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DETERGENT COMPOSITIONS CONTAINING METAL DISCOLORATION INHIBITORS

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The present invention relates to novel detergent compositions, and more particularly to detergent compositions having improved anti-tarnishing properties.

Certain detergent compositions have been known for many years and have been widely accepted since their lime resistance and other valuable properties make them advantageous for many uses, e. g., dishwashing, laundering, etc. An unexpected difficulty has been noted in the cleansing of certain metallic surfaces, such as articles made of German silver or having a German silver base, by solutions of such detergent compositions containing certain water-soluble polyphosphate compounds. For example, in the washing of household utensils such as tableware or "silverware" consisting of German silver with such compositions, the washed articles may exhibit tarnishing of the metallic surfaces.

Depending upon the nature of the material, the detergent composition and the conditions employed, the undesirable effects may range from a diminution or loss of luster of the highly polished metallic surfaces to a harsh discoloration or stain, or worse. The tarnish film, if it may be so called, is of such a nature that it is difficult to analyze, even with microscopic or X-ray means. The discoloration tarnishing effects appear to be particularly objectionable in non-soap detergent compositions containing complex polyphosphates, usually in aqueous alkaline solutions of such detergent compositions. Such adverse effects represent a significant problem from the standpoint of consumer appeal and in the cleansing and maintenance of such susceptible metals.

It has now been discovered that detergent compositions normally tending in solution to cause tarnishing of German silver and like metals and consisting essentially of water-soluble polyphosphate materials may be improved by incorporation of a minor amount of a mononuclear aromatic substituted thiourea to inhibit or retard the tarnishing by said detergent compositions in solution. As a preferred embodiment, the present invention relates to detergent compositions consisting essentially of a non-soap water-soluble synthetic detergent, a water-soluble polyphosphate compound, and a minute amount (e. g. up to about 1%) of an unsymmetrical mononuclear aryl substituted thiourea as a tarnish inhibitor. The specificity of action of these inhibitors in the relationship set forth is not completely understood at this time.

It is a principal feature of the present invention that the detergent composition may comprise water-soluble inorganic polyphosphate salts. These salts have the property of inhibiting precipitation of calcium material and the like in aqueous solution and may be considered as derived from orthophosphoric acid or the like by the removal of water, though any suitable means of manufacture may be employed if desired. These molecularly-dehydrated polyphosphate salts may be wholly or partially neutralized, such as the alkali metal or ammonium salts of tripolyphosphoric, tetraphosphoric, and pyrophosphoric acids. Suitable examples are sodium tripolyphosphate ($\text{Na}_3\text{P}_3\text{O}_{10}$), potassium tripolyphosphate, tetrasodium pyrophosphate, hexasodium hexametaphosphate (Graham's salt), hexasodium tetraphosphate, etc.

In detergent compositions consisting essentially of the indicated polyphosphates either with or without admixture with synthetic detergents, it will be observed that the tarnishing action manifests itself as a marked discoloration or stain on the German silver articles. Such discoloration, usually of a yellowish, purplish or blackish shade, appears to be due primarily to some phenomenon

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induced or existing in the presence of these complex polyphosphates in the detergent composition. This discoloration which is obviously highly undesirable may be either retarded or inhibited markedly and even substantially eliminated by the addition of a determinable amount of the indicated thiourea compounds. The mechanism by which these desired results are obtained is not completely understood at this time.

The novel compositions of the present invention may also contain as an active detergent ingredient a water-soluble non-soap organic synthetic detergent either in admixture with the polyphosphates. It is preferred to use the anionic sulphated or sulphonated synthetic detergents (including suitable mixtures thereof). Included therein are the aliphatic sulphated or sulphonated detergents, such as the sulphated aliphatic compounds having about 12 to about 26 carbon atoms and, more particularly, the aliphatic acyl-containing compounds having an acyl radical of about 8 to 22 carbon atoms such as the aliphatic carboxylic ester detergents. As suitable examples of aliphatic anionic detergents may be found the sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e. g. coconut oil monoglyceride monosulphate, tallow di-glyceride monosulphate; the long chain pure or mixed higher alkyl sulphates, e. g. lauryl sulphate, cetyl sulphate, higher fatty alcohol sulphates derived from reduced coconut fatty acids; the hydroxy sulphonated higher fatty acid esters, e. g. higher fatty acid esters of 2,3-dihydroxy propane sulphononic acid; the higher fatty acid esters of low molecular weight alkylol sulphononic acids, e. g. oleic ester of isothionic acid; the higher fatty acid ethanalamide sulphates; the higher fatty acid amides of amino alkyl sulphononic acids, e. g. lauric amide of taurine, and the like.

It is a feature of this invention that the desired effects are particularly enhanced with the alkyl aryl sulphonate detergents. These aromatic sulphonate detergents are also well known in the art. They may be mono- or polynuclear in structure. More particularly, the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresols, naphthalene, etc. The alkyl substituent on the aromatic nucleus may vary widely as long as the desired detergent power of such active ingredient is preserved.

More specific examples of suitable alkyl aromatic sulphonate detergents are the higher alkyl aromatic sulphonates. The higher alkyl substituent may vary widely. Thus, it may be branched or straight-chained in structure and comprise decyl, dodecyl, keryl, mixed long-chain alkyls from polymeric lower mono-olefins, etc. Preferred examples of this class are the higher alkyl mononuclear aryl sulphonates wherein the alkyl group is about 8 to about 22, and preferably about 12 to about 18 carbon atoms. More particularly, it is preferred to use the higher alkyl benzene sulphonates wherein the higher alkyl group averages about 12 to about 16 carbon atoms. For example, propylene may be polymerized to the tetramer and condensed with benzene in the presence of a Friedel-Crafts catalyst to yield essentially the dodecyl benzene derivative which is suitable for sulphonation to the desired sulphonate compounds.

These various anionic detergents are generally used in the form of the water-soluble salts, such as the alkali metal, alkaline earth metal, ammonium, amine and alkylamine salts. While the sodium, potassium, ammonium and alkylamine (e. g. mono-, di-, and triethanolamine) salts are preferred ordinarily, other salts such as the lithium, calcium, and magnesium salts may be used if desired. For general use, it is ordinarily preferred to use the sodium and potassium salts. For certain specialized uses, it may be preferred to select the ammonium and alkylamine salts in view of their generally greater solubility in aqueous solution.

It is within the scope of the present invention that non-ionic detergents may be present in the detergent composition and, if desired, in admixture with other compatible detergents such as suitable anionic sulphated or sulphonated ones described above. These non-ionic agents are also well known in the art and include the polyoxyethylene ethers of alkyl aromatic hydroxy bodies (e. g. the alkylated polyoxyethylene phenols) and the

polyoxyethylene ethers of long chain aliphatic alcohols, etc. Long chain derivatives of polyhydroxy compounds such as the appropriate ethers of polyalkylene glycols may also be employed therein.

The tarnish inhibitor is a mononuclear aromatic substituted thiourea compound. The unsymmetrical mononuclear aryl substituted thioureas are highly preferred in comparison to the symmetrical poly-substituted type. The monosubstituted mononuclear aryl derivatives have been found most effective in the relationship set forth. Suitable monosubstituted derivatives are monophenyl thiourea, ortho tolyl thiourea, para tolyl thiourea, 2, 4 dimethylphenyl thiourea, ethylphenyl thiourea, and their homologues (including isomers), particularly the homologues for example having alkyl substituents on the aromatic ring up to about four carbon atoms each. Suitable symmetrical di-substituted derivatives are di-o-tolyl thiourea, di-p-tolylthiourea and their homologues (and isomers) as indicated above. The aromatic nucleus in either the mono- or di-substituted derivatives may be further substituted by other groups, such as amino groups, provided the essential character of the inhibitor is preserved. The term "mononuclear aromatic" or "mononuclear aryl" in the specification and claims is limited to the aryl groups of the benzene series as indicated above.

The amount of the indicated tarnish inhibitor in the detergent composition is generally extremely small, usually up to a maximum of a few per cent (e. g. about 3%), and effective to produce the desired improvements in the tarnish inhibition or prevention. Generally, the amount for the unsymmetrical aryl thioureas will be less than about 1% by weight of the composition, and preferably a fraction of 1%, e. g. up to about 0.5%. While greater amounts may be employed if desired it will usually be found that amounts less than about 1% are satisfactory with commercial detergent compositions with effective results, particularly with built synthetic detergent compositions, being obtained at about 0.1% inhibitor of total solids.

The symmetrical di-substituted aryl thioureas will ordinarily be employed in larger amounts since equivalent effectiveness appears to require about 1% inhibitor of total solids, in comparison to the unsymmetrical type. Thus, these symmetrical poly-substituted mononuclear aryl thioureas will usually be employed in effective amounts up to about 3%, and preferably from about 1-3% though inhibition is obtained with lesser amounts also. Naturally the specific amount of the specific selected tarnish inhibitor to be incorporated in a selected detergent composition will vary somewhat with the nature and concentration of the synthetic detergent and particularly of the polyphosphate builders, and the contemplated field of application or manner of use. The appropriate amount of inhibitor to be employed however may readily be ascertained by means of relatively simple and standard tarnishing tests as indicated infra.

It has been found that particularly desirable effects are observed with such additives in "built" synthetic detergent compositions consisting essentially of the indicated synthetic detergents and the polyphosphates. More particularly, it is preferred to use compositions consisting essentially of about 10 to about 50% and usually about 15 to about 40% synthetic detergents, preferably of an anionic sulphated or sulphonated nature, and about 10 to about 80% and usually about 20 to about 60% of these water soluble polyphosphates, preferably tripolyphosphate, the above percentages being by weight of total solids of the detergent compositions. With such compositions it has been found that amounts of the unsymmetrical inhibitors of less than about 1%, and preferably up to about 0.5% e. g. .05-.5%, are usually highly effective in achieving the desired tarnish inhibiting action on German silver and the like.

Further conditions indicative of the complexity of the phenomenon involved and the specificity of action of these tarnish inhibitors and the like are the alkalinity of aqueous solutions of the detergent, and the concentration of solids therein. Illustratively, a built detergent composition consisting essentially of 35% sodium higher alkyl benzene sulphonate, 40% sodium tripolyphosphate and the balance essentially sodium sulphate with minor amounts of sodium silicate, carboxymethylcellulose, etc., and having a pH in 0.5% solution of about 9-11, and usually about 9.5-10, exhibits marked discoloration of

German silver within a relatively short time. Such adverse effects are largely eliminated by the addition of a suitable amount of inhibitor. If, however, the pH of the above detergent composition without inhibitor is lowered to substantially neutral values, the degree of tarnishing appears to be correspondingly diminished, and even to an extent that the results otherwise may not be objectionable visually. With the above composition and the like, the critical pH value appears to be within the range of about 7.5-8.5, and usually about 8. Above such values for aqueous solutions of the detergent composition, adverse effects are most marked and the use of the inhibitor yields optimum results.

It has been found moreover that more pronounced tarnishing is encountered using about 0.25% to 1% solids concentrations of the above detergent composition in aqueous solution than result from the use of more concentrated solutions. With the use of about 0.1% inhibitor such as phenylthiourea (based on total solids) in such aqueous solutions containing 1.5% solids or less, the presence of the inhibitor results in considerably reduced staining on German silver in comparison to controlled articles exposed to detergent solutions of similar strength but in the absence of inhibitor. Furthermore, a 2% or more solution of the above detergent composition without inhibitor does not appear to stain German silver in ordinary use. The reason for such criticality of action is not understood at this time.

The additives of the present invention may be incorporated with the detergent composition at any stage during the manufacture or use by the ultimate consumer, although it is preferred to incorporate them at the time of manufacture of the detergent composition so that the tarnish inhibitor and detergent composition may be sold to the user as a unitary composition. Thus, the additives may be incorporated at any point during the manufacturing process at which subsequent operations will not adversely modify the properties of the detergent compositions. The various ingredients may be dry-mixed or wet-mixed in any suitable manner. A procedure which is convenient, economical and productive of the best results with synthetic detergent compositions is the addition of the inhibitor in the form of an aqueous or alcoholic slurry to an aqueous slurry of the active detergent ingredients with vigorous stirring to form a relatively smooth, uniform and homogeneous paste. Thereafter these compositions may be prepared in the form of solutions, pastes or as dry or partially hydrated solid products, preferably in finely divided condition. Accordingly, the slurry of the detergent composition may be subjected to any suitable drying operation and converted to particle form. The mixture may thus be subjected to conventional spray-drying, roll-drying or drum-drying operations utilizing temperature of above 212° F. to obtain heat-dried homogeneous detergent particles.

It is common to employ various adjuvant materials in detergent compositions. The detergent compositions, particularly the organic synthetic type, may include any of these substances employed by the art in admixture with such detergent compositions, provided the use of any such materials does not completely neutralize or prevent the desired effects. These builders or additives may be inorganic or organic in structure and may be mixed with the active ingredients in any suitable manner and amount. Conventional builders are the various alkali metal phosphates (e. g. trisodium phosphate), the alkali metal silicates, sulphates, carbonates, etc. Suitable organic materials such as sodium carboxymethylcellulose, fatty acid amides, alcohols, esters may also be employed herein.

The following examples are additionally illustrative of the nature of the present invention and it will be understood that the invention is not limited thereto:

EXAMPLE I

A detergent composition is prepared by compounding 35% sodium dodecyl benzene sulphonate, 40% sodium tripolyphosphate, 3% sodium "N" silicate, 0.8% carboxymethylcellulose and 0.06% optical bleach (Blanco-phor MVI) and the balance sodium sulphate.

An aqueous 1% solution of the foregoing detergent composition stains German silver as indicated by the following simple test which involves the immersion of metal strips in the detergent solution to be tested under selected time and temperature conditions: Approximately 20 milliliters of the 1% detergent solution is poured into a 30

milliliter beaker and placed on a hot water bath until a temperature of about 50° C. is reached. German silver strips (Whitehead metal, 14 BS ¼ hard, approximately 18% nickel, 65% copper, 17% zinc) are cut to ¾" x 2" size. Each strip is abraded using wet #320 A Behr-Manning "Durite" abrasive paper. The strips are thoroughly rinsed in running tap water using a toothbrush, then dipped in denatured ethyl alcohol and air-dried on a clean towel. The strips are then half immersed in the above-mentioned 1% detergent solution and after 30 minutes at 50° C. are removed and patted dry with a clean towel. This procedure produces a dark stain on the surface of the German silver.

Similar results are obtained using 0.25% solution of the above detergent composition also.

To the identical detergent composition in separate aqueous solutions of similar strengths, phenyl thiourea is added in the proportions of 0.01–0.1% by weight of total solids. Repetition of the above tests with German silver strips discloses that the staining is reduced considerably with optimum effects obtained at 0.05 to 0.1% inhibitor. Starting at about 0.05% visual staining appears to be eliminated substantially completely in the relationship set forth.

These tests are repeated using the various aromatic thiourea compounds indicated in the table in the specified amounts.

Inhibitor	Percent Inhibitor of Total Solids	Total Solids in Solution, Percent	Results
None		2	Unstained.
Do		1	Purple stain.
Phenylthiourea	0.1	1	Unstained. ¹
Do	0.5	1	Unstained.
O-Tolylthiourea	0.1	1	Do.
Do	0.5	1	Do.
p-Tolylthiourea	0.1	1	Do.
s-Di-phenylthiourea	0.25	1	Blue.
Do	0.5	1	Slight yellow stain.
Do	1.0	1	Do.
s-Di-o-tolylthiourea	0.1	1	Very slight yellow stain.
s-Di-p-tolylthiourea	0.5	1	Light brown stain.

¹ Exhibits only a slight water-line mark at the air-liquid interface.

The effectiveness of the aromatic thiourea compounds is evident from the data. It is to be noted that the unsymmetrical monosubstituted aryl thioureas are markedly more effective in tarnish inhibition than the symmetrical disubstituted aryl thioureas.

EXAMPLE II

A detergent composition is prepared by forming about a 57% solids slurry containing on a solids basis about 35% sodium dodecyl benzene sulphonate (derived from a propylene tetramer), about 40% sodium tripolyphosphate, 15% sodium sulphate, and the remainder minor amounts of sodium chloride, sodium hydroxide, sodium carboxymethylcellulose, etc. This slurry is agitated at about 140° F. in a conventional soap crutcher to form a relatively homogeneous mixture. Phenylthiourea in an amount of 0.1% of total solids of the slurry is added in the form of an aqueous slurry to the detergent slurry which is further agitated to form a uniform mixture. The slurry is then subjected to spray-drying with heated air at a temperature of about 350° F. with a resultant moisture loss of about 40%. The resultant composition is recovered in the form of beads and has a pH of about 9.5–9.7 in 0.5% aqueous solution. This composition gives effective inhibition of tarnishing of German silver also.

EXAMPLE III

A detergent composition is prepared by the procedure of Example II with the modification that the organic detergent is sodium lauryl sulphate in 20% concentration of solids, and a proportionately increased amount of sodium sulphate. The presence of 0.1% p-tolylthiourea gives similarly satisfactory results.

Other formulations which are productive of desired results are:

EXAMPLE IV

Sodium dodecylbenzene sulphonate----- 9 85

Sodium lauryl sulphate	10
Sodium tripolyphosphate	50
Tetrasodium pyrophosphate	10
Sodium sulphate	17
Sodium carbonate	1.8
Sodium carboxymethylcellulose	0.5
Lauric monoethanolamide	1.5
Phenylthiourea	0.2

EXAMPLE V

	Percent
Sodium coconut monoglyceride sulphate	25
Sodium tripolyphosphate	40
Sodium sulphate	34.5
p-Tolylthiourea	0.5

EXAMPLE VI

	Percent
Sodium tripolyphosphate	99.5
Phenylthiourea	0.5

While the invention has been described in conjunction with its effect in substantially completely preventing the tarnishing of articles of German silver alloy, it is to be understood that it is also useful in conjunction with detergent compositions which are to be applied to other metals and alloys subject to tarnishing by such compositions. However, it is particularly effective with detergent compositions intended for use with the class of predominantly copper base alloys of which German silver and brass are well known members.

The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

Having described the invention what is desired to be secured by Letters Patent is:

1. A detergent composition tending normally in water solution to cause tarnishing of a copper base alloy consisting essentially of about 10 to about 50% of a water-soluble non-soap synthetic detergent selected from the group consisting of the anionic organic sulphated and sulphonated detergents, about 10 to about 80% of a water-soluble inorganic polyphosphate, and having incorporated therein monophenyl thiourea in an amount up to about 1% and sufficient to inhibit said tarnishing.

2. A detergent composition tending normally in water solution to cause tarnishing of a copper base alloy consisting essentially of about 10 to about 50% of a water-soluble non-soap synthetic detergent selected from the group consisting of the anionic organic sulphated and sulphonated detergents, about 10 to about 80% of a water-soluble inorganic polyphosphate, and having incorporated therein monotolyl thiourea in an amount up to about 1% and sufficient to inhibit said tarnishing.

3. A detergent composition tending normally in water solution to cause tarnishing of a copper base alloy consisting essentially of about 10 to about 50% of a water-soluble non-soap synthetic detergent selected from the group consisting of the anionic organic sulphated and sulphonated detergents, about 10 to about 80% of a water-soluble inorganic polyphosphate, and having incorporated therein di-tolyl thiourea in an amount up to about 3% and sufficient to inhibit said tarnishing.

4. A detergent composition consisting essentially of about 10 to 50% of a water-soluble anionic organic synthetic detergent selected from the class consisting of the water-soluble anionic organic detergents sulphates and sulphonates, and about 10 to 80% of water-soluble inorganic polyphosphate salts selected from the group consisting of tripolyphosphates, pyrophosphates, hexametaphosphates, tetraphosphates and mixtures thereof, and having incorporated therein about .05 to about 3% by weight of unsymmetrical mononuclear aryl thiourea.

5. A built detergent composition normally tending in water solution to cause tarnishing of a copper base alloy

consisting essentially of about 10 to about 50% of a water-soluble synthetic detergent selected from the group consisting of anionic organic sulphated and sulphonated synthetic detergents and about 10 to about 80% of a water-soluble inorganic tripolyphosphate salt, and having incorporated therein phenyl thiourea in an amount up to about 1% and sufficient to inhibit said tarnishing.

6. A built detergent composition normally tending in water solution to cause tarnishing of a copper base alloy consisting essentially of about 10 to about 50% of a water-soluble synthetic detergent selected from the group consisting of anionic sulphated and sulphonated synthetic detergents and about 10 to about 80% of a water-soluble inorganic tripolyphosphate salt, and having incorporated therein tolyl thiourea in an amount up to about 1% and sufficient to inhibit said tarnishing.

7. A built heat-dried detergent composition in particular form and normally tending in water solution to cause tarnishing of a copper base alloy which consists essentially of about 10 to about 50% of a water-soluble higher alkyl benzene sulphonate detergent and about 20 to about 60% of a water-soluble inorganic tripolyphosphate salt, and having incorporated therein a thiourea compound selected from the group consisting of mono-phenyl and mono-tolyl thiourea in an amount up to about 1% and sufficient to inhibit said tarnishing.

8. A detergent composition normally tending in water

solution to cause tarnishing of a copper base alloy consisting essentially of a water-soluble inorganic polyphosphate; and having incorporated therein a minor amount of a mononuclear aryl thiourea sufficient to inhibit said tarnishing.

9. A detergent composition in accordance with claim 8 which contains about 10 to 80% of a water-soluble inorganic polyphosphate and about 10 to about 50% of a water-soluble organic detergent selected from the group consisting of water-soluble organic sulfated and sulfonated detergents.

10. A detergent composition normally tending in water solution to cause tarnishing of a copper base alloy consisting essentially of a water-soluble inorganic tripolyphosphate salt, and having incorporated therein a minor amount of a thiourea derivative selected from the group consisting of mono-phenyl and mono-tolyl thiourea sufficient to inhibit said tarnishing.

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