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2,829,105

NONTARNISHING DETERGENT COMPOSITIONS CONTAINING WATER-SOLUBLE INORGANIC COLUMBATES

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This invention relates to detergent compositions containing tarnish inhibitors and more particularly to polyphosphate compositions containing water-soluble inorganic columbates 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 alloy 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 inorganic columbates, for example, sodium columbate and potassium columbate.

An amount of the water-soluble inorganic columbate 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 columbate in question, upon the tendency of the polyphosphate with which it is used to tarnish German silver, and upon the amount of polyphosphate present. In general, therefore, at least about 0.6%, and preferably at least about 2%, of the water-soluble inorganic columbate 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 columbate 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 15% based on the weight of polyphosphate.

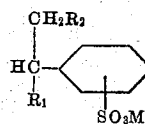
The tarnish inhibitors of the present invention are effective with water-soluble alkali metal polyphosphates at pH values where such polyphosphates tend to tarnish German silver, i. e., usually within the range of about pH 8 to about pH 11. The alkali metal polyphosphates may include, by way of example, pentasodium and pentapotassium triphosphates, 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 nonsoap detergents and builders which might be included in the detergent compositions.

Examples of such additional optional components are

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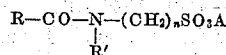
organic nonsoap detergents which may be either anionic, cationic, or nonionic detergents and builders, water, and inert materials. These detergent compositions may include alkali metal polyphosphate in any amount, usually between 15% and 50%; conventional proportions of nonsoap detergent, usually within the range between 5% and 40%; from about 0.6%, and preferably from about 2%, to about 15% of a water-soluble inorganic columbate 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 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 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 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:

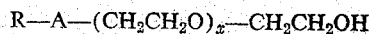


where A is hydrogen or alkali metal, i. e., ammonium, sodium, or potassium, n is a small whole number from one to about five, preferably two or three, R' is hydrogen or an alkyl, aryl, or cycloaliphatic group, such as methyl, and R is an alkyl or alkylene radical, such as myristyl, palmityl, oleyl, and 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, NH₂CH₂CH₂SO₃H, and the various N-substituted taurines, such as N-methyl taurine, or aminopropane sulfonic acid, NH₂(CH₂)₃SO₃H.

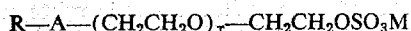
Other water-soluble alkyl aromatic sulfonic acids may constitute optional components such as those prepared by alkylating benzene or naphthalene with a kerosene fraction followed by sulfonation to aliphatic sulfonic acids, esters of sulfuric acid with aliphatic alcohols of ten to eighteen carbon atoms, 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, 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 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 thio-carboxylic 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:

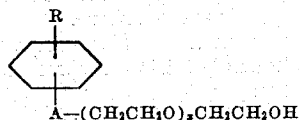


where M is hydrogen or an alkali metal or organic amine cation and x, A and R are as above.

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 8 to 17 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).

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 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 8 to 17 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, 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 may 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 8 or above. Preferably its pH lies in the range of about 8 to about 11, since solutions which are more alkaline may be irritating to the skin and tend to weaken some fabrics, particularly woolsens.

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 compositions may exist in any dry 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 in-

redients thereof in an aqueous solution or slurry and then drying the resulting mixture in a spray or drum dryer at elevated temperatures.

The tarnish inhibitors may be added to the polyphosphate composition in any stage of its manufacture, to the finished polyphosphate composition, or to the polyphosphate solution.

The compositions of the invention will be further illustrated by the following examples wherein a typical water-soluble inorganic columbate, namely potassium columbate, was employed in the compositions. The potassium columbate was tested as a solution of potassium columbate prepared by fusing 0.25 gram of columbium pentoxide with 2.0 grams of potassium carbonate, cooling the melt, and dissolving the resulting potassium columbate in 500 milliliters of water.

In these examples the following procedure was employed. Five grams of a polyphosphate composition (or an equivalent weight of a component thereof where specified) was dissolved in 600 milliliters of water. One-tenth of this volume, or 60 milliliters, was placed in a 200 milliliter beaker and the required volume of inhibitor solution added. The volume of solution in the beaker was made up to 95 milliliters. The final concentration of polyphosphate composition or component is equivalent to five grams whole composition per quart of water. The pH at room temperature was adjusted to the desired level with sodium hydroxide or hydrochloric acid solutions. The solution was then heated to 160-165° F., and placed in a water bath to maintain the temperature of the solution at 160-165° F. A German silver metal strip, one inch by six inches, cleaned with a Noxon metal polish, rinsed, and buffed with a cloth, was partially immersed in the solution and allowed to remain for one-half hour. At the end of that time, the strip was removed, rinsed, dried with a cloth, and visually examined for tarnish. The effectiveness of the tarnish inhibitor was 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.

Examples 1-4 below show that a water-soluble inorganic columbate inhibits the formation of tarnish by typical polyphosphates, such as pentasodium tripolyphosphate and tetrasodium pyrophosphate.

EXAMPLES 1-4

To separate portions of the polyphosphates listed below dissolved in distilled water were added varying proportions of potassium columbate and the volume diluted in accordance with the above test procedure. In Examples 1 and 2 the pH of the test solution was 8, while in Examples 3 and 4 the pH of the test solution was 10. All of the test solutions had a concentration of 2.25 grams of polyphosphate per quart of distilled water. The tarnish gradings upon German silver were as follows.

Polyphosphate	Percent Potassium Columbate (expressed as Columbium Pentoxide) (polyphosphate basis)		
	0.0	2.2	6.7
Tetrasodium Pyrophosphate (Examples 1-2)	6	3	2
Pentasodium Tripolyphosphate (Examples 3-4)	6	3	2

The addition of a water-soluble inorganic columbate to polyphosphate compositions containing an organic nonsoap detergent, which may be either anionic, nonionic, or cationic, as well as builders inhibits the formation of tarnish by such detergent compositions. This

is clearly illustrated by the examples set forth below wherein the eight compositions of Table I were employed.

Table I

Compositions.....	A	B	C	D	E	F	G	H
Sodium Dodecylbenzene Sulfonate.....	18.0	18.0					18.0	18.0
Lauric Ester of N-(beta-hydroxy-ethyl)-alpha-(chloropyridinium) acetamide [Emulsept].....			18.0	18.0				
Pluronic L-64.....					18.0	18.0		
Pentasodium Tripolyphosphate.....		45.0	45.0		45.0			
Tetrasodium Pyrophosphate.....	45.0			45.0		45.0		
Sodium Hexametaphosphate.....							45.0	
Hexasodium Tetrapolyphosphate.....								45.0
Sodium Silicate.....	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Sodium Carbonate.....	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sodium Carboxymethylcellulose.....	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water.....	10.0	10.0	7.0	7.0	7.0	7.0	7.0	7.0
Sodium Sulfate.....	17.5	17.5	20.5	20.5	20.5	20.5	20.5	20.5
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

In Compositions A through H the amounts of the various components are expressed in percent by weight. Pluronic L-64 is an organic nonionic nonsoap detergent 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.

Examples 5-14 show that at least about 0.6% of a water-soluble inorganic columbate based on the weight of polyphosphate inhibits the formation of tarnish by polyphosphate compositions containing an organic anionic nonsoap detergent and supplemental builders.

EXAMPLES 5-14

To five grams each of Compositions A and B there was added potassium columbate in the proportions shown below and the test procedure carried out with the following results. In Examples 5-8 the pH of the test solution was 8, while in Examples 9-14 the pH of the test solution was 10.

Percent Potassium Columbate (expressed as Columbum Pentoxide) (polyphosphate basis).....	0.0	0.6	1.1	2.2	4.4	6.7
Grading (Composition A) (Examples 5-8).....	6			2	2	2
Grading (Composition B) (Examples 9-14).....	6	3	3	3	3	2

A water-soluble inorganic columbate is effective as a tarnish inhibitor in polyphosphate compositions containing an organic nonsoap detergent as well as supplemental builders when the alkali metal polyphosphate is other than tetrasodium pyrophosphate or pentasodium tripolyphosphate, for example, sodium hexametaphosphate or hexasodium tetrapolyphosphate. This is clearly illustrated by Examples 15-18 set forth below.

EXAMPLES 15-18

Five grams each of Compositions G at pH 9 and H at pH 11 per quart of distilled water tested in accordance with the test procedure both tarnished German silver to a grading of 6, i. e., severe tarnish. When 6.7% of potassium columbate (expressed as columbum pentoxide) based on the weight of polyphosphate was added to Composition G, the tarnish grading of the composition upon German silver at pH 9 was reduced to grade 3. When 6.7% of potassium columbate (expressed as columbum pentoxide) based on the weight of polyphosphate was added to Composition H, the tarnish grading of the composition upon German silver at pH 11 was reduced to grade 1, indicating interface stain only.

Water-soluble inorganic columbates are also effective

as tarnish inhibitors in polyphosphate compositions containing either an organic cationic non-soap detergent or

an organic nonionic nonsoap detergent as well as supplemental builders, as illustrated by Examples 19-26.

EXAMPLES 19-26

Five grams each of Compositions C and D (cationic detergents) and E and F (nonionic detergents) per quart of distilled water were tested in accordance with the test procedure. Compositions C and E were tested at pH 11, while Compositions D and F were tested at pH 8. All four of these compositions tarnished German silver to grade 6. When 6.7% of potassium columbate (expressed as columbum pentoxide) based on the weight of polyphosphate was added to each of these compositions, Composition C then had a reduced tarnish grading at the specified pH value of 1, while Compositions D, E, and F then had a reduced tarnish grading at the specified pH values of 2.

The amount of the alkali metal polyphosphate present in the polyphosphate compositions may be as low as about 15% as noted above and as further illustrated by Examples 27-28.

EXAMPLES 27-28

15% of pentasodium tripolyphosphate was employed in Composition B with the amount of sodium sulfate being increased to offset the decrease in the pentasodium tripolyphosphate content of the composition (30% additional sodium sulfate). Five grams of this modified composition per quart of distilled water at pH 10 had a tarnish grading of 4 upon German silver metal, whereas five grams of the modified composition per quart of distilled water which also contained 6.7% of potassium columbate (expressed as columbum pentoxide) based on the weight of polyphosphate at pH 10 had a reduced tarnish grading of 2.

Examples 29-30 illustrate the fact that the water-soluble inorganic columbates 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 29-30

Five grams of Composition B per quart of water having a hardness of 180 p. p. m. at pH 11 tarnished German silver to grade 5, whereas five grams of Composition B containing 6.7% of potassium columbate (expressed as columbum pentoxide) based on the weight of polyphosphate per quart of water having a hardness of 180 p. p. m. at pH 11 tarnished German silver only to grade 1.

The effectiveness of water-soluble inorganic columbates as tarnish inhibitors with liquid polyphosphate detergent compositions is clearly illustrated in Examples 31-32.

EXAMPLES 31-32

Two 11.25 gram portions of the following liquid de-

tergent composition were dissolved separately in one quart of distilled water and potassium columbate added to one at the concentration indicated below. The tarnish grading of a strip of German silver metal inserted in each of the solutions at pH 9 is also set forth. It will be noted that 11.25 grams of the liquid product provides the same amount of polyphosphate (2.25 grams) as the standard five grams of granulated detergent containing 45% polyphosphate.

Composition	Percent by Weight	
Potassium Dodecylbenzene Sulfonate.....	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.....	100.0	
Example No.....	31	32
Percent Potassium Columbate (expressed as Columbium Pentoxide) (polyphosphate basis).....	0.0	0.7
Tarnish Grade.....	6	2

It should be borne in mind that this invention relates to tarnishing and tarnish inhibitors and does not pertain to alkaline corrosion or corrosion inhibitors. Tarnishing and corrosion of metals are two quite dissimilar phenomena. A discoloration is the principal manifestation of tarnishing, while a dissolving action characterizes corrosion of metal. Corrosion inhibitors are effective because they remove oxygen from the alkaline medium surrounding the metal being corroded. The antitarnishing action of a water-soluble inorganic columbate on German silver, on the other hand, is due to a different mechanism, since the presence of oxygen is not necessary to the tarnishing action of polyphosphates on German silver.

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

We claim:

1. A detergent composition consisting essentially of an alkali metal polyphosphate which in aqueous solution tarnishes German silver and a water-soluble inorganic columbate in an amount to lessen the tarnishing action of the polyphosphate.

2. A detergent composition consisting essentially of an alkali metal polyphosphate selected from the group

consisting of alkali metal triphosphates and pyrophosphates which in aqueous solution tarnishes German silver and from about 2% to about 15% of a water-soluble inorganic columbate to lessen the tarnishing action of the polyphosphate.

3. A detergent composition as set forth in claim 2 wherein the columbate is potassium columbate.

4. A detergent composition consisting essentially of from about 15% to about 50% of an alkali metal polyphosphate which in aqueous solution tarnishes German silver, from about 5% to about 40% of an organic non-soap detergent, and a water-soluble inorganic columbate in an amount from about 0.6% to about 15% based on the weight of the polyphosphate and sufficient to inhibit such tarnishing.

5. A detergent composition as set forth in claim 4 wherein the polyphosphate is an alkali metal triphosphate.

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

7. A detergent composition as set forth in claim 4 wherein the polyphosphate is an alkali metal hexametaphosphate.

8. A detergent composition as set forth in claim 4 wherein the polyphosphate is an alkali metal tetrapolyphosphate.

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

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

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

12. A detergent composition as set forth in claim 4 wherein the columbate is potassium columbate.

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