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2,870,093

POLYPHOSPHATE COMPOSITIONS CONTAINING
COCO-β-ALANINE AND 2-MERCAPTOTHIAZO-
LINE

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No Drawing. Application January 9, 1956
Serial No. 557,863

13 Claims. (Cl. 252—137)

This invention relates to detergent compositions con-
taining tarnish inhibitors and more particularly to spray-
dried polyphosphate compositions containing an alkali
metal coco-β-alanine and 2-mercaptothiazoline as syner-
gistic 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 tar-
nish 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 al-
lowed 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 nonsoap de-
tergent or an organic nonionic nonsoap 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 com-
positions contained 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 tripoly-
phosphate 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 nonsoap detergent
compound having the empirical formula



prepared by condensing ethylene oxide with a hydro-
phobic base formed by the condensation of propylene
oxide with propylene glycol, where *b* is an integer se-
lected 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 nonsoap detergent which is a poly-
propylene alkyl phenol averaging tetradecyl in the alkyl
radical condensed with ethylene oxide to an average of 9
ethylene oxide groups.

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TABLE I

Example No.	1	2	3	4	5	6
5 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 Tri- polyphosphate	35.00	35.00	35.00	35.00	35.00	35.00
Sodium Carboxy- methyl Hydroxy- ethyl Cellulose	0.50	0.50	0.50	0.50	0.50	0.50
10 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
15 2-Mercapto- thiazoline (based on tripolyphos- phate)	0.06	0.06	0.06	0.06	0.06	0.06
Tarnish Grade No.	1	2	3	5	5	5

The tarnishing action of each of the above tripolyphos-
phate detergent compositions on German silver was tested
by the following procedure. Five grams of the tripoly-
phosphate detergent composition was dissolved in some-
what less than one quart of water at a temperature under
170° F. More water was then added to give a total vol-
ume of one quart. 300 mls. 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 solu-
tion 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 tar-
nish 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 re-
maining examples herein set forth.

From Example 1 above it can be readily seen that a
tripolyphosphate detergent composition containing at
least one organic nonsoap detergent and containing 2-
mercaptothiazoline produces only interface stain upon
German silver when the composition does not contain an
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 effec-
tiveness 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 de-
composition upon spray-drying. It will be appreciated,

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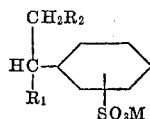
however, that the results noted above apply to spray-dried products.

In accordance with the instant invention it was found that spray-dried tripolyphosphate detergent compositions containing at least one organic nonsoap detergent and from about 10% to about 20% of an alkali metal carbonate could be provided with greatly improved tarnishing properties on German silver when such compositions contain 2-mercaptothiazoline and an alkali metal coco- β -alanine 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 nonsoap detergent selected from the group consisting of organic anionic nonsoap detergents and organic nonionic nonsoap detergents, from about 10% to about 20% of an alkali metal carbonate, about 10% of an alkali metal silicate, from about 0.03% to 0.06% of 2-mercaptothiazoline based upon the weight of tripolyphosphate, from about 0.07% to about 0.8% of an alkali metal coco- β -alanine based on the weight of tripolyphosphate, 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 tripolyphosphate 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.

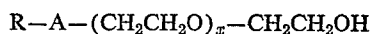
From about 5% to about 15% total, and preferably about 10% total, by weight of at least one organic nonsoap detergent is employed in the composition. The organic nonsoap detergents may be either organic anionic nonsoap detergents or organic nonionic nonsoap detergents.

The organic anionic nonsoap 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 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."

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

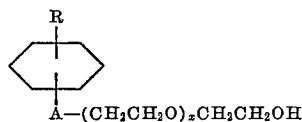
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or branched chain octyl, nonyl, decyl, lauryl, myristyl, cetyl or stearyl group or an alkylaryl group such as octylbenzene, nonylbenzene, decylbenzene, stearylbenzene, etc.

Where R is alkyl it will be evident that the detergent can be regarded as derived from an alcohol, mercaptan, oxy or thio fatty acid of high molecular weight, by condensation with ethylene oxide. Typical of this class 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," "Nonix 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 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 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 an alkali metal coco- β -alanine, from about 0.07% to about 0.8% thereof based on the weight of tripolyphosphate being employed in the detergent composition. The alkali metal coco- β -alanine has the following general formula:



where R is a mixed aliphatic hydrocarbon radical containing from 6 to 18 carbon atoms and M is an alkali metal, such as ammonium, sodium, or potassium. It may be prepared, for example, by reacting the mixture of aliphatic hydrocarbon amines derived from coconut oil and referred to in the art as cocoamine with methyl acrylate, followed by alkaline hydrolysis.

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 perfume 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

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then drying the resulting mixture in the 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 detergent 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 on German silver by the tripolyphosphate. This, however, is not true of spray-dried tripolyphosphate detergent compositions.

In the conventional spray-dried tripolyphosphate detergent compositions there is a decomposition of a portion of the alkali metal tripolyphosphate into such products as alkali metal pyrophosphate. For example, an aqueous slurry of the 35%-tripolyphosphate detergent composition in Example 9 below mixed at 160° F. without the synergistic tarnish inhibitors upon spray drying at an air inlet temperature of 400–450° F. 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 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 was 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 7–9 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.....	10.0
Pentasodium tripolyphosphate.....	35.0
Sodium silicate.....	10.0
Sodium carbonate.....	15.0
Sodium carboxymethyl hydroxyethyl cellulose.....	0.5
Fluorescent dye.....	0.03
Water.....	10.0
Sodium sulfate.....	19.45
2 - mercaptothiazoline ¹	0.02
Total.....	100

¹ 2-mercaptothiazoline (based on tripolyphosphate), 0.06%. 75

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PART B

Sodium dodecylbenzene sulfonate.....	10.0
Pentasodium tripolyphosphate.....	35.0
Sodium silicate.....	10.0
Sodium carbonate.....	15.0
Sodium carboxymethyl hydroxyethyl cellulose.....	0.5
Fluorescent dye.....	0.03
Water.....	10.0
Sodium sulfate.....	19.15
2 - mercaptothiazoline ¹	0.02
Sodium coco-β-alanine ²	0.3

Total..... 100

¹ 2-mercaptothiazoline (based on tripolyphosphate), 0.06%.

² Sodium coco-β-alanine (based on tripolyphosphate), 0.8%.

Example 8

PART A

Sodium hardened-tallow alcohol sulfate.....	10.0
Pentasodium tripolyphosphate.....	35.0
Sodium silicate.....	10.0
Sodium carbonate.....	15.0
Sodium carboxymethyl hydroxyethyl cellulose.....	0.5
Fluorescent dye.....	0.03
Water.....	10.0
Sodium sulfate.....	19.45
2 - mercaptothiazoline ¹	0.02

Total..... 100

¹ 2-mercaptothiazoline (based on tripolyphosphate), 0.06%.

PART B

	Percent
Sodium hardened-tallow alcohol sulfate.....	10.0
Pentasodium tripolyphosphate.....	35.0
Sodium silicate.....	10.0
Sodium carbonate.....	15.0
Sodium carboxymethyl hydroxyethyl cellulose.....	0.5
Fluorescent dye.....	0.03
Water.....	10.0
Sodium sulfate.....	19.15
2-mercaptothiazoline ¹	0.02
Sodium coco-β-alanine ²	0.3

Total..... 100

¹ 2-mercaptothiazoline (based on tripolyphosphate), 0.06%.

² Sodium coco-β-alanine (based on tripolyphosphate), 0.8%.

Example 9

PART A

Pluronic L-64.....	8.75
Oronite Dispersant NIW.....	1.25
Pentasodium tripolyphosphate.....	35.0
Sodium silicate.....	10.0
Sodium carbonate.....	15.0
Sodium carboxymethyl hydroxyethyl cellulose.....	0.5
Water.....	10.0
Fluorescent dye.....	0.03
Sodium sulfate.....	19.45
2-mercaptothiazoline ¹	0.02

Total..... 100

¹ 2-mercaptothiazoline (based on tripolyphosphate), 0.06%.

PART B

Pluronic L-64.....	8.75
Oronite Dispersant NIW.....	1.25
Pentasodium tripolyphosphate.....	35.0
Sodium silicate.....	10.0
Sodium carbonate.....	15.0
Sodium carboxymethyl hydroxyethyl cellulose.....	0.5
Water.....	10.0
Fluorescent dye.....	0.03
Sodium sulfate.....	19.15
2-mercaptothiazoline ¹	0.02
Sodium coco-β-alanine ²	0.3

Total..... 100

¹ 2-mercaptothiazoline (based on tripolyphosphate), 0.06%.

² Sodium coco-β-alanine (based on tripolyphosphate), 0.8%.

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The conditions set forth in Table II below were employed in the spray-drying of the compositions in Examples 7-9.

TABLE II

Example No.	7A	7B	8A	8B	9A	9B
Percent Water in Slurry	29	33	33	33	20	20
Slurry Temperature (° F.)	185	185	185	185	185	185
Total Mixing Time (min.)	30	30	30	30	30	30
Mixing Time after Phosphate addition (min.)	10	10	10	10	10	10
Lower air inlet temp. (° F.)	540	540	540	540	500-600	550

The tarnishing action of each of the spray-dried detergent compositions in Examples 7-9 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	3	Slight tarnish.
9A	4	Moderate tarnish.
9B	3	Slight tarnish.

The compositions in Part A of each of Examples 7-9 contain an alkali metal tripolyphosphate, at least one organic anionic or nonionic nonsoap 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 tarnish German silver to a degree of tarnish ranging from slight tarnish to moderate tarnish. The compositions in Part B of each of Examples 7-9 were as noted above with the exception that an alkali metal coco-β-alanine was also added thereto so that each of these compositions contains the synergistic tarnish inhibitors, namely, 2-mercaptothiazoline and an alkali metal coco-β-alanine. The compositions in Part B showed a 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 advantages 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 comprising 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 nonsoap detergent selected from the group consisting of organic anionic nonsoap detergents and organic nonionic nonsoap 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 about 0.8% of an alkali metal coco-β-alanine based on the weight of tripolyphosphate; the amounts of said thiazoline and alanine 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

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claim 1 containing about 10% total of at least one organic nonsoap detergent.

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

6. A spray-dried detergent composition as set forth in claim 1 wherein the organic nonsoap 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.

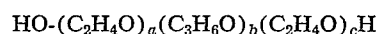
8. A spray-dried detergent composition as set forth in claim 1 wherein the alkali metal carbonate is sodium carbonate.

9. A spray-dried detergent composition as set forth in claim 1 wherein the alkali metal coco-β-alanine is sodium coco-β-alanine.

10. A spray-dried detergent composition comprising 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 about 0.8% of sodium coco-β-alanine based on the weight of tripolyphosphate; the amounts of said thiazoline and alanine 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 comprising 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 about 0.8% of sodium coco-β-alanine based on the weight of tripolyphosphate; the amounts of said thiazoline and alanine 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 comprising 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



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 about 0.8% of sodium coco-β-alanine based on the weight of tripolyphosphate; the amounts of said thiazoline and alanine being sufficient to inhibit the tarnishing and the components of the composition being expressed by weight

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at the time of mixing thereof and prior to spray-drying.

13. A spray-dried detergent composition comprising 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

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silicate; from about 0.03% to about 0.06% of 2-mercaptothiazoline based on the weight of tripolyphosphate; and about 0.8% of sodium coco- β -alanine based on the weight of tripolyphosphate; the amounts of said thiazoline and alanine 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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