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NONTARNISHING DETERGENT COMPOSITIONS CONTAINING FERRIC SALTS

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This invention relates to detergent compositions containing tarnish inhibitors and more particularly to polyphosphate compositions containing ferric salts as 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 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 inhibit the formation of tarnish upon German silver. The tarnish inhibitors of the invention are water-soluble ferric salts, for example, ferric chloride and ferric sulfate.

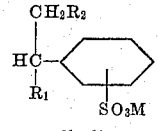
An amount of the water-soluble ferric salt is added to the polyphosphate composition to give tarnish inhibition when the composition is used in its normal way. It will be understood that the amount required will depend in part upon the tarnish inhibiting properties of the particular ferric salt in question, upon the tendency of the polyphosphate composition with which it is used to tarnish German silver and upon the amount of polyphosphate present. In general, therefore, at least about 1% of the water-soluble ferric salt based on the weight of the polyphosphate present in the detergent composition will inhibit the formation of tarnish by the composition. The maximum amount of the ferric 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 solution would not be used. In most cases, the maximum suggested would be about 15% by weight based on the weight of polyphosphate.

The polyphosphate detergent compositions must also contain an alkali metal silicate, for example, sodium or potassium silicate. From about 4% to about 27% by weight of an alkali metal silicate has been found to be satisfactory in the polyphosphate detergent compositions. The water-soluble ferric salts have been found to be effective as tarnish inhibitors in polyphosphate detergent compositions only when the compositions contain an alkali metal silicate, although an alkali metal silicate alone in the above amounts without the presence of a water-soluble ferric salt is ineffective in inhibiting the formation of tarnish by the polyphosphate detergent compositions.

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., usually within the range of about pH 7 to about pH 11, and preferably within the range of about pH 8 to about pH 9. The alkali metal polyphosphates include, by way of example, tetrasodium and tetrapotassium pyrophosphates, sodium and potassium hexametaphosphates, and hexasodium and hexapotassium tetrapolyphosphates. It was found that the tarnish inhibitors were ineffective against polyphosphate detergent compositions wherein the polyphosphate content was furnished by an alkali metal tripolyphosphate such as pentasodium tripolyphosphate. 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 nonsoap detergents and builders which might be included in the detergent compositions.

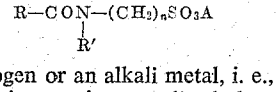
Examples of such additional optional components are organic nonsoap detergents which may be either anionic, cationic, or nonionic detergents, and builders, water, and inert materials. These detergent compositions may contain alkali metal polyphosphate in an amount between 30% to 50% if the compositions are in solid or liquid form and from 20% to 50% if the compositions are in liquid form; conventional proportions of organic nonsoap detergent, usually within the range between 5% to 40%; from about 4% to about 27% of an alkali metal silicate; and at least about 1% of a water-soluble ferric salt based on the weight of the polyphosphate; 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 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, 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 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 nonsoap 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 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, $NH_2CH_2CH_2SO_3H$, 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 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 2,3-dihydroxypropane 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 containing polyphosphates, such as 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 eight to eighteen carbon atoms or an aralkyl group having a straight or branched chain 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 alkylaryl group such as octylbenzene, nonylbenzene, decylbenzene, stearylbenzene, etc.

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

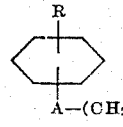
$$R—A—(CH_2CH_2O)_x—CH_2CH_2OSO_3M$$

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

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 of 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 chain 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 "NIW," "Antarox A–400," "Igepal CA" and "CO," Triton X–100," "Neutronyx 600" and "Tergitol NFX."

The optional supplemental builders may be alkali metal inorganic salts, typical examples of which include sodium and potassium sulfates, sodium and potassium chlorides 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 and acidic salts that the composition obtained in an aqueous 0.14% washing solution has a pH of about 7 to 11. Preferably, its pH lies within the range of about 8 to about 9. 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 of the invention inhibit the formation of tarnish upon German silver in either hard or soft water. It will be appreciated that the detergent composition may exist in any solid form such as drum dried or spray dried detergent compositions or may be in liquid form.

The polyphosphate-detergent compositions may be 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 composition in any stage of its manufacture, to the finished polyphosphate composition, or to the polyphosphate solutions.

The compositions of the invention will be further illustrated by the following examples wherein a typical water-soluble ferric salt, namely, ferric chloride, was employed in the compositions. In these examples the following test procedure was employed. A specified amount of the detergent composition was dissolved in somewhat less than one quart of water at a temperature under 170° F., and the ferric salt then added thereto in the form of a solution. More water was then added thereto to give a total volume of one quart. 300 mil. of the solution were placed in a beaker, and the temperature adjusted to 160–170° F. A strip of German silver metal, 6 inches by 1 inch, which had been cleaned with a metal polish and rinsed and dried, was partially immersed in the solution and allowed to remain for ½ hour at 160–170° F. The metal strip was then removed, rinced and dried with a cloth. The strip was visually examined for tarnish and the effectiveness of the tarnish inhibitor rated 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.

The polyphosphate detergent compositions set forth below in Table I were tested in many of the examples:

TABLE I

Compositions	A	B	C	D	E
Sodium Dodecylbenzene Sulfonate	18.0			18.0	18.0
Emulsept		18.0			
Pluronic L–64			18.0		
Tetrasodium Pyrophosphate	45.0	45.0	45.0		
Sodium Hexametaphosphate				45.0	
Hexasodium Tetrapolyphosphate					45.0
Sodium Carbonate	3.0	3.0	3.0	3.0	3.0
Sodium Silicate Solids (ratio of SiO_2:Na_2O is 2.4)	6.0	6.0	6.0	6.0	6.0
Sodium Carboxymethylcellulose	0.5	0.5	0.5	0.5	0.5
Water	10.0	7.0	7.0	7.0	7.0
Sodium Sulfate and Miscellaneous	17.5	20.5	20.5	20.5	20.5
	100.0	100.0	100.0	100.0	100.0

In Table I the components of the composition are expressed in percent by weight on the total composition. Sodium dodecylbenzene sulfonate is an anionic nonsoap detergent. Emulsept is a cationic nonsoap detergent

which is the lauric ester of N-(beta-hydroxy-ethyl)-alpha-(chloropyridinium) acetamide. Pluronic L-64 is a nonionic nonsoap detergent, and 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.

Examples 1–2 below show that a water-soluble ferric salt is ineffective as a tarnish inhibitor against an alkali metal polyphosphate alone, although a water-soluble ferric salt is effective as a tarnish inhibitor against an alkali metal polyphosphate when used in the presence of an alkali metal silicate.

Examples 1–2

2.25 grams of tetrasodium pyrophosphate were dissolved in distilled water and the volume diluted to one quart in accordance with the test procedure. 6.67% of ferric chloride based on the weight of pyrophosphate was added thereto and the pH adjusted to pH 9. This composition tarnished German silver to grade 6. 2.25 grams of tetrasodium pyrophosphate and 0.30 gram of sodium silicate (i. e., 12% by weight) were dissolved in distilled water and the volume diluted to one quart in accordance with the above test procedure. 6.67% of ferric chloride based on the weight of pyrophosphate was added thereto, and finally the pH of the solution was adjusted to pH 9. This composition tarnished German silver metal only to grade 3.

The addition of a water-soluble ferric salt to polyphosphate compositions containing an organic anionic nonsoap detergent, an alkali metal pyrophosphate, and an alkali metal silicate, and supplemental builders inhibits the formation of tarnish by such detergent compositions. This is clearly illustrated by Examples 3–8 set forth below wherein Composition A was employed. The tests were run at pH 9. It will be noted from these examples that at least about 1% of a water-soluble ferric salt based on the weight of polyphosphate in conjunction with about 6% of an alkali metal silicate inhibits the formation of tarnish upon German silver metal by such compositions.

Examples 3–8

To 5 grams of Composition A there was added ferric chloride in the proportions shown below and the test procedure carried out with the following results.

Percent Ferric Chloride, (polyphosphate basis)	0	0.67	1.11	2.2	4.4	6.67
Tarnish Grading	6	5	3	2	2	2

A water-soluble ferric salt is also effective as a tarnish inhibitor in polyphosphate detergent compositions containing either a hexametaphosphate or a tetrapolyphosphate, an organic nonsoap detergent, an alkali metal silicate, and supplemental builders. This is clearly illustrated by Examples 9–12 below which were conducted at a pH of 8.

Examples 9–12

5 grams of Composition D, i. e., the composition containing sodium hexametaphosphate, when dissolved in a quart of water and tested in accordance with the test procedure tarnished German silver to grade 6. When 6.67% of ferric chloride based on the weight of hexametaphosphate was added to the composition, German silver was tarnished only to grade 3. When 5 grams of Composition E, i. e., the composition containing hexasodium tetrapolyphosphate, was dissolved in a quart of water and tested in accordance with the test procedure, the composition tarnished German silver to grade 6. 6.67% of ferric chloride based on the weight of tetrapolyphosphate added to Composition E produced a reduced tarnish grade of 2 upon a strip of German silver metal.

The effectiveness of a water-soluble ferric salt used in conjunction with an alkali metal silicate in inhibiting the formation of tarnish upon German silver metal by a polyphosphate detergent composition containing either an organic nonionic nonsoap detergent or an organic cationic nonsoap detergent is clearly illustrated by Examples 13–16 below.

Examples 13–16

5 grams of Composition B, a composition containing an organic cationic nonsoap detergent, when dissolved in one quart of distilled water and tested in accordance with the test procedure tarnished the German silver metal strip to a tarnish grading of 6 at pH 8. When 6.67% of ferric chloride based on the weight of polyphosphate was added thereto, a strip of German silver metal tested in accordance with the test procedure had a reduced tarnish grading of 3 at pH 8. 5 grams of Composition C, a composition containing an organic nonionic nonsoap detergent, when dissolved in a quart of water and tested in accordance with the test procedure, produced a tarnish grading on a strip of German silver metal at pH 9 of 6. When 6.67% of ferric chloride based on the weight of polyphosphate was added to Composition C, a strip of German silver metal tested at pH 9 had a reduced tarnish grading of 2.

Examples 9, 11, 13 and 15 clearly show that an alkali metal silicate alone without the presence of a water-soluble ferric salt is ineffective in inhibiting the formation of tarnish on a strip of German silver metal by a polyphosphate detergent composition. From Example 1 it can be readily seen that a water-soluble ferric salt when used alone without the presence of an alkali metal silicate is ineffective in inhibiting the formation of tarnish by an alkali metal polyphosphate. Examples 2, 4–8, 10, 12, 14 and 16, on the other hand, clearly show that from about 1% to about 15% of a water-soluble ferric salt based on the weight of polyphosphate in conjunction with from about 4% to about 27% of an alkali metal silicate is effective in inhibiting the formation of tarnish upon German silver metal by a polyphosphate detergent composition.

The water-soluble ferric salts are effective as tarnish inhibitors when incorporated in a polyphosphate detergent slurry containing an alkali metal silicate and the slurry drum dried as shown by the following example.

Example 17

The composition shown below was prepared in the form of an aqueous slurry and drum dried. 5 grams of the drum dried product per quart of distilled water tarnished German silver at pH 9 only of grade 3.

Composition	Percent by Weight
Sodium Dodecylbenzene Sulfonate	18.0
Tetrasodium Pyrophosphate	45.0
Sodium Carbonate	3.0
Sodium Silicate	6.0
Sodium Carboxymethylcellulose	0.5
Ferric Chloride [1]	3.0
Water	7.0
Sodium Sulfate and Miscellaneous	17.5
Total	100.0

[1] Percent ferric chloride based on polyphosphate=6.67%.

Examples 18–19 illustrate the fact that the water-soluble ferric salts are effective as tarnish inhibitors in polyphosphate compositions containing an alkali metal silicate 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 18–19

5 grams of Composition A dissolved in a quart of water having a hardness of 180 p. p. m. and a pH of 8 tarnished German silver metal to grade 6, whereas 5 grams of Composition A containing 6.67% of ferric chloride based on the weight of polyphosphate dissolved in a quart of water having a hardness of 180 p. p. m. and a pH of 8 tarnished German silver only to grade 1.

The effectiveness of water-soluble ferric salts as tarnish inhibitors with liquid polyphosphate detergent compositions containing an alkali metal silicate is clearly illustrated by Examples 20–25.

Examples 20–25

Six 5 gram portions of the following liquid detergent composition were dissolved separately in one quart of distilled water and ferric chloride added thereto at the concentrations indicated below. The tarnish grading of a strip of German silver metal inserted in each of the solutions at pH 11 is also set forth.

Composition	Percent by Weight
Potassium Dodecylbenzene Sulfonate	10.0
Sodium Xylene Sulfonate (95%)	7.6
Lauric Isopropanolamide	3.2
Lauric Diethanolamide	3.8
Tetrapotassium Pyrophosphate	20.0
Sodium Silicate (37.5% solids) (ratio of SiO_2:Na_2O is 2.5)	7.0
Water	48.4
Total	100.0

Example No.	20	21	22	23	24	25
Percent Ferric Chloride (polyphosphate basis)	0	1.5	2.5	5.0	10.0	15.0
Tarnish Grade	6	3	2	2	2	3

From a study of all of the above examples it can be readily seen that from about 1% to about 15% of a water-soluble ferric salt based on the weight of polyphosphate inhibits the formation of tarnish by polyphosphate detergent compositions containing from about 4% to about 27% of an alkali metal silicate and optionally containing organic nonsoap detergents and supplemental builders.

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.

We claim:

1. A polyphosphate detergent composition consisting essentially of a water-soluble alkali metal polyphosphate selected from the group consisting of tetrasodium and tetrapotassium pyrophosphates, sodium and potassium hexametaphosphates, and hexasodium and hexapotassium tetrapolyphosphates which in aqueous solution tarnishes German silver; from about 1% to about 15% of a water-soluble ferric salt based on the weight of polyphosphate and from about 4% to about 27% of an alkali metal silicate having a SiO_2:M_2O ratio of about 2.5 where M is an alkali metal; the amounts of said ferric salt and silicate being sufficient to inhibit such tarnishing.

2. A polyphosphate detergent composition as set forth in claim 1 wherein the water-soluble ferric salt is ferric chloride.

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

4. A polyphosphate detergent composition consisting essentially of from about 30% to about 50% of a water-soluble alkali metal polyphosphate selected from the group consisting of tetrasodium and tetrapotassium pyrophosphates, sodium and potassium hexametaphosphates, and hexasodium and hexapotassium tetrapolyphosphates which in aqueous solution tarnishes German silver; from about 5% to about 40% of an organic nonsoap detergent; from about 1% to about 15% of a water-soluble ferric salt based on the weight of polyphosphate and from about 4% to about 27% of an alkali metal silicate having a SiO_2:M_2O ratio of about 2.5 where M is an alkali metal; the amounts of said ferric salt and silicate being sufficient to inhibit such tarnishing.

5. A polyphosphate detergent composition as set forth in claim 4 wherein the water-soluble ferric salt is ferric chloride.

6. A polyphosphate detergent composition as set forth in claim 4 wherein the alkali metal silicate is sodium silicate.

7. A polyphosphate detergent composition as set forth in claim 4 wherein the organic nonsoap detergent is an organic nonionic nonsoap detergent.

8. A polyphosphate detergent composition as set forth in claim 4 wherein the organic nonsoap detergent is an organic anionic nonsoap detergent.

9. A polyphosphate detergent composition as set forth in claim 4 wherein the organic nonsoap detergent is an organic cationic nonsoap detergent.

10. A liquid polyphosphate detergent composition consisting essentially of an aqueous solution of from about 20% to about 50% of an alkali metal polyphosphate selected from the group consisting of tetrasodium and tetrapotassium pyrophosphates, sodium and potassium hexametaphosphates, and hexasodium and hexapotassium tetrapolyphosphates which in aqueous solution tarnishes German silver; from about 5% to about 40% of an organic nonsoap detergent; from about 1% to about 15% of a water-soluble ferric salt based on the weight of polyphosphate and from about 4% to about 27% of an alkali metal silicate having a SiO_2:M_2O ratio of about 2.5 where M is an alkali metal; the amounts of said ferric salt and silicate being sufficient to inhibit such tarnishing.

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