the same concentrations of hydroxylamine hydrochloride. The German silver metal strip again had a tarnish grading of 6, i. e., severe tarnish, in all three tests.

A hydroxylamine salt is also ineffective in inhibiting the formation of tarnish upon German silver when added to polyphosphate compositions containing an organic nonsoap detergent. This is clearly illustrated in the following six examples.

Examples 7, 8 and 9

Three portions each of 0.9 gram of sodium dodecylbenzenesulfonate plus 2.25 grams of pentasodium tripolyphosphate were dissolved separately in three portions of somewhat less than one quart of distilled water at a temperature under 170° F., hydroxylamine hydrochloride was added respectively at three concentrations, i. e., 0.63%, 1.3% and 6.0%, based on total weight of the composition, and the three solutions were each diluted to one quart. A strip of German silver metal placed in each of the three solutions having a temperature of 160° F. to 170° F. had a tarnish grading of 6, indicating severe tarnish.

Examples 10, 11 and 12

Another polyphosphate, tetrasodium pyrophosphate, was substituted in an equal amount for the pentasodium tripolyphosphate of Examples 7, 8 and 9. The German silver metal strip again had a tarnish grading of 6, indicating severe tarnish.

A further attempt was made to solve the problem of the formation of tarnish upon metals such as German silver by polyphosphate compositions by including in such compositions an alkali metal silicate, such as sodium silicate. However, about 13% or less of an alkali metal silicate based on the weight of polyphosphate in the compositions was ineffective as a tarnish inhibitor as shown by the following two examples.

Examples 13 and 14

2.25 grams of pentasodium tripolyphosphate were dissolved in distilled water and 13.3% of sodium silicate based on the weight of polyphosphate added thereto and the solution diluted to one quart. Also 2.25 grams of tetrasodium pyrophosphate were dissolved in distilled water and 13.3% of sodium silicate based on the weight of polyphosphate added thereto and the solution diluted to one quart. A strip of German silver metal placed in each of these solutions had a tarnish grading of 6, indicating severe tarnish.

It can thus be readily seen that neither about 0.9% or less of a hydroxylamine salt based on the total weight of the composition nor about 13% or less of an alkali metal silicate based on the weight of polyphosphate when added separately to polyphosphate compositions act as tarnish inhibitors therein.

In accordance with the invention, however, it was found that polyphosphate compositions containing both an alkali metal silicate and a hydroxylamine salt had greatly improved tarnishing properties upon metals such as German silver, since the alkali metal silicate and the hydroxylamine salt act as synergistic tarnish inhibitors therein. Accordingly, the detergent compositions of the invention which inhibit the formation of tarnish upon copper and copper and nickel alloys comprise an alkali metal polyphosphate, at least about 0.2% of a water-soluble hydroxylamine salt, based on the total weight of the composition, and at least about 13% of an alkali metal silicate based on the weight of polyphosphate.

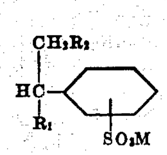
Any water-soluble hydroxylamine salt may be employed, examples thereof being hydroxylamine sulfate, hydroiodide, hydrobromide, hydrochloride, and nitrate. While the hydroxylamine salts are preferred, it will be understood that the more unstable hydroxylamine is an obvious equivalent thereof. While only 0.2% of a water-soluble hydroxylamine salt need be employed in conjunction with an alkali metal silicate, a greater amount may be employed if desired. The maximum amount of the hydroxylamine salt is not critical, but more than is necessary to give the desired effect usually would not be used, and, of course, an amount in excess of that soluble in the polyphosphate solution would not be used. In most cases, the maximum suggested would be about 12%.

Typical examples of suitable alkali metal silicates, i. e., metasilicates, include sodium and potassium silicates, also known as sodium and potassium metasilicates. At least about 13% of an alkali metal silicate based on the weight of the polyphosphate in conjunction with a hydroxylamine salt is added to the polyphosphate compositions, although greater amounts of an alkali metal silicate may be added thereto if desired. Hence, the maximum amount of alkali metal silicate is not critical, but more than is necessary to give the desired synergistic tarnish inhibiting effect usually would not be used, and, of course, an amount in excess of that soluble in the polyphosphate solution would not be used. Concentrations as high as 35% of alkali metal silicate based on the weight of polyphosphate have been satisfactorily employed.

The alkali metal polyphosphates may include by way of example pentasodium and pentapotassium triployphosphate, tetrasodium and tetrapotassium pyrophosphates, sodium and potassium hexametaphosphates, and hexasodium and hexapotassium tetrapolyphosphates. There is no critical amount of alkali metal polyphosphate which need be employed in the compositions, the amount of polyphosphate in the compositions being dictated only by the optional presence of organic non-soap detergents and builders which might be included in the detergent compositions.

Examples of such additional optional components are an organic non-soap detergent which may be either an anionic, cationic, or nonionic detergent and builders, water, and inert materials. These detergent compositions may contain an alkali metal polyphosphate in any amount, usually between 5% and 50%, at least about 0.2% of a water-soluble hydroxylamine salt, at least about 13% of an alkali metal silicate based on the weight of polyphosphate, conventional proportions of active organic non-soap detergent, usually within the range between 5% to 40%, and the balance builders and inert materials.

The alkylaryl sulfonates are a class of anionic detergents which may be included in the detergent compositions. One example thereof is the sulfonated phenyl polypropylene alkanes, characterized by the branched chain structure of polypropylene and a tertiary alkyl carbon at the benzene ring, and having the following general structure;



where M is hydrogen, an alkali metal or an organic amine cation, and R_1 and R_2 are alkyl, of the type formula C_nH_{2n+1}, and at least one R is a polypropylene group, the whole alkyl group containing preferably 12 to 15 carbon atoms. These are known compounds whose preparation and properties are set forth in United States Patent No. 2,477,383, to Lewis, issued July 26, 1949; they are available in commerce under the trade names "Oronite," "Ultrawet," and "Neolene."

Another class of useful non-soap detergents are the amidoalkane sulfonates which are characterized by the following structure:

$$R{-}CO{-}\underset{\substack{|\\ R'}}{N}{-}(CH_2)_nSO_3A$$

where A is hydrogen or an alkali metal, i. e., ammonium, sodium, or potassium, n is a small whole number from 1 to about 5, preferably 2 or 3, R′ is hydrogen or an alkyl, aryl, or cycloaliphatic group, such as methyl, and R is an alkyl or alkylene radical, such as myristyl, palmityl, oleyl and stearyl. Sodium palmitic tauride, sodium palmitic methyl tauride, sodium myristic methyl tauride, sodium palmiti-stearic methyl tauride and sodium palmitic methyl amidopropane sulfonate are typical examples.

These compounds are prepared by interacting the corresponding aliphatic acid anhydride or halide with an organic aliphatic aminosulfonic acid, such as taurine, $NH_2CH_2CH_2SO_3H$, and the various N-substituted taurines, such as N-methyl taurine, or aminopropane sulfonic acid, $NH_2(CH_2)_3SO_3H$.

Other water-soluble alkyl aromatic sulfonic acids may constitute optional components such as those prepared by alkylating benzene or naphthalene with a kerosene fraction followed by sulfonation to aliphatic sulfonic acids, esters of sulfuric acid with aliphatic alcohols of 10 to 18 carbon atoms, particularly those derived by the reduction of coconut oil, palm oil and the like long-chain fatty acids, sulfonated castor oil, esters and ethers of isethionic acid, long-chain fatty acid esters and long-chain alkyl ethers of 2,3-dihydroxy propane sulfonic acid and sulfuric acid esters of monoglycerides and glycerol monoethers. The salts of these acids are ordinarily employed.

The synergistic tarnish inhibitors are also useful with nonionic detergents containing polyphosphates, such as, for example, alkyl oxyether and ester and thioether and ester detergents having the following general formula: $R{-}A{-}(CH_2CH_2O)_x{-}CH_2CH_2OH$ where R is a straight or branched chain saturated or unsaturated hydrocarbon group having from 8 to 18 carbon atoms or an aralkyl group having a straight or branched chain saturated or unsaturated hydrocarbon group of from 8 to 18 carbon atoms attached to the aryl nucleus, and attached to A through the aryl nucleus, A is selected from the group consisting of ethereal oxygen and sulfur, carboxylic ester and thiocarboxylic ester groups and x is a number from 8 to 20. R can, for example, be a straight or branched chain octyl, nonyl, decyl, lauryl, myristyl, cetyl, or stearyl group, or an alkylaryl group such as octylbenzene, nonylbenzene, decylbenzene, stearylbenzene, etc.

The sulfated ethoxynated derivatives of the above are also useful anionic detergents:

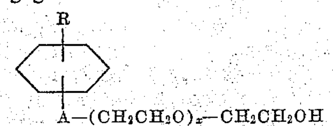
$$R{-}A{-}(CH_2CH_2O)_x{-}CH_2CH_2OSO_3M$$

where M is hydrogen or an alkali metal or organic amine cation and x, A and R are as above.

Where R is alkyl it will be evident that the detergent can be regarded as derived from an alcohol, mercaptan, oxy or thio fatty acid of high molecular weight, by condensation with ethylene oxide. Typical of this class of alkyl ether are the condensation products of oleyl or dodecyl alcohol or mercaptan with from 8 to 17 moles of ethylene oxide such as "Emulfor ON." Typical alkyl esters are the polyoxyethylene ester of tall oil acids, "Renex," and the higher fatty acid esters of polyethylene glycol, "Neutronyx 330."

Where R is aralkyl, the detergent can be derived from an alkyl phenol or thiophenol.

The ethoxynated alkyl phenols and thiophenols have the following general formula:



where R is a straight or branched chain saturated or unsaturated hydrocarbon group having at least 8 carbon atoms up to approximately 18 carbon atoms, A is oxygen or sulfur and x is a number from 8 to 20. R can, for example, be a straight or branched chain octyl, nonyl, decyl, lauryl, cetyl, myristyl, or stearyl group. Typical are the condensation products of octyl and nonyl phenol and thiophenol with from 8 to 17 moles of ethylene oxide such as "Igepal CA."

The detergent compositions can contain supplemental inorganic builders in small amounts including alkali metal sulfates, chlorides, and carbonates, such as sodium and potassium sulfate, sodium and potassium chloride, and sodium and potassium carbonate.

In addition to or instead of the above mentioned supplemental inorganic salts, organic materials, such as salts of carboxymethylcellulose, can be used as builders.

The detergent compositions inhibit the formation of tarnish upon copper, and nickel and copper alloys such as German silver in either hard or soft water. It will be appreciated that the detergent compositions may exist in any dry form, such as drum-dried or spray-dried detergent compositions, or may be in liquid form.

The detergent compositions containing a polyphosphate may be prepared by conventional methods, as by blending the components thereof in an aqueous solution or slurry and then drying the resulting mixture in a spray or drum dryer at elevated temperatures. The hydroxylamine salt may be added to solutions of the heat-dried detergent compositions containing a polyphosphate and silicate or may be added in the powdered state to heat-dried polyphosphate detergent compositions containing a silicate and have excellent inhibiting qualities. It was found, however, that the inhibiting properties of a hydroxylamine salt were almost completely lost if the hydroxylamine salt is added to the crutcher slurry and the slurry subsequently drum dried.

Illustrative examples of the polyphosphate detergent compositions of this invention and the synergistic tarnish inhibiting action of a hydroxylamine salt and an alkali metal silicate upon such compositions are set forth below.

In Examples 15 and 16 the compositions consisted of a polyphosphate, a hydroxylamine salt, and a silicate.

Examples 15 and 16

2.25 grams of pentasodium tripolyphosphate and 2.25 grams of tetrasodium pyrophosphate were dissolved respectively in two portions of distilled water; 0.01 grams of hydroxylamine hydrochloride, i. e., 0.4%, and 13.3% of sodium silicate based on the weight of polyphosphate were added to each of the solutions, and each of the solutions was then diluted to one quart. A strip of German silver metal immersed therein had a tarnish grading of 2, barely noticeable tarnish, for the pentasodium tripolyphosphate solution and a grading of 3, slight tarnish, for the tetrasodium pyrophosphate solution. This constituted a considerable improvement over the comparable compositions shown in Examples 1 through 6 and 13 and 14 wherein either a water-soluble hydroxylamine salt or an alkali metal silicate respectively was added to a polyphosphate.

Further examples showing how the synergistic tarnish inhibitors minimize the formation of tarnish upon copper and copper and nickel alloys by polyphosphate compositions are Examples 17 through 21. In these examples the amount of alkali metal silicate was varied with two different polyphosphates. It will be noted from these examples that only about 9% of an alkali metal silicate based on the weight of polyphosphate need be used in detergent compositions containing at least about 0.2% by weight of a hydroxylamine salt when the polyphosphate in the compositions is an alkali metal tripolyphosphate.

Examples 17, 18 and 19

Three 2.25 gram portions of pentasodium tripolyphosphate were dissolved in distilled water. 0.02 gram of hydroxylamine hydrochloride was added to each of the three solutions. 8.9%, 13.3%, and 22.2%, of sodium silicate based on the weight of polyphosphate were added respectively to the three solutions. Accordingly, the compositions contained 0.80%, 0.77% and 0.73%, respectively, of hydroxylamine hydrochloride. A strip of German silver metal immersed in each of the three solutions had a tarnish grading of 2 indicating barely noticeable tarnish.

Examples 20 and 21

Two 2.25 gram portions of tetrasodium pyrophosphate were dissolved in distilled water. 0.02 gram of hydroxylamine hydrochloride was added to each of the solutions. 13.3% and 22.2% of sodium silicate was added respectively to the two solutions. Accordingly, the compositions contained 0.77% and 0.73%, respectively, of hydroxylamine hydrochloride. A strip of German silver metal immersed in each of the solutions had a tarnish grading of 3 indicating slight tarnish.

Illustrative examples showing the synergistic tarnishing action of a hydroxlyamine salt and an alkali metal silicate upon a composition containing a polyphosphate and an anionic non-soap detergent are Examples Nos. 22, 22A, 23 and 23A wherein the concentrations are given in grams per liter and wherein the compositions were evaluated by the test procedure described above.

Examples 22, 22A, 23 and 23A

Example No.	22	22A	23	23A
Sodium Dodecylbenzenesulfonate	0.9	0.9	0.9	0.9
Pentasodium Tripolyphosphate	2.25	2.25	------	------
Tetrasodium Pyrophosphate	------	------	2.25	2.25
Hydroxylamine Hydrochloride [1]	------	0.02	------	0.02
Sodium Silicate [2]	0.3	0.3	0.3	0.3
Tarnish Grading	6	2	6	3
[1] Percent inhibitor, total weight basis	------	0.6	------	0.6
[2] Percent inhibitor, phosphate basis	13.3	13.3	13.3	13.3

In Examples 22 and 23 hydroxylamine hydrochloride, one of the synergistic tarnish inhibitors, was omitted from the compositions while it was included in Examples 22A and 23A. A noticeable improvement in the tarnish forming properties of the compositions is apparent in Examples 22A and 23A wherein the synergistic tarnish inhibitors were included in the compositions.

The remaining examples make use of the following two drum-dried compositions or modifications thereof as described in the examples.

Composition	X	Y
Sodium Dodecylbenzenesulfonate	18.0	18.0
Tetrasodium Pyrophosphate	45.0	------
Pentasodium Tripolyphosphate	------	45.0
Sodium Carbonate	3.0	3.0
Sodium Silicate [1]	6.0	6.0
Sodium Carboxymethyl-cellulose	0.5	0.5
Water	7.0	7.0
Sodium Sulfate and Miscellaneous Inert Materials	20.5	20.5
Total	100.0	100.0
[1] Percent inhibitor, phosphate basis	13.3	13.3

The components of the above compositions are given in percent by weight of the total composition. Both compositions X and Y thus contain one of the synergistic tarnish inhibitors, namely, sodium silicate, an alkali metal polyphosphate, an organic anionic non-soap detergent, and supplemental organic and inorganic builders.

Examples 24 through 29 show that when at least about 0.2% of a water-soluble hydroxylamine salt based on the total weight of the composition and at least about 13% of an alkali metal silicate based on the weight of the polyphosphate are added to a detergent composition containing tetrasodium pyrophosphate and an anionic non-soap detergent plus organic and inorganic supplemental builders that the formation of tarnish upon German silver is greatly reduced.

Examples 24–29

Six 5.0 gram portions of Composition X were dissolved separately in one liter of distilled water and hydroxylamine hydrochloride added thereto at the concentrations indicated below. The tarnish grading of the German silver metal strips is also indicated.

Example No.	24	25	26	27	28	29
Percent Hydroxylamine hydrochloride, total weight basis	0	0.1	0.2	0.4	4	6
Tarnish grade	6	5	3	2	1	1

The following Examples 30 through 35 show that at least about 0.2% of a water-soluble hydroxylamine salt based on the total weight of the composition and at least about 13% of an alkali metal silicate based on the weight of polyphosphate when added to a detergent composition containing a different polyphosphate from that used in Examples 24–29, that is, pentasodium tripolyphosphate, and an anionic non-soap detergent plus inorganic and organic supplemental builders that the composition had improved tarnish formation properties.

Examples 30–35

Six 5.0 gram portions of Composition Y were dissolved in one liter of distilled water and hydroxylamine hydrochloride was added at the concentrations indicated below. The tarnish grading of strips of German silver metal inserted in each of the solutions is also set forth.

Example No.	30	31	32	33	34	35
Percent Hydroxylamine hydrochloride, total weight basis	0	0.1	0.2	0.4	4	6
Tarnish grading	5	5	3	1	2	3

Examples 36–39 show that the synergistic tarnish inhibitors are effective in compositions containing still other alkali metal polyphosphates, namely, sodium hexametaphosphate and hexasodium tetrapolyphosphate.

Examples 36–39

Sodium hexametaphosphate and hexasodium tetrapolyphosphate both tarnished German silver to grade 6 when these polyphosphates were substituted for the tetrasodium pyrophosphate in 5.0 gram portions of Composition X. The tarnish was reduced to grade 1 with 0.4% hydroxylamine hydrochloride, total weight basis, added thereto when the polyphosphate was sodium hexametaphosphate and to grade 2 when the polyphosphate was hexasodium tetrapolyphosphate.

Examples 40 and 40A show that the synergistic tarnish inhibitors are effective in detergent compositions containing an organic cationic non-soap detergent.

Examples 40 and 40A

The lauric ester of N-(beta-hydroxyethyl)-alpha-(chloropyridinium) acetamide was substituted for sodium dodecylbenzenesulfonate in two 5.0 gram portions of Composition X. 4% of hydroxylamine hydrochloride based on the total weight of the composition was added to one portion of the composition. A strip of German silver metal was tarnished to grade 6 by the composition which contained the alkali metal silicate but which did not contain a hydroxylamine salt whereas a strip of German silver metal was tarnished only to grade 2 when immersed in a solution of the composition which contained the synergistic tarnish inhibitors.

Examples 41 and 41A show that the synergistic tarnish inhibitors are effective in polyphosphate compositions containing an organic nonionic non-soap detergent.

Examples 41 and 41A

When 4% of hydroxylamine hydrochloride based on the total weight of the composition was added to a 5.0 gram portion of Composition X wherein the organic nonionic non-soap detergent, Pluronic L–64 [a compound having the empirical formula

$$HO—(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$$

prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol where b is an integer selected from the group consisting of 26 to 30 and a plus b is an integer such that the molecule contains from 40% to 50% ethylene oxide], was substituted for the sodium dodecylbenzenesulfonate, the composition tarnished German silver metal only to grade 3. A 5.0 gram portion of the same composition in the absence of hydroxylamine hydrochloride tarnished German silver metal to grade 6.

When other anionic non-soap detergents, namely, the sodium salt of N-palmitoyl-N-methyl taurine and sodium-3-dodecyloxy-2-hydroxypropane sulfonate, were substituted for the sodium dodecylbenzenesulfonate in Composition X, both compositions tarnished German silver metal to grade 6. The tarnish was reduced to grade 3 in both instances when 0.4% hydroxylamine hydrochloride (total weight basis) was included in the formula.

That the syngeristic tarnish inhibitors are also effective in hard water is shown by the following Example 42.

Example 42

A 5.0 gram portion of Composition X tarnished German silver metal to grade 6 in water of 180 p. p. m. hardness without the presence of hydroxylamine hydrochloride while a strip of German silver metal was tarnished only to grade 3 when 0.4% of hydroxylamine hydrochloride, total weight basis, was added to a 5.0 gram portion of Composition X in water having a hardness of 180 p. p. m.

As noted above, the hydroxylamine salt may be added in a powdered state to the heat-dried polyphosphate detergent compositions containing an alkali metal silicate. This is illustrated in Example 43.

Example 43

To 10 grams of Composition X were added 0.04 grams of powdered hydroxylamine hydrochloride, i. e., 0.4% hydroxylamine hydrochloride based on the total weight of the composition. The two powders were thoroughly mixed and 5 grams removed and tested for tarnishing tendencies. A grade 3 rating was obtained, indicating satisfactory tarnish inhibition.

The effectiveness of the synergistic tarnish inhibitors in inhibiting tarnish formation by polyphosphate compositions on metals other than German silver was tested by the procedure given above using a 5 gram portion of Composition X to which was added 0.5% of hydroxylamine hydrochloride based on the total weight of the composition. The results of these tests are presented below in Table 1.

TABLE 1

Metal or Alloy	Tarnish Grading
Brass (alloy of copper and zinc)	6
Coinage Nickel (alloy of nickel and copper)	1
Copper	4
Monel (alloy of nickel, copper, manganese and iron)	1

The test data indicates that the synergistic tarnish inhibitors when used in polyphosphate compositions are effective against the tarnishing of copper and copper and nickel alloys, such as coinage nickel, copper and Monel. The synergistic tarnish inhibitors are less effective when used in the cleaning of copper and are ineffective when used in the cleaning of brass which is an alloy of copper and zinc.

The effectiveness of the synergistic tarnish inhibitors with liquid polyphosphate detergent compositions is clearly illustrated in Examples 44–47.

Examples 44–47

Four 5 gram portions of the following liquid detergent composition were dissolved separately in one liter of distilled water and hydroxylamine hydrochloride added thereto at the concentrations indicated below. The tarnish grading of strips of German silver metal inserted in each of the solutions is also set forth.

Composition	Percent by weight
Potassium Dodecylbenzenesulfonate	10.0
Sodium Xylene Sulfonate	7.6
Lauric Isopropanolamide	3.2
Lauric Diethanolamide	3.8
Tetrapotassium Pyrophosphate	20.0
Sodium Silicate [1]	7.0
Water	48.4
Total	100.0

[1] Percent inhibitor, phosphate basis, 35.

Example No.	44	45	46	47
Percent hydroxylamine hydrochloride, total weight bases	0	0.2	0.4	2.6
Tarnish grade	6	3	3	2

Many modifications and variations may be made in the invention herein set forth without departing from the spirit thereof, and only such limitations of the invention should be imposed as are indicated by the scope of the appended claims.

We claim:

1. A detergent composition consisting essentially of an alkali metal polyphosphate which in aqueous solution tarnishes copper and copper and nickel alloys, from about 0.2% to about 12% of a water-soluble inorganic hydroxylamine salt, and from about 13% to about 35% of an alkali metal metasilicate based on the weight of polyphosphate; the amounts of said hydroxylamine salt and metasilicate being sufficient to inhibit such tarnishing.

2. A detergent composition as set forth in claim 1 wherein the alkali metal polyphosphate is pentasodium tripolyphosphate.

3. A detergent composition as set forth in claim 1 wherein the alkali metal polyphosphate is tetrasodium pyrophosphate.

4. A detergent composition as set forth in claim 1 wherein the water-soluble inorganic hydroxylamine salt is hydroxylamine hydrochloride.

5. A detergent composition as set forth in claim 1 wherein the alkali metal metasilicate is sodium metasilicate.

6. A detergent composition consisting essentially of from about 5% to about 50% of an alkali metal polyphosphate which in aqueous solution tarnishes copper and copper and nickel alloys, from about 5% to about 40% of an organic non-soap detergent, from about 0.2% to about 12% of a water-soluble inorganic hydroxylamine salt, and from about 13% to about 35% of an alkali metal metasilicate based on the weight of polyphosphate; the amounts of said hydroxylamine salt and metasilicate being sufficient to inhibit such tarnishing.

7. A detergent composition as set forth in claim 6 wherein the alkali metal polyphosphate is pentasodium tripolyphosphate.

8. A detergent composition as set forth in claim 6 wherein the alkali metal polyphosphate is tetrasodium pyrophosphate.

9. A detergent composition as set forth in claim 6 wherein the water-soluble inorganic hydroxylamine salt is hydroxylamine hydrochloride.

10. A detergent composition as set forth in claim 6 wherein the alkali metal metasilicate is sodium metasilicate.

11. A detergent composition as set forth in claim 6 wherein the organic non-soap detergent is an organic anionic non-soap detergent.

12. A detergent composition as set forth in claim 6 wherein the organic non-soap detergent is an organic cationic non-soap detergent.

13. A detergent composition as set forth in claim 6 wherein the organic non-soap detergent is an organic nonionic non-soap detergent.

14. A detergent composition as set forth in claim 11 wherein the organic anionic non-soap detergent is sodium dodecylbenzenesulfonate.

15. A detergent composition as set forth in claim 12 wherein the organic cationic non-soap detergent is the lauric ester of N-(beta-hydroxyethyl)-alpha-(chloropyridinium) acetamide.

16. A detergent composition as set forth in claim 13 wherein the organic nonionic non-soap detergent is a compound having the empirical formula

$$HO—(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$$

prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol where b is an integer selected from the group consisting of 26 to 30 and a plus c is an integer such that the molecule contains from 40% to 50% of ethylene oxide.

17. A detergent composition consisting essentially of an alkali metal tripolyphosphate which in aqueous solution tarnishes copper and copper and nickel alloys, from about 0.2% to about 12% of a water-soluble inorganic hydroxylamine salt, and from about 9% to about 35% of an alkali metal metasilicate based on the weight of tripolyphosphate; the amounts of said hydroxylamine salt and metasilicate being sufficient to inhibit such tarnishing.

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