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2,903,431

NONTARNISHING DETERGENT COMPOSITIONS CONTAINING STANNOUS SALTS

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No Drawing. Application August 16, 1955 Serial No. 528,814

16 Claims. (Cl. 252-135)

This invention relates to detergent compositions containing tarnish inhibitors and more particularly to polyphosphate compositions containing water-soluble stannous salts as tarnish inhibitors.

Compositions containing polyphosphates are now widely used for detergent and other purposes. Aqueous solutions of polyphosphates tend, when at certain pH values to tarnish copper, and nickel and copper alloys such as 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 or alloy for several minutes. Since German silver is frequently used for household articles commonly washed in polyphosphatebuilt 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 copper, and nickel and copper alloys such as German silver. The tarnish inhibitors of the invention are water-soluble inorganic and organic stannous salts, for example, stannous chloride, bromide, fluoride, tartrate, iodide, and sulfate. Stannic salts on the other hand are ineffective to inhibit the formation of tarnish.

It has not been possible to determine the exact form of the tin compounds present in washing solutions of the detergent compositions due to the complexity of the system. It is believed that a minor proportion of the water-soluble stannous salt may be converted into a stannite or a soluble tin-polyphosphate complex. For the 45 sake of clarity, therefore, the tarnish inhibitors are referred to as water-soluble stannous salts, especially since on a production basis the tarnish inhibitors are added to the crutcher slurry of the detergent product in the form of water-soluble stannous salts.

An amount of the water-soluble stannous salt 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 stannous salt in question, upon the tendency of the polyphosphate with which it is used to tarnish copper, and nickel and copper alloys, and upon the amount of polyphosphate present. In general, therefore, at least about 1.3% of the water-soluble stannous salt based on the weight of the polyphosphate present in the detergent composition will inhibit the formation of tarnish by the composition. The maximum amount of the stannous salt 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 6.7%.

The tarnish inhibitors of the present invention are effective with water-soluble alkali metal polyphosphates

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at pH values where such polyphosphates tend to tarnish German silver, i.e., usually within the range of about pH 7 to about pH 11. The alkali metal polyphosphates may include, by way of example, pentasodium and pentapotassium tripolyphosphates, 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 organic nonsoap detergents which may be either anionic, cationic, or nonionic detergents and builders, water, and inert materials. These detergent compositions may contain alkali metal polyphosphate in any amount, usually between 5% and 50%; conventional proportions of organic nonsoap detergent, usually within the range between 5% and 40%; at least about 1.3% of a water-soluble stannous salt based on the weight of the polyphosphate; and the balance builders and inert materials.

The alkylaryl sulfonates are a class of anionic detergents which may be included in the detergent compositions. One example thereof 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_1 and R_2 are alkyl, of the type formula C_nH_{2n+1} , and at least one R is a polypropylene group, the whole alkyl group containing preferably twelve to fifteen carbon atoms. These are known compounds, whose preparation and properties are set forth in U.S. Patent No. 2,477,383 to Lewis, issued July 26, 1949; they are available in commerce under the trade names "Oronite," "Ultrawet," and "Neolene."

Another class of useful nonsoap detergents are the amidoalkane sulfonates which are characterized by the following structure:

Where A is hydrogen or 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 of alkylene radical, such as myristyl, palmityl, oleyl and stearyl. Sodium palmitic tauride, sodium palmitic methyl tauride, sodium myristic methyl tauride, sodium palmitic 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 of aliphatic sulfonic acids, esters of sulfuric acid with aliphatic alcohols of ten

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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 10 formation of tarnish upon copper, and nickel and copper detergents having the following general formula:

-A—(CH₂CH₂O)_x—<math>CH₂CH₂OH

where R is a straight or branched chain saturated or unsaturated hydrocarbon group having from eight to 15 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 20 of ethereal oxygen and sulfur, carboxylic ester and thiocarboxylic ester groups and x is a number from eight to twenty. R can, for example, be a straight or branched chain octyl, nonyl, decyl, lauryl, myristyl, cetyl or stearyl group, or an alkyl aryl group such as octylbenzene, nonyl- 25 benzene, decylbenzene, stearylbenzene, etc.

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

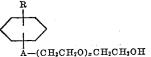
$$R$$
— A — $(CH2CH2O)x— $CH2CH2OSO3M$$

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 con- 35 densation with ethylene oxide. Typical of this type of alkyl ether are the condensation products of oleyl or dodecyl alcohol or mercaptan with from eight to seventeen moles of ethylene oxide, such as "Emulfor ON," "Nonic 218" and "Sterox SE" and "SK." Typical alkyl 40 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 45 an alkyl phenol or thiophenol.

The ethoxynated alkyl phenols and thiophenols have the following general formula:



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

The optional supplemental builders may be alkali metal inorganic salts, typical examples of which include sodium and potassium sulfates, sodium and potassium chlorides, 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 carboxymethyl cellulose can be used as builders.

The builder mixture is so chosen among alkaline, neutral, and acidic salts that the composition obtained in an aqueous 0.14% washing solution has a pH of about 7 or above. Preferably its pH lies within the range of about 7 to about 11, since solutions which are more alkaline may be irritating to the skin and tend to weaken some fabrics, particularly woolens. In general, the alkali metal carbonates are preferred agents for bringing the pH of the solution to a high alkaline value within the preferred range.

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The detergent compositions of the invention inhibit the alloys such as 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 spraydried detergent compositions, or may be in liquid form.

The polyphosphate detergent compositions may be prepared by conventional methods, as by blending the ingredients thereof in an aqueous solution or slurry and then drying the resulting mixture in a spray or drum dryer at elevated temperatures.

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

The compositions of the invention will be further illustrated by the following examples wherein a typical watersoluble stannous salt, namely stannous chloride dihydrate, was employed in the compositions. In these examples the following test procedure was employed. An amount of the polyphosphate composition was dissolved in somewhat less than one quart of water at a temperature under 170° F. to provide 2.25 grams of polyphosphate per quart of solution. A tarnish inhibitor was then added thereto in the form of a solution. More water was then added thereto to give a total volume of one quart. 300 mls. of the solution were placed in a beaker and the temperature adjusted to 160° F. to 170° F. A strip of metal, such as German silver, 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. to 170° F. The metal strip was then removed, rinsed and dried with a cloth. The strip was visually examined for tarnish and the effectiveness of the tarnish inhibitor rated as follows:

45	Grade No.	Degree of Tarnish
50	0	No tarnish. Interface stain only. Barely noticeable tarnish. Slight tarnish. Moderate tarnish. Considerable (heavy) tarnish. Severe, as when inhibitor is absent.

Examples 1-18 below show that at least about 3% of a water-soluble stannous salt based on the weight of polyphosphate inhibits the formation of tarnish by typical polyphosphates, such as pentasodium tripolyphosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, and hexasodium tetrapolyphosphate. More specifically, the examples show that at least about 3% of stannous chloride based on the weight of polyphosphate is effective in inhibiting the formation of tarnish by pentasodium tripolyphosphate and tetrasodium pyrophosphate, while at least about 0.3% of stannous chloride is effective in inhibiting the formation of tarnish by sodium hexametaphosphate and at least about 1% of stannous chloride is effective in inhibiting the formation of tarnish by hexasodium tetrapolyphosphate.

EXAMPLES 1-18

To separate 2.25 gram portions of the four polyphosphates listed below dissolved in distilled water were added varying proportions of stannous chloride, and the volume diluted to one quart in accordance with the above test procedure. The tarnish grading upon German silver was as follows.

Percent Stannous Chloride (polyphosphate basis)	0	0.3	0.6	1.1	2.2	3.3	4.4	
Polyphosphate			Tar	nish (₹rade			
Pentasodium Tripolyphosphate (Examples 1-5). Tetrasodium Pyrophosphate (Examples 6-10) Sodium Hexametaphosphate (Examples 11-15).	6 6	3	2	6 5 2	5 5	4 2	3 2	3
Hexasodium Tétrapolyphos- phate (Examples 16–18)	6			. 4	2			

A water-soluble stannous salt is effective as a tarnish inhibitor in polyphosphate compositions which contain an organic nonsoap detergent as shown by Examples 19–22.

EXAMPLES 19-22

0.9 gram of sodium dodecylbenzenesulfonate and 2.25 grams of pentasodium tripolyphosphate were dissolved in distilled water, and 4.4% of stannous chloride based on the weight of the polyphosphate added thereto, and the solution diluted to a volume of one quart. This solution tarnished German silver only to grade 1 while an identical solution without the presence of the stannous chloride tarnished German silver to grade 6. Tetra sodium pyrophosphate was substituted in the same amount for the pentasodium tripolyphosphate in the above composition. A strip of German silver metal placed in the solution of the composition containing stannous chloride was tarnished only to grade 1, whereas a strip of German silver metal placed in the solution of the composition without the presence of the stannous chloride tarnished to grade 6.

The addition of a water-soluble stannous salt to polyphosphate compositions containing an organic nonsoap detergent, which may be either anionic, nonionic, or cationic, as well as supplemental builders inhibits the formation of tarnish by such detergent compositions. This is clearly illustrated by the examples set forth below wherein the following two compositions, or specified modifications thereof, were employed.

Compositions	x	Y	
Sodium Dodecylbenzene-sulfonate Tetrasodium Pyrophosphate Pentasodium Tripolyphosphate Sodium Carbonate Sodium Silicate Sodium Carboxymethylcellulose Water Sodium Sulfate and Miscellaneous Inert Materials	18. 0 45. 0 3. 0 6. 0 0. 5 7. 0 20. 5	18.0 45.0 3.0 6.0 0.5 7.0 20.5	Ē
Total	100	100	ŧ

In compositions X and Y the amounts of the various components are expressed in percent by weight.

EXAMPLES 23-34

To 5 grams each of compositions X and Y there was added stannous chloride in the proportions shown below and the test procedure carried out with the following results.

Percent Stannous Chloride, Polyphosphate Basis	0	1.1	1.3	1.7	2. 2	6.7
Grading (Composition X) (Examples 23-28). Grading (Composition Y) (Examples 29-34)	6	6	4	2	1	1

Examples 23-34 show that at least about 1.3% of stannous chloride based on the weight of polyphosphate inhibits the formation of tarnish by polyphosphate compositions containing an organic anionic nonsoap detergent and supplemental builders.

A stannous salt is effective as a tarnish inhibitor in polyphosphate compositions containing an organic non5 soap 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 10 35-38 set forth below.

EXAMPLES 35-38

Sodium hexametaphosphate and hexasodium tetrapolyphosphate were each substituted for the same amount of tetrasodium pyrophosphate in composition X and the compositions tested in accordance with the test procedure. 5 grams of each of these compositions in a quart of water tarnished German silver to a grading of 6, i.e., severe tarnish. When 4.4% of stannous chloride based on the weight of polyphosphate was added to each of these compositions, the tarnish grading of both compositions upon German silver was reduced to grade 1, indicating interface stain only.

A stannous salt is also effective as a tarnish inhibitor in polyphosphate compositions containing other organic anionic nonsoap detergents as well as supplemental builders as shown by Examples 39–42.

EXAMPLES 39-42

30 The organic anionic nonsoap detergents, the sodium salt of N-palmitoyl-N-methyl taurine and sodium-3-do-decyloxy-2-hydroxypropane sulfonate, were substituted separately for the same amount of sodium dodecylbenzene-sulfonate in composition X. When 5 grams of each of these compositions was tested in accordance with the test procedure, both compositions tarnished German silver to grade 6, indicating severe tarnish. The tarnish was reduced to grade 4 when 2.2% of stannous chloride based on the weight of polyphosphate was included in the composition containing the sodium salt of N-palmitoyl-N-methyl taurine, while the tarnish was reduced to grade 2 when 2.2% of stannous chloride based on the weight of polyphosphate was included in the composition containing sodium-3-dodecyloxy-2-hydroxypropane sulfonate.

A water-soluble stannous salt is also effective as a tarnish inhibitor in polyphosphate compositions containing either an organic cationic nonsoap detergent or an organic nonionic nonsoap detergent as well as supplemental builders, as illustrated by Examples 43–46.

EXAMPLES 43-46

18% of an organic cationic nonsoap detergent, namely the lauric ester of N-(beta-hydroxyethyl)-alpha-(chloropyridinium) acetamide, was substituted for the sodium dodecylbenzenesulfonate in composition X. A second composition was prepared wherein 18% of an organic nonionic nonsoap detergent, namely Pluronic L-64, a compound having the empirical formula

$HO - (C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$

prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol where b is an integer selected from the group consisting of 26 to 30 and a plus c is an 65 integer such that the molecule contains from 40% to 50% of ethylene oxide, was substituted for the sodium dodecylbenzenesulfonate in composition X. 5 grams of each of these compositions when dissolved in one quart of water and tested in accordance with the test procedure 70 tarnished German silver to grade 6. When 2.2% of stannous chloride based on the weight of polyphosphate was added to each of these compositions, they both then had a tarnish grading of 4, thereby showing a considerable improvement.

The amount of the organic nonsoap detergent present

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in the polyphosphate composition may be varied within the range from about 5% to about 40% as noted above and as further illustrated by Examples 47-50.

EXAMPLES 47-48

5% of sodium dodecylbenzenesulfonate was employed in composition X with the amount of sodium sulfate being increased to offset the decrease in the sodium dodecylbenzenesulfonate content of the composition. 5 grams of this modified composition dissolved in a quart of distilled water and a tarnish grading of 6 upon German silver metal, whereas 5 grams of the composition which also contained 2.2% of stannous chloride based on the weight of polyphosphate had a reduced tarnish grading

EXAMPLES 49-50

The following composition was prepared having a high detergent content:

Composition	Percent by Weight	
Sodium Dodecy lbenzenesulfonate	40. 0 45. 0 3. 0 6. 0 0. 5 5. 5	
Total	100	

When 5 grams of this composition was tested in accordance with the test procedure upon German silver metal the metal had a tarnish grade of 6. When 1.7% of stannous chloride based on the weight of polyphosphate was added to the above composition, the composition tarnished German silver only to grade 3.

The water-soluble stannous salts are effective as tarnish inhibitors when incorporated in a detergent-polyphosphate slurry and the slurry drum-dried as shown by the following example.

EXAMPLE 51

The composition shown below was prepared in the form of an aqueous slurry having a 30% water content and drum-dried. 5 grams of the drum-dried product per quart of distilled water tarnished German silver only to grade 1.

Composition	Percent by Weight
Sodium Dodecylbenzenesulfonate	6.0
Total	100

¹ Percent stannous chloride based on polyphosphate 2.2%.

Examples 52-53 illustrate the fact that the stannous salts 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 52-53

5 grams of composition X dissolved in a quart of water having a hardness of 180 p.p.m. tarnished German silver to grade 6, whereas 5 grams of composition X containing 2.2% of stannous chloride based on the weight of polyphosphate dissolved in a quart of water having a hardness of 180 p.p.m. tarnished German silver only to grade 2.

The effectiveness of water-soluble stannous salts as

tarnish inhibitors with liquid polyphosphate detergent compositions is clearly illustrated in Examples 54-57.

EXAMPLES 54-57

Four 11.25 gram portions of the following liquid detergent composition were dissolved separately in one quart of distilled water and stannous chloride added thereto at the concentrations indicated below. The tarnish grading of a strip of German silver metal inserted in each of the solutions 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 5 grams of granulated detergent containing 45% polyphosphate.

Composition		Percent by Weight		
Potassium Dodecylbenzenesulfonate Sodium Xylenesulfonate Lauric Isopropanolamide Lauric Diethanolamide Tetrapotassium Pyrophosphate Sodium Silicate Water Total				10. 0 7. 6 3. 2 3. 8 20. 0 7. 0 48. 4
Example No	54	55	56	67
Percent Stannous Chloride, polyphosphate basis. Tarnish Grade.	0	1. 1 5	1.3 2	1.

The effectiveness of a water-soluble stannous salt in inhibiting the formation of tarnish upon metals and alloys other than German silver when the metals or alloys are immersed in a solution of the polyphosphate composition was tested in accordance with the test procedure given above using 5 grams of composition X containing stannous chloride and the results of the test given below in Table I.

Table I

Metal or Alloy	Stannous Chloride, 3.3% by weight based on polyphosphate
Brass (alloy of copper and zinc) Coinage Nickel (alloy of nickel and copper) Copper Monel (alloy of nickel, copper, manganese and iron)	2 1 4 1

The results of the test show that a stannous salt is highly effective in inhibiting the formation of tarnish upon brass, coinage nickel, and Monel, and is moderately effective in inhibiting the formation of tarnish upon conner.

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

We claim:

- 1. The process of cleaning articles formed of copper and copper and nickel alloys without imparting appreciable tarnish thereto which comprises washing said articles with a detergent composition consisting essentially of an alkali metal polyphosphate which in aqueous solution having a pH of from about 7 to about 11 tarnishes copper and copper and nickel alloys and a water soluble stannous salt in an amount to lessen the tarnishing action of the polyphosphate.
- 2. The process as set forth in claim 1 wherein the detergent composition contains at least about 3% by weight of the stannous salt based on the weight of the polyphosphate present in the composition.

3. The process as set forth in claim 1 wherein the water-soluble stannous salt is stannous chloride.

4. The process as set forth in claim 1 wherein the alkali metal polyphosphate is tetrasodium pyrophosphate.

5. The process as set forth in claim 1 wherein the alkali metal polyphosphate is sodium hexametaphosphate.

6. The process as set forth in claim 1 wherein the alkali metal polyphosphate is hexasodium tetrapolyphosphate.

alkali metal polyphosphate is pentasodium tripolyphos-

- 8. The process of cleaning articles formed of copper and copper and nickel alloys without imparting appreciable tarnish thereto which comprises washing said 15 articles with a detergent composition consisting essentially of from about 5% to about 50% of an alkali metal polyphosphate which in aqueous solution having a pH of from about 7 to about 11 tarnishes copper and copper and nickel alloys, from about 5% to about 40% of an organic nonsoap detergent, and a water-soluble stannous salt in an amount of at least about 1.3% based on the weight of the polyphosphate and sufficient to inhibit such tarnishing.
- 9. The process as set forth in claim 8 wherein the 25 alkali metal polyphosphate is pentasodium tripolyphosphate.
 - 10. The process as set forth in claim 8 wherein the

10 alkali metal polyphosphate is tetrasodium pyrophosphate.

11. The process as set forth in claim 8 wherein the alkali metal polyphosphate is sodium hexametaphosphate.

12. The process as set forth in claim 8 wherein the alkali metal polyphosphate is hexasodium tetrapolyphos-

13. The process as set forth in claim 8 wherein the water-soluble stannous salt is stannous chloride.

14. The process as set forth in claim 8 wherein the 7. The process as set forth in claim 1 wherein the 10 organic nonsoap detergent is an organic cationic nonsoap detergent.

> 15. The process as set forth in claim 8 wherein the organic nonsoap detergent is an organic nonionic nonsoap detergent.

16. The process as set forth in claim 8 wherein the organic nonsoap detergent is an organic anionic nonsoap detergent.

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