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**POLYPHOSPHATE COMPOSITIONS CONTAINING SOAP AND 2-MERCAPTOTHIAZOLINE**

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This invention relates to detergent compositions containing tarnish inhibitors and more particularly to spray-dried tripolyphosphate compositions containing a soap and 2-mercaptothiazoline as synergistic tarnish inhibitors.

Tripolyphosphate compositions are now widely used for detergent and other purposes. Aqueous solutions of such compositions when at certain pH values tend 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 tripolyphosphate-built detergent compositions, it is evident that this is a serious problem.

In developing a spray-dried tripolyphosphate detergent composition containing an organic anionic non-soap detergent or an organic nonionic non-soap detergent it was found that 2-mercaptothiazoline was an effective tarnish inhibitor for such compositions. However, it was also found that when such spray-dried tripolyphosphate compositions contain from about 10% to about 20% of an alkali metal carbonate that 2-mercaptothiazoline no longer was effective as a tarnish inhibitor. This is clearly shown by the six examples presented below in Table I wherein the amounts of the components in the tripolyphosphate detergent compositions are expressed in percent by weight of the total composition at the time of mixing the components together with the exception of the 2-mercaptothiazoline tarnish inhibitor, the percent thereof being based upon the weight of the tripolyphosphate present in the compositions. In the following six examples Pluronic L-64 is an organic nonionic non-soap detergent 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 and Oronite Dispersant NIW is an organic nonionic non-soap detergent which is a polypropylene alkyl phenol averaging tetradecyl in the alkyl radical condensed with ethylene oxide to an average of 9 ethylene oxide groups.

TABLE I

Example No. ....	1	2	3	4	5	6
Pluronic L-64 .....	8.75	8.75	8.75	8.75	8.75	8.75
Oronite Dispersant NIW .....	1.25	1.25	1.25	1.25	1.25	1.25
Pentasodium Tripolyphosphate .....	35.00	35.00	35.00	35.00	35.00	35.00
Sodium Carboxymethyl Hydroxyethyl Cellulose .....	0.50	0.50	0.50	0.50	0.50	0.50
Water .....	10.00	10.00	10.00	10.00	10.00	10.00
Sodium Sulfate .....	44.50	40.75	37.00	33.25	29.50	24.50
Sodium Carbonate .....	0.00	3.75	7.50	11.25	15.00	20.00
Total .....	100.00	100.00	100.00	100.00	100.00	100.00
2-Mercaptothiazoline (based on tripolyphosphate) .....	0.06	0.06	0.06	0.06	0.06	0.06
Tarnish Grade No. ....	1	2	3	5	5	5

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The tarnishing action of each of the above tripolyphosphate detergent compositions on German silver was tested by the following procedure. Five grams of the tripolyphosphate detergent composition was dissolved in somewhat less than one quart of water at a temperature under 170° F. More water was then added to give a total volume of one quart. 300 ml. of the solution was placed in a beaker, and the temperature adjusted to 160° F.-170° F. A 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.-170° F. The metal strip was then removed and dried with a cloth. The strip was visually examined for tarnish and the tarnish graded as follows.

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

This test procedure was employed throughout the remaining examples herein set forth.

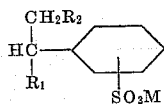
From Example 1 above it can be readily seen that a tripolyphosphate detergent composition containing at least one organic non-soap detergent and containing 2-mercaptothiazoline produces only interface stain upon German silver when the composition does not contain any alkali metal carbonate. As the amount of alkali metal carbonate is increased and the amount of alkali metal sulfate supplemental builder correspondingly decreased it can be seen that the 2-mercaptothiazoline loses its effectiveness as a tarnish inhibitor and becomes ineffective when the alkali metal carbonate content is in the range from about 10% to about 20%. The compositions of Examples 1-6 were prepared as mechanical mixes rather than as spray-dried products in order that the proportions of sodium carbonate would not be altered by possible decomposition upon spray drying. It will be appreciated, however, that the results noted above also apply to spray-dried products.

In accordance with the instant invention it was found that spray-dried tripolyphosphate detergent compositions containing at least one organic non-soap detergent and from about 10% to about 20% of an alkali metal carbonate could be provided with greatly improved tarnishing properties upon German silver when such compositions contain 2-mercaptothiazoline and soap as synergistic tarnish inhibitors. The spray-dried detergent compositions of the present invention which will inhibit the formation of tarnish upon German silver therefore comprise by weight from about 20% to about 50% of an alkali metal tripolyphosphate, from about 5% to about 15% total of at least one organic non-soap detergent selected from the group consisting of organic anionic non-soap detergents and organic nonionic non-soap detergents, from about 10% to about 20% of an alkali metal carbonate, about 10% of an alkali metal silicate, from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate, from about 1.4% to about 3.0% of a soap based on the weight of tripolyphosphate, said soap being selected from the group consisting of alkali metal salts of fatty acids having an acyl-group of from 8 to 22 carbon atoms, and the balance water and supplemental builders. These components and percentages thereof are expressed at the time of mixing the components together and prior to spray drying.

Any water-soluble alkali metal tripolyphosphate may be employed, examples thereof being pentasodium tri-

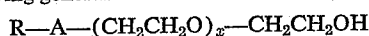
polyphosphate and pentapotassium tripolyphosphate. From about 20% to about 50%, and preferably about 35%, by weight of the alkali metal tripolyphosphate is present in the detergent composition as the heavy duty component thereof. From about 5% to about 15% total, and preferably about 10% total, by weight of at least one organic non-soap detergent is employed in the composition. The organic non-soap detergents may be either organic anionic non-soap detergents or organic nonionic non-soap detergents. It was found that the synergistic tarnish inhibitors were ineffective with organic cationic non-soap detergents and hence such detergents are excluded from the detergent compositions.

The organic anionic non-soap detergents include by way of example the alkylaryl sulfonates, a class of anionic detergents well known in the art under this name. One example thereof is the sulfonated phenyl polypropylene alkanes, characterized by the branched chain structure of polypropylene and a tertiary alkyl carbon at the benzene ring, and having the following general structure:



where M is hydrogen, an alkali metal or an organic amine cation, and R<sub>1</sub> and R<sub>2</sub> are alkyl, of the type formula C<sub>n</sub>H<sub>2n+1</sub>, 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 "Neolene."

Nonionic detergents include, for example, alkyl oxy-ether and ester and thioether and ester detergents having the following general formula:

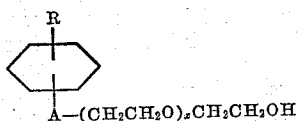


where R is a straight or branched chain saturated or unsaturated hydrocarbon group having from 8 to 18 carbon atoms or an aralkyl group having a straight or branched chain saturated or unsaturated hydrocarbon group of from 8 to 18 carbon atoms attached to the aryl nucleus, and attached to A through the 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.

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 class of alkyl ether are the condensation products of oleyl or dodecyl alcohol or mercaptan with from 8 to 17 moles of ethylene oxide, such as "Emulfor On," "Nonic 218" and "Sterox SE" and "SK." Typical alkyl esters are "G1226" "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 8 carbon

atoms up to approximately 18 carbon atoms, A is oxygen or sulfur and x is a number from 8 to 20. R can, for example, be a straight or branched chain octyl, nonyl, decyl, lauryl, cetyl, myristyl or stearyl group. Typical are the condensation products of octyl and nonyl phenol and thiophenol with from 8 to 17 moles of ethylene oxide, available commercially under the trade names "NIW," "Antarox A-400," "Igepal CA" and "CO," "Triton X-100," "Neutronyx 600," and "Tergitol NFX."

The alkali metal carbonate may be by way of example sodium carbonate or potassium carbonate, from about 10% to about 20%, and preferably 15%, by weight thereof being employed in the detergent composition.

The alkali metal silicate may be sodium or potassium silicate, for example, the amount thereof being about 10%.

As noted above one of the synergistic tarnish inhibitors is 2-mercaptothiazoline. From about 0.03% to about 0.06% thereof based on the weight of tripolyphosphate is employed in the spray-dried detergent composition.

The other synergistic tarnish inhibitor is a soap, from about 1.4% to about 3.0% thereof based on the weight of tripolyphosphate being employed in the detergent composition. The soap is an alkali metal salt of one or more of the higher saturated or unsaturated fatty acids having an acyl group of from 8 to 22 carbon atoms and may include, for example, the alkali metal salts, such as the sodium salts of myristic acid, palmitic acid, tallow fatty acid, and coconut oil fatty acid.

The balance of the spray-dried detergent composition is made up of water and supplemental builders. The supplemental builders may include alkali metal and alkaline earth metal sulfates, chlorides, and borates, such as sodium tetraborate, sodium sulfate, calcium sulfate, calcium chloride, sodium chloride, and sodium borate. The builders should be water-soluble.

In addition to or instead of the above mentioned supplemental inorganic salts, organic material, such as starch, polyethylene glycols, polyvinyl alcohols and salts of carboxymethylcellulose and carboxymethyl hydroxyethyl cellulose and perfumes and dyes can be used in minor proportions as builders.

The tripolyphosphate detergent compositions may be prepared by the conventional method of blending the ingredients thereof in an aqueous solution or slurry and then drying the resulting mixture in a spray dryer at elevated temperatures. It was found that with drum-dried tripolyphosphate detergent compositions that the synergistic tarnish inhibitors were not necessary in order to prevent the formation of tarnish by such compositions upon German silver. Accordingly, drum-dried tripolyphosphate detergent compositions are excluded from this invention.

The invention will be further explained by the following discussion. Drum-dried tripolyphosphate detergent compositions do not need the presence of the synergistic tarnish inhibitors, since the components of such compositions do not decompose upon drum drying. Accordingly, the 10% of alkali metal silicate added to the mixture of the composition prior to drum drying remains present in the same amount in the drum-dried product and is sufficient by itself in this amount to inhibit the formation of tarnish upon German silver by the tripolyphosphate. This, however, is not true of spray-dried tripolyphosphate detergent compositions.

In the conventional spray drying of tripolyphosphate detergent compositions there is a decomposition of a portion of the alkali metal tripolyphosphate into such products as alkali metal pyrophosphate. For example, a mixture of the tripolyphosphate detergent composition in Example 9 without the synergistic tarnish inhibitors upon spray drying contained about 10% of tetrasodium pyrophosphate as determined by wet analysis. There is also a decomposition of a portion of the alkali metal silicate into silica floc by the acidic breakdown products of the

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alkali metal tripolyphosphate, thereby reducing the silicate content to about 6-8%. Accordingly, there is an insufficient amount of silicate present in the spray-dried product to inhibit the formation of tarnish. Moreover, the presence of pyrophosphate in the spray-dried product resulting from the decomposition of tripolyphosphate increases the tarnishing effect of the spray-dried product, since alkali metal silicate is much less effective as a tarnish inhibitor against pyrophosphates than against tripolyphosphates.

The 10% of alkali metal silicate would be effective as a tarnish inhibitor in tripolyphosphate detergent compositions containing from 10% to 20% of alkali metal carbonate if there were no decomposition of the tripolyphosphate and silicate upon spray drying. Since there is such decomposition, it is necessary in accordance with the invention to employ the synergistic tarnish inhibitors therein.

The compositions of the invention will be further illustrated in connection with the following examples. Spray-dried tripolyphosphate detergent compositions were prepared having the following percentage compositions by weight, at the time of mixing the components together and prior to spray drying. In Examples 9 and 10 the fluorescent dye was the disodium salt of 4,4'-bis[4-phenylamino - 6 - [bis(2 - hydroxyethyl)]amino - s - triazine - 2-ylamino]-2,2' stilbene disulfonic acid.

## Example 7

## PART A

	Percent
Sodium dodecylbenzene sulfonate	10
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Sodium sulfate	19.48
2 - mercaptothiazoline <sup>1</sup>	0.02

Total ----- 100

<sup>1</sup> 2-mercaptothiazoline (based on tripolyphosphate) 0.06%.

## PART B

	Percent
Sodium dodecylbenzene sulfonate	10
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Sodium sulfate	18.48
2 - mercaptothiazoline <sup>1</sup>	0.02
Sodium tallow soap <sup>2</sup>	1.00

Total ----- 100

<sup>1</sup> 2-mercaptothiazoline (based on tripolyphosphate) 0.06%.

<sup>2</sup> Sodium tallow soap (based on tripolyphosphate) 2.9%.

## Example 8

## PART A

	Percent
Sodium hardened-tallow alcohol sulfate	10
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Sodium sulfate	19.48
2-mercaptothiazoline <sup>1</sup>	0.02

Total ----- 100

<sup>1</sup> 2-mercaptothiazoline (based on tripolyphosphate) 0.06%.

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## PART B

	Percent
Sodium hardened-tallow alcohol sulfate	10
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Sodium sulfate	18.48
2-mercaptothiazoline <sup>1</sup>	0.02
Sodium tallow soap <sup>2</sup>	1.00

Total ----- 100

<sup>1</sup> 2-mercaptothiazoline (based on tripolyphosphate) 0.06%.

<sup>2</sup> Sodium tallow soap (based on tripolyphosphate) 2.9%.

## Example 9

## PART A

	Percent
Pluronic L-64	8.75
Oronite dispersant NIW	1.25
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Fluorescent dye	0.03
Sodium sulfate	19.47

Total ----- 100

2-mercaptothiazoline (based on tripolyphosphate) ----- 0.03

## PART B

	Percent
Pluronic L-64	8.75
Oronite dispersant NIW	1.25
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Fluorescent dye	0.03
Sodium sulfate	19.47

Total ----- 100

2-mercaptothiazoline (based on tripolyphosphate) ----- 0.03

Sodium tallow soap (based on tripolyphosphate) ----- 1.4

## Example 10

## PART A

	Percent
Pluronic L-64	8.75
Oronite dispersant NIW	1.25
Pentasodium tripolyphosphate	35
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Water	10
Fluorescent dye	0.03
Sodium sulfate	19.47

Total ----- 100

2-mercaptothiazoline (based on tripolyphosphate) ----- 0.06

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## PART B

	Percent
Pluronic L-64 -----	8.75
Oronite dispersant NIW -----	1.25
Pentasodium tripolyphosphate -----	35
Sodium silicate -----	10
Sodium carbonate -----	15
Sodium carboxymethyl hydroxyethyl cellulose --	0.5
Water -----	10
Fluorescent dye -----	0.03
Sodium sulfate -----	19.47

Total ----- 100

2-mercaptothiazoline (based on tripolyphosphate) -----	0.06
Sodium tallow soap (based on tripolyphosphate) -----	2.9

The conditions set forth in Table II below were employed in the spray-drying of the compositions in Examples 7-10.

TABLE II

Example No.-----	7A	7B	8A	8B	9A	9B	10A	10B
Percent Water in Slurry-----	29	29	33	33	35	35	20	20
Slurry Temperature (° F)-----	185	185	185	185	160	160	185	185
Total Mixing Time (minutes)-----	30	30	30	30	-----	-----	30	30
Mixing Time After Phosphate Addition (minutes)-----	10	10	10	10	-----	-----	10	10
Tower Air Inlet Temperature (° F)-----	540	540	540	540	400-450	400-450	500-600	520

Examples 9A and 9B were prepared by adding 2-mercaptothiazoline (and soap) in solution to a solution of the product, which was spray-dried without 2-mercaptothiazoline or other synergist. These examples differ in this respect from the others which were spray-dried after addition of 2-mercaptothiazoline (and soap) to the crutcher slurry.

The tarnishing action of each of the spray-dried detergent compositions in Examples 7-10 upon German silver was tested in accordance with the above described test procedure. The following results were noted.

Example No.	Tarnish Grade No.	Degree of Tarnish
7A-----	3	Slight tarnish.
7B-----	1	Interface stain only.
8A-----	4	Moderate tarnish.
8B-----	2	Barely noticeable tarnish.
9A-----	5	Considerable (heavy) tarnish.
9B-----	1	Interface stain only.
10A-----	5	Considerable (heavy) tarnish.
10B-----	1	Interface stain only.

The compositions in part A of each of Examples 7-10 contained an alkali metal tripolyphosphate, at least one organic anionic or nonionic non-soap detergent, an alkali metal carbonate, an alkali metal silicate, supplemental builders and one of the synergistic tarnish inhibitors, namely 2-mercaptothiazoline. In these compositions 2-mercaptothiazoline alone was ineffective as a tarnish inhibitor, since the compositions tarnished German silver to a degree of tarnish ranging from slight tarnish to considerable tarnish. The compositions in part B of each of Examples 7-10 were as noted above with the exception that an alkali metal soap was also added thereto so that each of these compositions contained the synergistic tarnish inhibitors, namely, 2-mercaptothiazoline and an alkali metal soap. The compositions in part B showed a very noticeable improvement over the corresponding compositions in part A, thereby demonstrating the remarkable effectiveness of the synergistic tarnish inhibitors.

Various modifications and changes may be made in the compositions of this invention without departing from the spirit of the invention or sacrificing any of the advan-

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tages thereof. Accordingly, it will be understood that the invention is to be limited only within the scope of the appended claims.

I claim:

1. A spray-dried detergent composition consisting essentially of from about 20% to about 50% of an alkali metal tripolyphosphate which in aqueous solution tarnishes German silver, from about 5% to about 15% total of at least one organic non-soap detergent selected from the group consisting of organic anionic non-soap detergents and organic nonionic non-soap detergents, from about 10% to about 20% of an alkali metal carbonate, about 10% of an alkali metal silicate, from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate, and from about 1.4% to about 3.0% of a water-soluble alkali metal soap based on the weight of tripolyphosphate, said soap being selected from the group consisting of the alkali metal salts of fatty acids having an acyl group of from 8 to 22 carbon atoms; the amounts of said thiazoline and soap being sufficient to inhibit the tarnishing and the components of

the composition being expressed by weight at the time of mixing thereof and prior to spray drying.

2. A spray-dried detergent composition as set forth in claim 1 wherein the amount of alkali metal tripolyphosphate is about 35%.

3. A spray-dried detergent composition as set forth in claim 1 wherein the alkali metal tripolyphosphate is pentasodium tripolyphosphate.

4. A spray-dried detergent composition as set forth in claim 1 containing about 10% total of at least one organic non-soap detergent.

5. A spray-dried detergent composition as set forth in claim 1 wherein the organic non-soap detergent is sodium dodecylbenzene sulfonate.

6. A spray-dried detergent composition as set forth in claim 1 wherein the organic non-soap detergents are a mixture of (1) a compound having the empirical formula  $\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$  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, and (2) a polypropylene alkyl phenol averaging tetradecyl in the alkyl radical condensed with ethylene oxide to an average of 9 ethylene oxide groups.

7. A spray-dried detergent composition as set forth in claim 1 containing about 15% of an alkali metal carbonate.

8. A spray-dried detergent composition as set forth in claim 1 wherein the alkali metal carbonate is sodium carbonate.

9. A spray-dried detergent composition as set forth in claim 1 wherein the water-soluble alkali metal soap is sodium tallow soap.

10. A spray-dried detergent composition consisting essentially of from about 20% to about 50% of pentasodium tripolyphosphate which in aqueous solution tarnishes German silver, from about 5% to about 15% of sodium dodecylbenzene sulfonate, from about 10% to about 20% of sodium carbonate, about 10% of sodium silicate, from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate, and from about 1.4% to about 3.0% of sodium tallow soap

based on the weight of tripolyphosphate; the amounts of said thiazoline and soap being sufficient to inhibit the tarnishing and the components of the composition being expressed by weight at the time of mixing thereof and prior to spray drying.

11. A spray-dried detergent composition consisting essentially of about 35% of pentasodium tripolyphosphate which in aqueous solution tarnishes German silver, about 10% of sodium dodecylbenzene sulfonate, about 15% of sodium carbonate, about 10% of sodium silicate, from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate, and from about 1.4% to about 3.0% of sodium tallow soap based on the weight of tripolyphosphate; the amounts of said thiazoline and soap being sufficient to inhibit the tarnishing and the components of the composition being expressed by weight at the time of mixing thereof and prior to spray drying.

12. A spray-dried detergent composition consisting essentially of from about 20% to about 50% of pentasodium tripolyphosphate which in aqueous solution tarnishes German silver; from about 5% to about 15% total of a mixture of (1) a compound having the empirical formula  $\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$  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, and (2) a polypropylene alkyl phenol averaging tetradecyl in the alkyl radical condensed with ethylene oxide to an average of 9 ethylene oxide groups; from about 10% to about 20% of sodium carbonate; about 10% of sodium silicate; from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate; and from about 1.4% to about 3.0% of sodium tallow soap based on the weight of tripolyphosphate; the amounts of said thiazoline and soap being

sufficient to inhibit the tarnishing and the components of the composition being expressed by weight at the time of mixing thereof and prior to spray drying.

13. A spray-dried detergent composition consisting essentially of about 35% of pentasodium tripolyphosphate which in aqueous solution tarnishes German silver; about 10% total of a mixture of (1) a compound having the empirical formula  $\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$  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, and (2) a polypropylene alkyl phenol averaging tetradecyl in the alkyl radical condensed with ethylene oxide to an average of 9 ethylene oxide groups; about 15% of sodium carbonate; about 10% sodium silicate; from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate; and from about 1.4% to about 3.0% of sodium tallow soap based on the weight of tripolyphosphate; the amounts of said thiazoline and soap being sufficient to inhibit the tarnishing and the components of the composition being expressed by weight at the time of mixing thereof and prior to spray drying.

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