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2,733,215

CLEANING COMPOSITIONS CONTAINING TARNISH INHIBITORS

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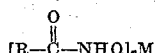
20 Claims. (Cl. 252—137)

This invention relates to cleaning compositions containing tarnish inhibitors and more particularly to polyphosphate and synthetic detergent compositions containing hydroxamic compounds as tarnish inhibitors.

Compositions containing polyphosphates and/or synthetic detergents are now widely used for detergent and other purposes. Aqueous solutions of polyphosphates and some synthetic detergents 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 and detergent compositions are provided containing a tarnish inhibitor which compositions will not tarnish copper, and nickel and copper alloys such as German silver. The tarnish inhibitor of the invention is a hydroxamic compound which can take the form of a hydroxamic acid or water-soluble salt thereof.

The hydroxamic compounds of the invention are described by the following formula:



M is a cation such as hydrogen or a metal and n is an integer equal to the valence of the metal. R is an aliphatic hydrocarbon group having either a straight or branched chain and can be saturated or unsaturated. The number of carbon atoms in the R chain is not critical, but R should have at least seven carbon atoms. Optimum tarnish inhibiting properties are displayed by compounds in which R has from nine to fifteen carbon atoms. As the chain increases in molecular weight above seventeen carbon atoms, tarnish-inhibiting properties tend to diminish, and larger amounts of compound have to be employed to achieve good inhibition. Therefore usually compounds in which R has over seventeen carbon atoms would not be employed.

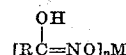
Typical R radicals having either straight or branched chains are heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, decynyl, dodecenyl, octadecenyl, octadecadienyl and dodecynyl.

The hydroxamic compound can be used either in the form of the acid or as a water-soluble salt depending upon which is most readily available and least expensive. In some instances the salts have not been isolated but apparently exist in solution. The alkali metal salts such as the sodium, potassium and ammonium salts are preferred. The salts of other metals, such as barium, silver, iron (ferric), copper, calcium and magnesium, can be used as well, since it is not the salt-forming cation but the hydroxamic acid or its anion which displays the tarnish

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inhibiting properties. In solutions of the detergent composition the hydroxamic acid may exist in the form of a salt different from that present in the dry composition, due to ion exchange with other cations.

It may be noted that the hydroxamic compounds are also capable of existing in the following form:



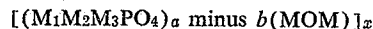
where R has the same significance as above. The hydroxamic compounds are represented as well by the above formula as by that given first, but for consistency are referred to throughout the specification and claims by the name of the first-given form.

These acids and their salts are known compounds and are readily prepared by the general procedure appearing in Organic Syntheses, collective vol. II, page 67 (1944). A procedure for their preparation is given in U. S. Patent No. 2,397,508, dated April 2, 1946, to Rouault and Rhodes. These acids and their salts are non-toxic, sparingly water soluble substances but sufficiently water-soluble to permit their incorporation in polyphosphate and synthetic detergent solutions in the amounts required to impart tarnish inhibition thereto.

An amount of hydroxamic compound would be added to the polyphosphate and/or synthetic detergent composition sufficient to give tarnish inhibition when the composition is used in its normal way. Usually about 0.13% of the hydroxamic compound gives adequate tarnish inhibition, but larger amounts can be used if desired. From 0.13 to 5% is effective under nearly all conditions and therefore is preferred. The maximum amount of hydroxamic compound 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 solution would not be used. It will be understood that the amount required will depend in part upon the tarnish inhibiting properties of the particular hydroxamic compound in question, upon the tendency of the polyphosphate and/or synthetic detergent with which it is used to tarnish copper and nickel alloys and copper alloys, and upon the amounts of polyphosphate and synthetic detergent present.

The hydroxamic compounds are effective as tarnish inhibitors in both hard and soft water.

The tarnish inhibitors of the invention are effective with water-soluble polyphosphates as a class at pH values where such polyphosphates tend to tarnish German silver (usually pH 6 or above) and particularly those polyphosphates identified by the following general formula from which it is seen that both the acids and their various salts are contemplated:



where:

M_1 , M_2 and M_3 are hydrogen or an alkali metal, such as sodium, potassium and ammonium, and can be the same or different, and M is M_1 and/or M_2 and/or M_3 . a is an integer of 1 or more, usually 1 to 4, b is an integer of 1 or more, usually 1 or 2, x is an integer of 1 or more, usually 1 to 6.

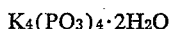
In the case where a is 2, b is 1 and x is 1, the compound is a pyrophosphate. When a is 1, b is 1 and x is 1, the compound is a metaphosphate. Others will be evident to those skilled in the art.

The upper limit of a , b and x is not critical, but will be determined by the increasingly lower water-solubility as molecular weight increases. The sodium polyphosphates are preferred.

As the general formula shows, both the normal and

acid salts of the phosphates are within the scope of the invention.

Among the polyphosphoric acids and their alkali metal salts coming within the invention are the polymetaphosphoric acids $(\text{HPO}_3)_x$, (a is 1, b is 1, x is more than 1), pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$ (a is 2, b is 1, x is 1), triphosphoric acid $\text{H}_5\text{P}_3\text{O}_{10}$ (a is 3, b is 2, x is 1), and tetraphosphoric acid $\text{H}_6\text{P}_4\text{O}_{13}$ (a is 4, b is 3, x is 1). $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{K}_4\text{P}_2\text{O}_7$, $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_6\text{P}_4\text{O}_{13}$, sodium polyphos ($\text{Na}_{12}\text{P}_{10}\text{O}_{31}$ =Blockson),



Pascal's salt, sodium dimetaphosphate, sodium trimetaphosphate (Knorre's salt), sodium tetrametaphosphate and sodium hexametaphosphate (Graham's salt) are examples.

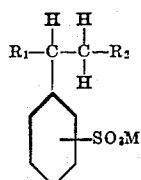
The hydroxamic compound tarnish inhibitors can be incorporated in compositions containing polyphosphates, and in compositions containing synthetic detergents, and are effective to reduce tarnish due to polyphosphate or detergent in each of these types of compositions. They are particularly useful in synthetic detergent compositions which contain one or more polyphosphates as builders and one or more synthetic detergents, i. e., anionic detergents, nonionic detergents, and mixtures thereof. In many instances they display an enhanced tarnish-inhibiting action in the presence of both polyphosphate and detergent.

The polyphosphate-built detergent compositions should contain conventional proportions of active detergent, usually within the range between 5 and 40%, polyphosphate in any amount, usually between 5 and 50%, based on the total composition, and the residue builders and inert materials.

The hydroxamic compounds are not compatible with cationic detergents and display very poor tarnish inhibiting action in their presence.

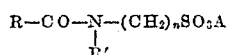
The hydroxamic compounds are useful with a wide variety of anionic and nonionic synthetic detergents, with and without polyphosphates.

The alkyl aryl sulfonates are a class of detergents well known in the art under this name. One example thereof are the sulfonated phenylpolypropylene 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 $\text{C}_n\text{H}_{2n+1}$, and at least one R is a polypropylene group, the whole alkyl group containing preferably twelve to fifteen 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 "Neolene."

Another class of useful detergents are the amidoalkane sulfonates 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 one to about five, preferably two or three, 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 palmitic-stearic methyl tauride and sodium palmitic methyl amidopropane sulfonate have been found to be particularly suitable for use in the compositions of the invention.

These compounds are prepared by interacting the corresponding aliphatic acid anhydride or halide with an organic aliphatic aminosulfonic acid, such as taurine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, and the various N -substituted taurines, such as N -methyl taurine, or aminopropane sulfonic acid, $\text{NH}_2(\text{CH}_2)_3\text{SO}_3\text{H}$.

The invention is also applicable to other water-soluble alkyl aromatic sulfonic acids, 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 ten to eighteen carbon atoms, particularly those derived by the reduction of coconut oil, palm oil and 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 1,2-dihydroxy propane-3-sulfonic acid and sulfuric acid esters of monoglycerides and glycerol monoethers. The salts of these acids are ordinarily employed.

The tarnish inhibitors are also useful with nonionic detergents, such as, for example, alkyl oxyether and ester and thioether and ester detergents having the following general formula:

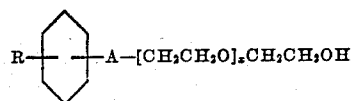


where R is a straight or branched chain saturated or unsaturated hydrocarbon group having from eight to eighteen carbon atoms or an aralkyl group having a straight or branched saturated or unsaturated hydrocarbon group of from eight to eighteen carbon atoms attached to the aryl nucleus, and attached 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 eight to twenty. R can for example be a straight or branched chain octyl, nonyl, decyl, lauryl, myristyl, cetyl or stearyl group, or an alkyl aryl group such as octyl benzene, nonylbenzene, decylbenzene, stearyl benzene, etc.

When 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 or oleyl or dodecyl alcohol or mercaptan with from eight to seventeen moles of ethylene oxide, such as Emulfor ON, Nonic 218 and Sterox SE and SK. Typical alkyl esters are G1226 and Renex (polyoxyethylene ester of tall oil acids), Sterox CD and Neutronyx 330 and 331 (higher fatty acid esters of polyethylene glycol).

When 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 saturated or unsaturated hydrocarbon group having at least eight carbon atoms up to approximately eighteen carbon atoms, A is oxygen or sulfur and x is a number from eight to twenty. 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 eight to seventeen moles of ethylene oxide, available commercially under the trade names NI 8586, Antarox A-400, Igepal CA and CO, Triton X-100, Neutronyx 600 and Tergitol NFX.

The detergent composition can contain supplemental

builders including alkali metal and alkaline earth metal sulfates, chlorides, silicates, borates, carbonates, metaphosphates, and orthophosphates, such as sodium silicate, magnesium sulfate, sodium tetraborate, sodium carbonate, sodium sulfate, trisodium phosphate, potassium carbonate, disodium orthophosphate, sodium metaphosphate, calcium sulfate, calcium chloride, sodium chloride, sodium borate and potassium metaphosphate. The builder should but need not be water-soluble.

In addition to or instead of the above-mentioned supplemental inorganic salts, organic materials such as starch, polyethylene glycols, polyvinyl alcohols and salts of carboxymethylcellulose can be used as builders. It has been found that between about 0.1 and 1% of an alkali metal carboxymethylcellulose increases detergency and sudsing.

The builder mixture is so chosen among alkaline, neutral and acidic salts that the composition obtained in an aqueous 0.14% solution has a pH of 7 or above. Preferably, its pH lies within the range from 7 to about 10 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 composition is prepared by conventional methods, as by blending the ingredients thereof in an aqueous solution or slurry and then drying the resulting mixture in a spray or drum dryer at elevated temperatures.

The tarnish inhibitor may be added to the polyphosphate or detergent composition at any stage of its manufacture, to the finished polyphosphate or detergent composition, or to the polyphosphate or detergent solution.

In the examples the tarnishing action of the compositions was evaluated by this test:

Five grams (dry solids basis) of the composition to be tested is dissolved in one quart of distilled water and 300 ml. of the test solution placed in a suitable container and brought to 160° F. A strip of German silver metal is polished with a metal polish, washed and dried, placed in the solution and the solution held at 160 to 170° F. for one half hour. The effectiveness of the inhibitor is rated as follows:

Excellent (1)=Perfect protection except for slight interface stain
Excellent (2)=Barely noticeable cast, uniform or spotted
Good=Very slight attack
Fair=Considerable attack
Poor=Badly tarnished

EXAMPLES 1 TO 6

Detergent compositions were prepared having the following formulation:

	Percent
Sodium Oronite (active) (sodium phenylpolypropylene sulfonate).....	18.0
Tetrasodium pyrophosphate.....	30.0
Sodium tripolyphosphate.....	15.0
Sodium carboxymethylcellulose.....	0.5
Sodium silicate.....	6.0
Sodium carbonate.....	3.0
Sodium sulfate and misc.....	20.5
Water	7.0
	100.0
Hydroxamic compound.....	0.067 to 0.53% based on the weight of the polyphosphates.

To solutions of these compositions for testing for tarnish inhibition were added the hydroxamic compounds listed in the amount indicated.

Table I¹

Ex-ample No.	Inhibitor	Grading at Concentration of Agent				
		None	0.067	0.133	0.27	0.53
1.....	Caprylyl hydroxamic acid.	Tarn(2)	Poor..	Poor..	Poor..	Fair.
2.....	Capryl hydroxamic acid.	Tarn(2)	Poor..	Good..	Exc...	Exc.
3.....	Potassium lauryl hydroxamate.	Tarn(2)	Fair...	Good..	Exc...	Exc.
4.....	Potassium myristyl hydroxamate.	Tarn(2)	Poor..	Fair...	Exc.	Exc.
5.....	Potassium palmityl hydroxamate.	Tarn(2)	Poor..	Poor..	Good..	Exc.
6.....	Potassium stearyl hydroxamate.	Tarn(2)	Poor..	Poor..	Fair...	Exc.

¹ Exc.=excellent; Tarn(2)=severe tarnish.

The caprylyl hydroxamic acid having a seven carbon alkyl radical and the potassium stearyl hydroxamate having a seventeen carbon atom alkyl group display the poorest tarnishing inhibiting properties, but even these give fair to excellent protection at the higher inhibitor concentrations. The potassium lauryl hydroxamate, having an eleven carbon alkyl group, gives the best results. These results show the effect of the chain length of the alkyl group on the potency of the tarnishing inhibiting properties of the hydroxamic compound.

The results show that when the compound has poor tarnishing inhibiting properties at a low concentration good tarnish inhibition can be obtained by increasing the amount of hydroxamic compound.

EXAMPLE 7

A test was conducted to determine whether cotton cloth washed with detergent compositions of the invention using water containing 50 p. p. m. ferric iron would become discolored due to formation of the red colored ferric salt-hydroxamate complex. A solution was prepared having a 0.14% concentration of the composition of Example 3, and the cloth stirred in the solution for twenty minutes at 140° F. The cloth was identical in appearance after drying and pressing with a similar cloth washed in a similar solution without the hydroxamate. In another test, simulated rust spots were applied to a cotton cloth which was then washed as described above except that no iron was added to the water. Although the iron spots were still evident after the washing, the hydroxamate had not changed their color.

EXAMPLES 8 TO 14

Solutions of the detergent composition of Examples 1 to 6 were prepared containing 5 g./qt. of the composition and 0.27% and 0.53% respectively, of the following tarnish inhibitors of the invention. The solutions were tested with the results listed in the table:

Table II

Example No.	Inhibitor	Grading	
		0.27%	0.53%
8.....	Magnesium dodecanohydroxamate.	Excellent..	
9.....	Ammonium dodecanohydroxamate.	Fair.....	Excellent.
10.....	Calcium dodecanohydroxamate.	Excellent..	
11.....	Barium dodecanohydroxamate.	do.....	
12.....	Ferric dodecanohydroxamate.	Fair.....	Excellent.
13.....	Copper dodecanohydroxamate.	Poor.....	Good.
14.....	Silver dodecanohydroxamate.	do.....	Excellent.

Those rated as excellent at a 0.27% concentration were not tested at the 0.53% level. Those inhibitors which were poor or fair at the 0.27% concentration were good or excellent at a 0.53% concentration.

EXAMPLES 15 TO 21

Detergent solutions were prepared of compositions having the formulations listed in the table. The solution concentrations were equivalent to 5 g. of the dry composition per quart of water. The inhibitor used in each case was potassium dodecanohydroxamate (0.27%).

the solutions then subjected to the tarnish inhibitor test. The composition of the solutions was as follows:

	G./qt. of solution
Detergent	0.90
Sodium tripolyphosphate	2.25
Potassium dodecanohydroxamate	0.006

Table III¹

	Percent Composition of Example No. —						
	15	16	17	18	19	20	21
Sodium phenylpolypropylene sulfonate	8.....	40.....	18.....	40.....	18.....	40.....	18.....
Sodium lauryl sulfate ²	45.....	45.....	45.....	50.....	50.....	50.....	5.....
Grading:							
without inhibitor	T(2)...	T(2)...	T(2)...	T(2)...	T(2)...	(T2)...	Slight tarn. Exc.
with inhibitor	Exc...	Good...	Exc...	Fair...	Exc...	Exc...	Exc.

¹ T(2)=severe tarnish; Exc.=excellent.

² Commercial grade, principally sodium lauryl sulfate with small proportion of other higher fatty alcohol sulfates (sodium salt).

These results show that the inhibitor is effective at 8%, 18%, and 40% concentrations of the detergent and at 5%, 45% and 50% concentrations of the tripolyphosphate.

EXAMPLES 22 TO 25

Four solutions of each of the detergents listed in the following table were prepared at a detergent concentration of 0.09%. Two solution pairs of each were brought to a pH of 6 and 9.5, respectively, potassium dodecanohydroxamate (0.67% by weight of the detergent) as the tarnish inhibitor added to one solution of each pair, and all of the solutions subjected to the tarnish inhibitor test.

Table IV

Example No.	Surfactant	Degree of Tarnish	
		pH 6	pH 9.5
22.....	Sodium phenylpolypropylene sulfonate: without inhibitor.....	slight.....	barely noticeable. trace.
	with inhibitor.....	very slight.....	Do.
23.....	Sodium lauryl sulfate: ¹ without inhibitor.....	moderate.....	substantially none. Do.
	with inhibitor.....	slight.....	Do.
24.....	Sodium palmitic methyl-tauride: without inhibitor.....	severe.....	slight. substantially none.
	with inhibitor.....	moderate.....	Do.
25.....	Nonylphenol ether of polyethylene glycol: ² without inhibitor.....	very slight.....	barely noticeable. Do.
	with inhibitor.....	substantially none.	Do.

¹ Commercial grade, principally sodium lauryl sulfate with small proportion of other higher fatty alcohol sulfates (sodium salt).

² Average 9.5 moles of ethylene oxide.

It is evident from the above data that at pH 6 the detergent solutions tested tarnish German silver. This tarnish is not as evident at pH 9.5. In the presence of the inhibitor the tarnishing effect is greatly diminished.

EXAMPLES 26 TO 35

Detergent solutions were prepared, dissolving the detergent (listed in the table below) polyphosphate and inhibitor separately to make up a concentration equivalent to 5 g. of the complete formula per quart of water, and

The following detergents were employed:

Table V

Example No.	Detergent	Grading
26.....	Magnesium phenylpolypropylene sulfonate.....	Excellent.
27.....	Sodium phenylpolypropylene sulfonate.....	Do.
28.....	Sodium octadecyl sulfonate.....	Fair.
29.....	Sodium lauryl sulfate.....	Excellent.
30.....	Sodium salt of the palmitamide of N-methyl taurine.	Do.
31.....	Tallow fatty acid ester of isethionic acid.....	Do.
32.....	Sodium salt of the lauric ether of 1,2 dihydroxy propane-3-sulfonic acid.	Do.
33.....	Nonyl phenol ether of polyethylene glycol ¹	Do.
34.....	Octyl phenol ether of polyethylene glycol ²	Do.
35.....	Polyethylene glycol ester of tall oil fatty acids ³	Do.

¹ Average 9.5 moles of ethylene oxide.

² Eight to ten moles ethylene oxide.

³ Average ten moles ethylene oxide.

EXAMPLES 36 TO 43

To 0.9 g. (18%) of sodium phenylpolypropylene sulfonate and 2.25 g. (45%) of sodium tripolyphosphate was added 1 g. (20%) (anhydrous basis) of a builder selected from the group listed in the following table.

The mixtures were dissolved in one quarter of distilled water and to the solutions were added 0.27% of potassium dodecanohydroxamate. The tarnish properties were evaluated according to the test and the solutions graded for tarnish protection.

Table VI

Example No.	Builder	Grading
36.....	Disodium orthophosphate.....	Excellent.
37.....	Sodium tetraborate.....	Do.
38.....	Calcium chloride.....	Do.
39.....	Calcium sulfate.....	Do.
40.....	Potassium carbonate.....	Do.
41.....	Sodium chloride.....	Do.
42.....	Polyethylene glycol 600.....	Do.
43.....	Starch.....	Do.

It is evident from this data that the builders tested do not affect the tarnish inhibiting properties of the hydroxamate.

EXAMPLE 44

A detergent composition was prepared having the following formulation:

	Percent
Sodium phenylpolypropylene sulfonate	18.0
Tetrasodium pyrophosphate	30.0
Sodium tripolyphosphate	15.0
Sodium carboxymethylcellulose	0.5
Sodium silicate	6.0
Sodium carbonate	3.0
Sodium sulfate and misc.	20.5
Water	7.0
	100.0

The components listed in the table were slurried in sufficient water to provide 40% in the slurry and potassium dodecanohydroxamate (0.27%) added to the slurry. The mixture was agitated at 165° F. to obtain a smooth slurry and then spray dried. The moisture content of the product was 5.4%. This composition was evaluated for tarnishing action by the test and rated Excellent (1).

EXAMPLES 45 TO 49

Solutions were prepared containing 2.25 g. (in one quart of water) of one of the polyphosphates listed in the following table, with and without 0.27% of potassium dodecanohydroxamate and with and without 0.90 g. sodium phenylpolypropylene sulfonate. The pH values of the solutions in each case were adjusted to within the range from 9.5 to 10.0 before testing. During the test, the pH of the trimetaphosphate solution dropped to about 7.5.

Table VII¹

Example No.	Polyphosphate	Grading			
		With polyphosphate, Without sulfonate		With sulfonate and polyphosphate	
		Without Inhibitor	With Inhibitor	Without Inhibitor	With Inhibitor
45	(NaPO ₃) ₃	Tarn(1)	Exc.(1)	Tarn(2)	Exc.(1)
46	Calgon (NaPO ₃) ₃	Tarn(2)	Exc.(1)	Tarn(2)	Exc.(1)
47	Quadrafos (Na ₅ P ₄ O ₁₃)	Tarn(2)	Exc.(1)	Tarn(2)	Exc.(1)
48	Na ₅ P ₄ O ₁₃	Tarn(2)	Fair	Tarn(2)	Exc.(1)
49	Na ₃ P ₃ O ₇	Tarn(2)	Good	Tarn(2)	Exc.(1)

¹ Exc.=excellent; Tarn(1)=moderate tarnish; Tarn(2)=severe tarnish.

In the presence of both detergent and polyphosphate, protection from tarnish by the inhibitor was excellent in all cases, and protection was excellent to fair in the presence of polyphosphate alone.

Compositions containing tarnish inhibitors of the invention do not tarnish copper, nickel-copper-zinc alloys such as German silver, coinage nickel or brass, which normally tarnish when exposed to aqueous solutions containing polyphosphates and/or synthetic detergents. It is not possible at this time to explain why the compounds of the invention are effective tarnish inhibitors. However it has been observed that when a German silver utensil is immersed for a period in an inhibitor- and polyphosphate-containing detergent solution, and then immersed in a polyphosphate-containing detergent solution not containing inhibitor, only slight tarnishing results. This is taken as an indication that the inhibitor is preferentially adsorbed by the metal, and that this is important in tarnish prevention, but of course such evidence is not conclusive.

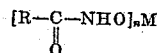
Obviously, many modifications and variations may be made in the invention herein set forth without departing from the spirit and scope thereof, and only such limitations should be imposed as are indicated in the appended claims.

All parts and percentages in the specification and claims are by weight. Proportions of hydroxamic compound are based on the weight of the tarnish-producing substance, i. e., polyphosphate and/or detergent. In the

examples, when both polyphosphate and detergent were present, the weights of hydroxamic compound were based on the polyphosphate since this amount was adequate, due to the enhanced effectiveness of the inhibitor compound in the presence of both polyphosphate and detergent, but when no polyphosphate was present the amount was based on the weight of detergent.

I claim:

1. A cleaning composition comprising a water-soluble polyphosphate which in aqueous solution tarnishes copper and copper and nickel alloys and a tarnish inhibitor in an amount to lessen the tarnishing action of the polyphosphate and having the general formula:



where M is selected from the group consisting of hydrogen and a metal, R is an aliphatic hydrocarbon radical having from seven to seventeen carbon atoms, and n is the valence of M.

2. A composition in accordance with claim 1 in which the tarnishing inhibitor is capryl hydroxamic acid.

3. A composition in accordance with claim 1 in which the tarnish inhibitor is potassium dodecanohydroxamate.

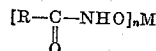
4. A composition in accordance with claim 1 in which the tarnish inhibitor is potassium myristyl hydroxamate.

5. A composition in accordance with claim 1 in which the tarnish inhibitor is potassium palmityl hydroxamate.

6. A composition in accordance with claim 1 in which the tarnish inhibitor is magnesium dodecanohydroxamate.

7. A non-soap detergent composition comprising an active detergent selected from the group consisting of

anionic and nonionic detergents which in aqueous solution tarnishes copper and copper and nickel alloys and a tarnish inhibitor in an amount to lessen the tarnishing action of the detergent and having the general formula:



where M is selected from the group consisting of hydrogen and a metal, R is an aliphatic hydrocarbon radical having from seven to seventeen carbon atoms, and n is the valence of M.

8. A composition in accordance with claim 7 in which the tarnishing inhibitor is capryl hydroxamic acid.

9. A composition in accordance with claim 7 in which the tarnish inhibitor is potassium dodecanohydroxamate.

10. A composition in accordance with claim 7 in which the tarnish inhibitor is potassium myristyl hydroxamate.

11. A composition in accordance with claim 7 in which the tarnish inhibitor is potassium palmityl hydroxamate.

12. A composition in accordance with claim 7 in which the tarnish inhibitor is magnesium dodecanohydroxamate.

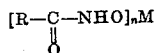
13. A detergent composition in accordance with claim 7 in which the detergent is magnesium phenylpolypropylene sulfonate.

14. A detergent composition in accordance with claim 7 in which the detergent is sodium phenylpolypropylene sulfonate.

15. A non-soap detergent composition comprising an

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active detergent selected from the group consisting of anionic and nonionic detergents, a water-soluble polyphosphate which in aqueous solution tarnishes copper and copper and nickel alloys and a tarnish inhibitor in an amount to lessen the tarnishing action of the polyphosphate and having the general formula:



where M is selected from the group consisting of hydrogen and a metal, R is an aliphatic hydrocarbon radical having from seven to seventeen carbon atoms, and n is the valence of M.

16. A composition in accordance with claim 15 in which the tarnishing inhibitor is potassium dodecanohydroxamate.

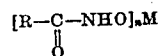
17. A composition in accordance with claim 15 in which the tarnish inhibitor is potassium myristyl hydroxamate.

18. A composition in accordance with claim 7 in which the tarnish inhibitor is potassium palmityl hydroxamate.

19. A composition in accordance with claim 15 in which the tarnish inhibitor is magnesium dodecanohydroxamate.

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20. A cleaning composition comprising a water-soluble substance selected from the group consisting of polyphosphates and synthetic detergents selected from the group consisting of anionic and nonionic detergents which in aqueous solution tarnish copper and copper and nickel alloys and a tarnish inhibitor in an amount to lessen the tarnishing action of the substance and having the general formula:



where M is selected from the group consisting of hydrogen and a metal, R is an aliphatic hydrocarbon radical having from seven to seventeen carbon atoms, and n is the valence of M.

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