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NONTARNISHING DETERGENT COMPOSITIONS CONTAINING A HYDRAZINE SALT

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This invention relates to detergent compositions containing tarnish inhibitors and more particularly to polyphosphate compositions containing a hydrazine salt as a tarnish inhibitor.

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 the 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.

In accordance with the instant invention polyphosphate compositions are provided containing a tarnish inhibitor which compositions will inhibit the formation of tarnish upon copper, and copper and nickel alloys such as German silver. The tarnish inhibitors of the invention are water-soluble hydrazine salts, typical examples of which include hydrazine sulfate, hydrochloride, hydroiodide, hydrobromide, and nitrate. It will be appreciated that hydrazine is an obvious equivalent of such hydrazine salts and may also be employed in the compositions in lieu of a hydrazine salt.

An amount of the hydrazine salt is added to the polyphosphate composition which is sufficient to give tarnish inhibition when the composition is used in its normal way. It will be understood that the amount required will depend in part upon the tarnish inhibiting properties of the particular hydrazine salt in question, on the tendency of the polyphosphate with which it is used to tarnish copper and nickel and copper alloys, and upon the amount of polyphosphate present. In general, at least about 1% of the hydrazine salt will inhibit the formation of tarnish by the composition. The maximum amount of the hydrazine salt is not critical, but more than is necessary to give the desired effect will usually not be used, and of course an amount in excess of that soluble in an aqueous solution of the composition would not be used. In most cases, the maximum suggested would be about 12%.

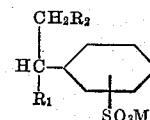
The tarnish inhibitors of the present invention are effective with water-soluble alkali metal polyphosphates at pH values where such polyphosphates tend to tarnish German silver, i. e., within the range of about pH 7 to about pH 11. Typical examples of suitable alkali metal polyphosphates include pentasodium and pentapotassium tripolyphosphates, tetrasodium and tetrapotassium pyrophosphates, sodium and potassium hexametaphosphates, and hexasodium and hexapotassium tetraphosphates. 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

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and builders which might be included in the detergent compositions.

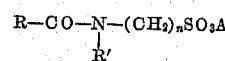
Examples of such additional optional components are an organic non-soap detergent which may be either an anionic, cationic, or nonionic detergent, and builders, water, and inert materials. The detergent compositions may contain conventional proportions by weight of an organic non-soap detergent, usually within the range between 5% and 40%; an alkali metal polyphosphate in any amount, usually between 5% and 50%; at least about 1% of a water-soluble hydrazine salt; and the balance supplemental builders and inert materials.

The alkylaryl sulfonates are a class of anionic detergents well known in the art under this name which may be included in the detergent compositions. One example thereof are 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, R₁ and R₂ 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 U. S. Patent No. 2,477,383 to Lewis, issued July 26, 1949; they are available in commerce under the trade names "Oronite," "Ultrawet," and "Neoleene."

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



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 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 palmitic-stearic methyl tauride and sodium palmitic methyl amidopropyl sulfonate are typical examples thereof.

These compounds are prepared by interacting the corresponding aliphatic acid anhydride or halide with an organic aliphatic aminosulfonic acid, such as taurine, NH₂CH₂CH₂SO₃H, and the various N-substituted taurines, such as N-methyl taurine, or aminopropane sulfonic acid, NH₂(CH₂)₃SO₃H.

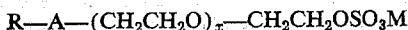
Other water-soluble alkyl aromatic sulfonic acids may constitute optional components such as those prepared by alkylating benzene or naphthalene with a kerosene fraction followed by sulfonation to aliphatic sulfonic acids, esters of sulfuric acid with aliphatic alcohols of 10 to 18 carbon atoms, particularly those derived by the reduction of coconut oil, palm oil and the like long-chain fatty acids, sulfonated castor oil, esters and ethers of isenthionic 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.

Examples of organic nonionic non-soap detergents include alkyl oxyether and ester and thioether and ester detergents having the following general formula:



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 also are useful anionic detergents:

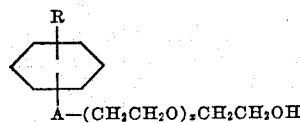


where M is hydrogen or an alkali metal or an organic amine cation and x, A and R are as above.

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 type 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 "Renex" (polyoxyethylene ester of tall oil acids) and "Neutronyx 331" (higher fatty acid ester of polyethylene glycol).

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, 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, available commercially under the trade name "Igepal CA."

The optional supplemental builders may be alkali metal inorganic salts, typical examples of which include sodium and potassium sulfates, sodium and potassium chlorides, sodium and potassium silicates, and sodium and potassium carbonates.

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

The builder mixture is so chosen among alkaline, neutral or acidic salts that the composition obtained in an aqueous 0.14% washing solution has a pH of 7 or above. Preferably its pH lies within the range of 7 to about 11, since solutions which are more alkaline may be irritating to the skin and tend to weaken some fabrics, particularly woolens. In general, the alkali metal carbonates are preferred agents for bringing the pH of the solution to a high alkaline value within the preferred range.

The detergent compositions containing a polyphosphate are 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. 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 water-soluble hydrazine salt tarnish inhibitor may be added to solutions of heat-dried detergents containing polyphosphates, or to the crutcher slurry if it is to be cold-dried and ground, or may be added in the powdered state to heat-dried detergents and have excellent inhibiting qualities. However, it was found that the inhibiting properties of 2% hydrazine salt are completely lost if added to the crutcher slurry, and the slurry subsequently drum-dried.

The compositions of the invention will be further illustrated by the following examples wherein a typical hydrazine salt, namely the monobasic form of hydrazine sulfate, was employed in the compositions. In these examples the following test procedure was employed. A specified amount of the polyphosphate detergent composition was dissolved in somewhat less than one quart of water at a temperature under 170° F., and the hydrazine salt then 20 added thereto in the form of a solution. More water was then added thereto to give a total volume of one quart and the pH adjusted when necessary to 7-11. 300 mls. of the solution were placed in a beaker and the temperature adjusted within the range from 160° F. to 170° F. A 25 strip of German silver metal, six inches by one inch, which had been cleaned with a metal polish and rinsed and dried, was partially immersed in the solution and allowed to remain for one-half hour at 160° F. to 170° F. The metal strip was then removed, rinsed, and dried with a cloth. The strip was visually examined for tarnish and the effectiveness of the hydrazine salt in inhibiting the formation of tarnish graded as follows:

| | Grade No. | Degree of Tarnish |
|----|-----------|--------------------------------------|
| 35 | 0 | No tarnish. |
| | 1 | Interface stain only. |
| | 2 | Barely noticeable tarnish. |
| | 3 | Slight tarnish. |
| | 4 | Moderate tarnish. |
| | 5 | Considerable (heavy) tarnish. |
| 40 | 6 | Severe, as when inhibitor is absent. |

Examples 1-19 below show that at least about 1% of a water-soluble hydrazine salt inhibits the formation of tarnish by typical polyphosphates, such as pentasodium

45 tripolyphosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, and hexasodium tetrapolyphosphate. More specifically, the examples show that at least 1.6% of hydrazine sulfate is effective in inhibiting the formation of tarnish by pentasodium tripolyphosphate and tetra-50 sodium pyrophosphate, while at least 1.1% of hydrazine sulfate is effective in inhibiting the formation of tarnish by sodium hexametaphosphate and hexasodium tetrapolyphosphate.

Examples 1-19

55 To separate 2.25 gram portions of the four polyphosphates listed below dissolved in distilled water were added varying proportions of hydrazine sulfate, and the volumes diluted to one quart in accordance with the above test procedure. The tarnish grading upon German silver was as follows:

| Percent Hydrazine Sulfate | 0 | 1.1 | 1.6 | 2.2 | 8.2 | 11.8 |
|------------------------------------------------|---|-----|-----|-----|-----|------|
| Pentasodium Tripolyphosphate (Examples 1-6) | 6 | 6 | 3 | 3 | 1 | 1 |
| Tetrasodium Pyrophosphate (Examples 7-11) | 6 | 6 | 2 | 1 | | 1 |
| Sodium Hexametaphosphate (Examples 12-15) | 6 | 2 | 2 | 2 | | |
| Hexasodium Tetrapolyphosphate (Examples 16-19) | 6 | 2 | 1 | 1 | | |

| 65 | Polyphosphate | Tarnish Grade | | | | | |
|------------------------------------------------|---------------|---------------|---|---|---|--|---|
| Pentasodium Tripolyphosphate (Examples 1-6) | 6 | 6 | 3 | 3 | 1 | | 1 |
| Tetrasodium Pyrophosphate (Examples 7-11) | 6 | 6 | 2 | 1 | | | |
| Sodium Hexametaphosphate (Examples 12-15) | 6 | 2 | 2 | 2 | | | |
| Hexasodium Tetrapolyphosphate (Examples 16-19) | 6 | 2 | 1 | 1 | | | |

Tarnishing of German silver by polyphosphates does not depend upon the presence of oxygen as is true in

corrosion, and thus the inhibiting action of water-soluble hydrazine salts does not consist merely in removing oxygen from the solution. This is clearly shown in Examples 20-27 below wherein oxygen was excluded from the solutions and yet German silver was tarnished in the absence of the inhibitor and the tarnish was considerably reduced when the inhibitor was present in the polyphosphate compositions.

Examples 20-27

The standard procedure was employed but modified in that the oxygen was removed from the solution at 160° F. by bubbling nitrogen gas for one-half hour before inserting the German silver metal strip and then continued in the succeeding one-half hour during which the strip was allowed to remain immersed. The solutions each contained 2.25 grams of the designated polyphosphates and had a pH of 10.

| Percent Hydrazine Sulfate..... | 0.0 | 0.3 | 0.5 | 1.1 |
|----------------------------------------------------|---------------|-----|-----|-----|
| Polyphosphate | Tarnish Grade | | | |
| Pentasodium Tripolyphosphate (Examples 20-23)..... | 6 | 4 | 2 | 1 |
| Tetrasodium Pyrophosphate (Examples 24-27)..... | 6 | 6 | 1 | 1 |

A water-soluble hydrazine salt is effective as a tarnish inhibitor in polyphosphate compositions which contain an organic non-soap detergent as shown by Examples 28-31.

Examples 28-31

0.9 gram of sodium dodecylbenzenesulfonate and 2.25 grams of pentasodium tripolyphosphate were dissolved in distilled water, and 0.05 gram (1.6%) of hydrazine sulfate added thereto, and the solution diluted to a volume of one quart. This solution tarnished German silver only to grade 1, while an identical solution without the presence of the hydrazine sulfate tarnished German silver to grade 6. Tetrasodium pyrophosphate was substituted in the same amount for the pentasodium tripolyphosphate in the above composition. A strip of German silver metal placed in the solution of the composition containing hydrazine sulfate was tarnished only to grade 1, whereas a strip of German silver metal placed in a solution of the composition without the presence of the hydrazine sulfate tarnished to grade 6.

The addition of a water-soluble hydrazine salt to polyphosphate compositions containing an organic non-soap detergent, which may be either anionic, nonionic, or cationic, as well as supplemental builders inhibits the formation of tarnish by such detergent compositions. This is clearly illustrated by the examples set forth below wherein the following two compositions, or specified modifications thereof, were employed.

| Compositions..... | X | Y |
|-------------------------------------------------------|------|------|
| Sodium Dodecylbenzenesulfonate..... | 18.0 | 18.0 |
| Tetrasodium Pyrophosphate..... | 45.0 | |
| Pentasodium Tripolyphosphate..... | | 45.0 |
| Sodium Carbonate..... | 3.0 | 3.0 |
| Sodium Silicate..... | 6.0 | 6.0 |
| Sodium Carboxymethylcellulose..... | 0.5 | 0.5 |
| Water..... | 7.0 | 7.0 |
| Sodium Sulfate and Miscellaneous Inert Materials..... | 20.5 | 20.5 |
| Total..... | 100 | 100 |

In Compositions X and Y the amounts of the various components are expressed in percent by weight.

Examples 32-43

To 5 grams each of Compositions X and Y there was added hydrazine sulfate in the proportions shown below.

and the test procedure carried out with the following results.

| Percent Hydrazine Sulfate..... | 0.4 | 0.45 | 0.5 | 0.6 | 1.0 | 1.2 | 6.0 |
|-----------------------------------------------|-----|-------|-----|-----|-----|-------|-----|
| Grading (Composition X) (Examples 32-37)..... | 6 | 6 | 4 | 3 | 1 | ----- | 1 |
| Grading (Composition Y) (Examples 38-43)..... | 5 | ----- | 4 | 3 | 3 | 1 | 1 |

Examples 32-43 show that at least about 1% and more particularly 0.5%, of hydrazine sulfate inhibits the formation of tarnish by polyphosphate compositions containing an organic anionic non-soap detergent and supplemental builders.

A hydrazine salt is effective as a tarnish inhibitor in polyphosphate compositions containing an organic non-soap detergent as well as supplemental builders when the alkali metal polyphosphate is other than tetrasodium pyrophosphate or pentasodium tripolyphosphate, for example sodium hexametaphosphate and hexasodium tetrapolyphosphate. This is clearly illustrated by Examples 44-47 set forth below.

Examples 44-47

Sodium hexametaphosphate and hexasodium tetrapolyphosphate were each substituted for the same amount of tetrasodium pyrophosphate in Composition X and the composition tested in accordance with the test procedure. Five grams of each of these compositions in a quart of water tarnished German silver to a grading of 6, i. e., severe tarnish. When 1.0% of hydrazine sulfate was added to each of these compositions the tarnish grading of both compositions upon German silver was reduced to grade 2 indicating barely noticeable tarnish.

At least about 1% of a hydrazine salt is also effective as a tarnish inhibitor in polyphosphate compositions containing other organic anionic non-soap detergents as well as supplemental builders as shown by Examples 48-51.

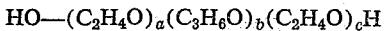
Examples 48-51

The organic anionic non-soap detergents, the sodium salt of N-palmitoyl-N-methyl taurine and sodium-3-dodecyloxy-2-hydroxypropane sulfonate, were substituted separately for the same amount of sodium dodecylbenzenesulfonate in Composition X. When 5 grams of each of these compositions was tested in accordance with the test procedure, both compositions tarnished German silver to grade 6 indicating severe tarnish. The tarnish was reduced to grade 1 in both instances when 1.0% of hydrazine sulfate was included in each of the two compositions.

A hydrazine salt is also effective as a tarnish inhibitor in polyphosphate compositions containing either an organic cationic non-soap detergent or an organic nonionic non-soap detergent as well as supplemental builders, as illustrated by Examples 52-55.

Examples 52-55

18% of an organic cationic non-soap detergent, namely the lauric ester of N-(beta-hydroxyethyl)-alpha-(chloropyridinium) acetamide, was substituted for the sodium dodecylbenzenesulfonate in Composition X. A second composition was prepared wherein 18% of an organic nonionic non-soap detergent, namely Pluronic L-64, a compound having the empirical formula



prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of pyropylene 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, was substituted for the sodium dodecylbenzenesulfonate in Composition X. Five grams of each of these compositions when dissolved in one quart of water and tested in accordance with the test procedure tarnished German silver to grade 6. When 1.0% of hydrazine sul-

fate was added to each of these compositions, they both then had a tarnish grading of 2, indicating barely noticeable tarnish.

As noted above the water-soluble hydrazine salts are effective as tarnish inhibitors in polyphosphate compositions containing an organic non-soap detergent as well as supplemental builders wherein the alkali metal polyphosphate may vary within the range of about 5% to about 50%. Data showing the effect of the reduction in the amount of alkali metal polyphosphate present in the detergent composition is set forth below in Examples 56-57.

Examples 56-57

Composition X was modified by employing 5% of tetrasodium pyrophosphate therein with the remainder of the composition being the same with the exception that the amount of sodium sulfate was increased to offset the corresponding decrease in the tetrasodium pyrophosphate content. Five grams of the modified composition dissolved in a quart of distilled water having a temperature of 160° F.-170° F. had a tarnish grading upon German silver of grade 4. When 0.11% of hydrazine sulfate was added to the composition and five grams thereof dissolved in a quart of water, the composition had a tarnish grading of 1 upon German silver metal, indicating considerable improvement.

The amount of the organic non-soap detergent present in the polyphosphate composition may be varied within the range of about 5% to about 40% as noted above and as further illustrated by Examples 58-61.

Examples 58-59

5% of sodium dodecylbenzenesulfonate was employed in Composition X with the amount of sodium sulfate being increased to offset the decrease in the sodium dodecylbenzenesulfonate content of the composition. Five grams of this modified composition dissolved in a quart of distilled water had a tarnish grading of 6 upon German silver metal, whereas five grams of the composition which also contained 1% of hydrazine sulfate had a reduced tarnish grading of 2.

Examples 60-61

Five grams of the following product was mechanically mixed (not heat-dried) and had a tarnish grading of 6 when tested by the standard procedure.

| Composition | Percent by Weight |
|-------------------------------------|-------------------|
| Sodium Dodecylbenzenesulfonate..... | 40.0 |
| Tetrasodium Pyrophosphate..... | 45.0 |
| Sodium Carbonate..... | 3.0 |
| Sodium Silicate..... | 6.0 |
| Sodium Carboxymethylcellulose..... | 0.5 |
| Water..... | 5.5 |
| Total..... | 100 |

When 0.5% of hydrazine sulfate was added thereto, the polyphosphate detergent composition had a reduced tarnish grading of 3.

The hydrazine salt may be incorporated in the polyphosphate detergent composition by mechanically mixing the inhibitor with the heat-dried product as shown by Examples 62-63.

Examples 62-63

To ten grams of Composition X (a drum-dried granulated product) were added 0.1 gram of powdered hydrazine sulfate, i. e., 1% of hydrazine sulfate. The two powders were thoroughly mixed in a flask, and five grams removed and tested for tarnishing tendencies. This polyphosphate detergent composition had a tarnish grading of 1, whereas the composition without the presence of the hydrazine sulfate had a tarnish grade of 6.

Examples 64-65 illustrate the fact that the hydrazine salts are effective as tarnish inhibitors in polyphosphate

compositions when the polyphosphate compositions are used in hard water. It will be noted that in all of the previous examples the water was soft water, i. e., distilled water.

Examples 64-65

Five grams of Composition X dissolved in a quart of water having a hardness of 180 p. p. m. tarnished German silver to grade 6, whereas five grams of Composition X containing 1% of hydrazine sulfate dissolved in a quart of water having a hardness of 180 p. p. m. tarnished German silver only to grade 1.

The effectiveness of the hydrazine salt in inhibiting the formation of tarnish upon metals and alloys other than German silver when the metals or alloys are immersed in a solution of a polyphosphate composition was tested in accordance with the test procedure given above using five grams of Composition X containing hydrazine sulfate and the results of the tests given below in Table I.

TABLE I

| Metal or Alloy | Hydrazine Sulfate, 0.5% by Weight |
|----------------------------------------------------------|-----------------------------------|
| Brass (alloy of copper and zinc)..... | 4 |
| Coinage Nickel (alloy of nickel and copper)..... | 1 |
| Copper..... | 4 |
| Monel (alloy of nickel, copper, manganese and iron)..... | 1 |

30 The results of the tests show that a hydrazine salt is highly effective in inhibiting the formation of tarnish upon coinage nickel and Monel, and is moderately effective in inhibiting the formation of tarnish upon brass and copper.

35 The effectiveness of at least about 1%, and more specifically 0.5%, of a water-soluble hydrazine salt as a tarnish inhibitor with liquid polyphosphate detergent compositions is clearly illustrated by Examples 66-71.

Examples 66-71

40 Six 5 gram portions of the following liquid detergent composition were dissolved separately in one quart of distilled water and hydrazine sulfate added thereto at 45 the concentrations indicated below. The tarnish grading of strips of German silver metal inserted in each of the solutions at pH 10 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..... | 7.0 |
| Water..... | 48.4 |
| Total..... | 100 |

| Example No. | 66 | 67 | 68 | 69 | 70 | 71 |
|--------------------------------|----|-----|-----|-----|-----|-----|
| Percent Hydrazine Sulfate..... | 0 | 0.4 | 0.5 | 0.8 | 1.0 | 2.6 |
| Tarnish Grade..... | 6 | 5 | 3 | 3 | 2 | 1 |

65 Many modifications and variations may be made in the invention herein set forth without departing from the spirit thereof, and accordingly the invention is to be limited only within the scope of the appended claims.

We claim:

70 1. A detergent composition comprising an alkali metal polyphosphate which in aqueous solution tarnishes copper and copper and nickel alloys and a water-soluble inorganic hydrazine salt in an amount of at least about 1% based on the weight of polyphosphate and sufficient 75 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 alkali metal polyphosphate is sodium hexametaphosphate.

5. A detergent composition as set forth in claim 1 wherein the alkali metal polyphosphate is hexasodium tetrapolyphosphate.

6. A detergent composition as set forth in claim 1 wherein the water-soluble inorganic hydrazine salt is hydrazine sulfate.

7. A detergent composition comprising 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, and a water-soluble inorganic hydrazine salt in an amount of at least about 1% based on the weight of polyphosphate and sufficient to inhibit such tarnishing.

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

9. A detergent composition as set forth in claim 7 wherein the alkali metal polyphosphate is tetrasodium pyrophosphate.

10. A detergent composition as set forth in claim 7 wherein the alkali metal polyphosphate is sodium hexametaphosphate.

11. A detergent composition as set forth in claim 7 wherein the alkali metal polyphosphate is hexasodium tetrapolyphosphate.

12. A detergent composition as set forth in claim 7 wherein the water-soluble inorganic hydrazine salt is hydrazine sulfate.

13. A detergent composition as set forth in claim 7 wherein the organic non-soap detergent is an organic cationic non-soap detergent.

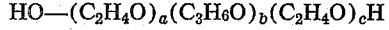
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14. A detergent composition as set forth in claim 7 wherein the organic non-soap detergent is an organic nonionic non-soap detergent.

15. A detergent composition as set forth in claim 7 wherein the organic non-soap detergent is an organic anionic non-soap detergent.

16. A detergent composition as set forth in claim 13 wherein the organic cationic non-soap detergent is the lauric ester of N-(beta-hydroxyethyl)-alpha-(chloropyridinium) acetamide.

17. A detergent composition as set forth in claim 14 wherein the organic nonionic non-soap detergent is a compound having the empirical formula



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.

18. A detergent composition as set forth in claim 15 wherein the organic anionic non-soap detergent is sodium dodecylbenzenesulfonate.

19. A detergent composition as set forth in claim 15 wherein the organic anionic non-soap detergent is the sodium salt of N-palmitoyl-N-methyl taurine.

20. A detergent composition as set forth in claim 15 wherein the organic anionic non-soap detergent is sodium-3-dodecyloxy-2-hydroxypropane sulfonate.

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