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SILVER ANTITARNISH COMPOSITIONS

Harry Kroll, Warwick, Alderic R. Therrien, Jr., Woonsocket, and Phyllis W. Bennett, North Scituate, R.I., assignors, by mesne assignments, to Philip A. Hunt Chemical Corporation, a corporation of Delaware

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This invention relates to a composition for cleaning and polishing silver and protecting the cleaned polished surface. Of course, it is evident it is useful for cleaning and polishing metals which act chemically like silver.

The physical properties of silver make this metal useful in a number of important applications. One of the more important properties of the metal is its high reflectivity. It is this physical characteristic which makes it desirable for use in tableware, art objects, in jewelry, and in electrical components. Although silver is considered to be a chemically inert element, the metal when exposed to an atmosphere containing sulfur forms unsightly brown to black surface films. The tarnish which is a result of the formation of silver sulfide and silver oxide, detracts from the appearance of the metal and may also interfere with its use in specific applications.

It is the purpose of this invention to provide a composition of matter, containing several components, which (1) removes existing tarnish, (2) cleanses the metal surface, (3) protects the silver against further tarnish, and (4) imparts a high lustre to the surface.

Metallic silver is used commercially in several different forms. The most common are pure silver, silver alloys, and silverplate. Each of these has its resistance to tarnishing. For example, sterling silver develops tarnish less rapidly than electroplated silver. To complicate this problem further, electroplating baths for depositing silver contain additives which function as brighteners. These substances are plated with the silver on the base metal thus modifying the electrodeposited surface and its reaction to tarnish producing chemicals.

There are other factors which influence the rate of tarnish formation on silverplate or sterling silver. Cutlery, flatware, and holloware are exposed to proteinaceous foodstuffs. Depending on their prior treatment, these foods contain varying amounts of hydrogen sulfide and sulfur-containing natural products. Tarnish produced by eggs on silverware is a well known example. The combustion of solid and liquid fuels is perhaps the most common source of sulfur contamination in the atmosphere. All forms of silver when exposed to atmospheres containing minute amounts of combustion products develop a tenacious brown tarnish.

It is the purpose of this deview of the factors contributing to the formation of silver tarnish to point out the complexity of this process and to emphasize that different types of tarnish may be produced on silver surfaces. Despite the complicated nature of tarnish formation, it is the object of this invention to disclose novel compositions of matter for removing all types of silver tarnish and to protect silver against the formation of tarnish regardless of the causative factors.

A number of chemical treatments have been proposed for preventing the tarnishing of silver. In the electronics industry, silver contacts have been plated with rhodium, gold, or platinum. This process is expensive and is unsuitable for many items produced from silver and its alloys. Various types of chromate treatments have also been described. These include both chemical and electrochemical depositions. These protective coatings afford silver a limited protection but because of the toxicity of chromium salts, they cannot be used on silver plate or silverware in contact with edibles. A further disadvantage of chromate treatment is the difficulty in producing consistent protection. Lacquer and silicone coatings have also been used, but these coatings are only effective as long as the film remains intact. Abrasions and other breakthroughs of the protective film exposes the silver to the tarnishing process.

More recently, high molecular weight straight chain alkyl mercaptans, such as octadecyl mercaptan, have been proposed as antitarnishing agents. Although these compounds provide a temporary protection, they tend to dull the lustre of bright silver and its alloys and they leave an objectionable greasy film on the surface of the metal.

The removal of tarnish from the surface of metallic silver and depositing simultaneously a protective film is a delicate process involving several chemical reactions and requires the blending of several components, which if not compatible, will fail to produce the desired effect. The removal of the tarnish film from the surface of the silver while at the same time depositing a protective film is obviously a complex process but the formulations of this invention achieve this objective.

Other objects and advantages of this invention will in part be obvious and in part appear hereinafter.

This invention accordingly is in a composition of matter comprising a liquid carrier, or solid, finely divided abrasive carrier, containing 0.1–10% of a mercapto ester having a structure corresponding to

$$\mathrm{HS(CH_2)_n{-}\overset{\overset{\large O}{\|}}{C}{-}OR}$$

wherein

$n=1$ or 2, and R is a straight or branched alkyl group containing 12 to 18 carbon atoms, and

0.1% to 10% of an amine salt having a formula corresponding to

$$\left[\begin{array}{c} \quad\ R_2 \\ \quad \diagup \\ R_1{-}\overset{+}{N} \\ \ |\ \diagdown \\ \ H \quad R_3 \end{array}\right] X^-$$

where

R_1 is a straight or branched chain alkyl group containing 8 to 20 carbon atoms,

R_2 and R_3 are hydrogen, methyl, or ethyl, and X is the anion derived from a low molecular weight water soluble organic acid,

said composition being capable of preventing silver and its alloys from tarnishing when exposed to hydrogen sulfide and hydrogen sulfide generating chemicals.

The composition is characterized by the presence of a pair of components, the long chain alkyl thio ester of a mercaptan and the long chain alkyl amine salt of water soluble acid. It is these ingredients which dissolve the tarnish and deposit the protective finish on silver. The abrasive carrier may be any usual polishing abrasive, e.g., pumice, rouge, diatomaceous earth, calcium carbonate etc., the degree of fineness being consistent with the high polished surface and hardness enough to work on the film.

The liquid carrier may be water, in which the active ingredients are emulsified, or dissolved, or it may be an organic solvent such as isopropanol, or chlorinated hydrocarbon.

Within this family of compounds mercapto esters such as lauryl thiogylcolate, lauryl 2-mercaptopropionate, cetyl thioglycolate, stearyl thioglycolate, stearyl 2-mercaptopropionate, etc. are capable of imparting antitarnish protection to silver. This protective film is essentially monomolecular and is different from that described for the high molecular weight mercaptan, in that this protection is transient in nature, because the effect wears off after a few days. However, in contrast to the tenacious mercaptan film, produced by the high molecular weight alkyl mercaptans, which produce a yellowish and undesirable hue on the polished silver surface, the mercapto esters form protective films which are colorless and enhance the reflective properties of the silver. This formation of colorless film is highly desirable for silverware, tableware, decorative items, and other objects where the bright natural lustre of silver is desired.

This invention therefore is concerned with compositions of matter which improve the antitarnish properties of the mercapto esters. To produce a more lasting protective action, we have found that the organic salts of high molecular weight amines when blended with the mercapto esters increase the durability of the antitarnish protection. The amines which can be used in these formulations are straight chain alkyl groups containing 12 to 18 carbon atoms. The amines may be primary, secondary or tertiary. Dodecylamine, dimethyl hydrogenated tallow amine, N-ethyl, N-hexadecylamine, octadecylamine are examples of the amines which have been used. Unsaturated amines such as octadecenyl amine, amines derived from the unsaturated fatty acids present in soy bean oil or peanut oil have also been used. The organic acids which are used to neutralize the amines are acetic acid, formic acid, citric acid, malic acid, maleic acid, fumaric acid, etc.

When a mixture of the mercapto ester and amine is formulated with abrasive agents such as calcium carbonate, finely powdered pumice, or selected forms of diatomaceous earths, the composition of matter may be used for removal of tarnish and imparting a protective film in a single treatment. The incorporation of a nonionic surfactant in the formulation will provide a cleansing action and a means of dispersing the tarnish removed by the polishing action. The surfactant will also aid in the rinsing and cleaning of the polished silver, which on drying will exhibit a high lustre.

Mixtures of mercapto ester and amine salt may be emulsified in water, and these emulsions are capable of imparting a protective film to silver immersed in the liquid. These compositions are not limited to use in aqueous vehicles. Mixtures of mercapto esters and amine salts may be dissolved in organic solvents such as trichlorethylene or isopropanol. Silver plated test panels, sterling silver dinnerware and other objects immersed in these solutions develop an invisible protective coating which will protect the metal from tarnishing when exposed to sulfur contaminated atmospheres and especially highconcentration s of water soluble inorganic sulfides.

Another novel way in which the compositions of matter of this invention may be used is to impregnate a soft cotton flannel cloth or cellulose sponge with a mixture of mercapto ester, amine salt, and abrasive. This cloth, when moistened with water, can be used to polish silver. The polishing process will remove tarnish and produce an antitarnish protective film on the metal.

The following examples illustrate the compositions of matter and demonstrate the novel features of the invention.

Example I

	Parts
Stearyl 2-mercaptopropionate	3
Octadecylamine acetate	1
(Surfactant nonylphenol plus 6 moles ethylene oxide)	2

The above chemicals were mixed to yield a clear solution and added to 86 parts of water. To this emulsion was added 8 parts of calcium carbonate.

Copper panels, 2 inch x 2 inch, plated with silver and polished to a high lustre were thoroughly rubbed with the above composition. After rinsing the treated panels in running water, they were wiped clean with a soft cloth. The treated panels were immersed in an 0.3% solution of potassium sulfide in water for five minutes. No tarnish was evident after 5 minutes immersion. An untreated panel turned black in 30 seconds.

Example II

	Parts
Octadecyl thioglycolate	3.0
Tallow amine acetate	0.5
Calcium carbonate	7.0
Pumice, fine	1.0
Water	86.0

The above composition was formulated in a manner similar to that described in Example I.

Silver plated panels were immersed in 0.3% potassium sulfide solution for five minutes and a brownish-black tarnish formed on the metal surface.

The panels were polished with a cloth which had been dipped in the above formulation. The removal of the tarnish was readily accomplished leaving a lustrous silver surface. The treated silver panels were reimmersed in the potassium sulfide solution for ten minutes. There was no sign of tarnish on the panels after the second exposure to the tarnishing agent.

Example III

	Parts
Lauryl thioglycolate	3.0
N-methyl N-dodecylamine formate	1.0
Pumice, fine	4.0
Calcium carbonate	4.0
Water	86.0

The above formulation was made up according to the procedure in Example I.

Two sterling silver candy bowls, 3 inches in diameter, were polished with the paste described in this example. One of the bowls was placed in an 0.3% solution of potassium sulfide for ten minutes. No tarnish was detected on the bowl. The second bowl was stored for 2 hours in an atmosphere of hydrogen sulfide generated from a solution of ammonium sulfide. At the end of this time, there was only a faint trace of tarnish on the treated bowl whereas an untreated control had a black film.

Example IV

The following test was carried out to demonstrate the difference between a silver polish containing a straight chain alkyl mercaptan and a mercapto ester.

The following formulation was prepared by the process of Example I.

	Percent
Stearyl thioglycolate	4.0
Tallow dimethylamine acetate	0.1
Lauryl alcohol plus 4 ethylene oxide	3.9
Calcium carbonate	2.0
Diatomaceous earth	1.0
Methyl cellulose	1.0
Water	86.0

This product was compared to a commercial silver polish "A" which contains a high molecular weight straight mercaptan.

Two silver plated panels were immersed in an 0.3% potassium sulfide solution for five minutes. A blue black tarnish formed on the two test panels.

One panel was polished with commercial silver polish "A" and the second panel was polished with the composition described in this example.

The polished panels were rinsed in lukewarm tap water and dried with soft flannel cloths. The panel which had been cleaned with the commercial polish had a faint yellowish color whereas the second test panel retained the bright metallic lustre of the original silverplate.

Both panels were immersed in a fresh 0.3% solution of potassium sulfide maintained at a temperature of 25° C. After five minutes, the panel treated with commercial polish began to show brown spots of tarnish whereas the panel cleaned with the composition described in this example showed no stains. After 10 minutes, the first panel (polished with the commercial polish) showed a uniform golden brown tarnish whereas the second panel (treated with the composition in this example) remained untarnished.

Example V

The mixture of mercapto ester and amine salt is useful for preparation of silver antitarnish polishing cloths.

The cloths were prepared as follows: stearyl thioglycolate, 10 grams, and tallow amine acetate, 3.0 grams, was dissolved in 33 grams of isopropanol. The solution was added to 54 grams of a commercial suspension of pumice. The solution was uniformly dispersed and coated on a No. 4 cotton flannel weighing 2.7 grams. The pickup of the dispersion by the cloth was 12.0 grams. The treated cloth was air dried for 12 hours. The pickup of solid on the dried cloth was 6.9 grams or 2.5 grams of solid/gram of cloth.

A similar cloth was prepared using the suspension of pumice only and omitting the stearyl thioglycolate and tallow amine acetate.

Two 2 inch x 2 inch silver plated panels were immersed in a 1% solution of potassium sulfide until thoroughly stained. The panels were rinsed and dried.

Panel 1 was cleaned with a moistened cloth treated with pumice suspension but not containing stearyl thioglycolate and tallow amine acetate. The cloth removed the tarnish readily.

Panel 2 was treated similarly with cloth containing the pumice, stearyl thioglycolate, and tallow amine acetate. This cloth removed the tarnish readily.

Panel 1 and panel 2 were immersed in a 1% solution of potassium sulfide for 15 minutes.

The results were that panel 1 was badly tarnished whereas panel 2 remained untarnished.

One the basis of this and a long sequence of like experiments with various combinations of mercapto ester and amine salt, it was concluded that the mercapto ester and amine salt plus a polishing agent could be impregnated on a suitable fabric which in turn can be used to impart an antitarnish preventative on silver.

Example VI

The following formulation was used to treat silver plated samples by immersion into an organic solvent.

Octadecyl thioglycolate, 120 grams, is dissolved in 3800 milliliters of trichloroethylene. Tallow amine acetate, 40.0 grams, is dissolved in this solution.

A sterling silver mug was immersed in this solution for 15 minutes. The mug was removed from the solution and rinsed in clean trichloroethylene. The sterling silver mug did not tarnish when immersed in an 0.5% solution of potassium sulfide for 10 minutes.

Example VII

Octadecylamine acetate, 4.0 grams, was added to 12.0 grams of octadecyl thioglycolate, and the mixture was warmed to 80° C. A clear amber liquid was obtained. The oil was dispersed in 300 milliliters of water heated to 70° C. A milky white emulsion was obtained.

Silver plated panels were immersed in this emulsion for ten minutes and then rinsed rapidly in isopropanol and dried in a jet of warm dry air.

The treated panels were bright and lustrous, and no superficial films could be detected visually. The panels were treated in a closed container having atmosphere equivalent to 200 parts per million of hydrogen sulfide. The panels did not develop a tarnish film in six hours whereas untreated controls were tarnished within 15 minutes.

What is claimed is:

1. A composition wherein active ingredients consist essentially of 0.1–10 parts of a mercapto ester having the structure

$$HS(CH_2)_n-\overset{\overset{O}{\|}}{C}-OR$$

where

n is an integer of value in the range 1 and 2, and R is any alkyl group containing 12 to about 18 carbon atoms, and

0.1 to 10 parts of an amine salt having the formula

$$\left[\begin{array}{c} \quad\;\; R_2 \\ R_1-\overset{+}{N} \\ \;\; H \quad R_3 \end{array}\right] X^-$$

where

R_1 is an alkyl group containing 8 to about 20 carbon atoms, R_2 and R_3 are selected from the group consisting of hydrogen, methyl, and ethyl, and

X is the anion derived from a low molecular weight water soluble organic acid,

said composition being capable of preventing silver and its alloys from tarnishing when exposed to hydrogen sulfide and hydrogen sulfide generating compositions.

2. A composition of matter as defined in claim 1 which includes 0.1 to about 10 parts of a polishing abrasive agent, said composition being capable of removing tarnish from the surface of silver and its alloys, and imparting a film to the metal surface which will prevent the formation of new tarnish.

3. A polishing cloth impregnated with the composition of matter described in claim 2, capable of removing tarnish from silver and its alloys, and imparting a protective film to the metal surface which prevents the formation of new tarnish.

4. A process for preventing the formation of tarnish on silver and its alloys, which comprises cleaning the surface of said silver with a composition of matter described in claim 1.

5. A process for removing tarnish from silver and its alloys and preventing the formation of tarnish which comprises cleaning the surface of said silver with the composition in claim 2.

6. A process for removing tarnish from silver and its alloys and preventing the formation of tarnish which comprises cleaning the surface of said silver with the polishing cloth described in claim 3.

7. A composition of matter described in claim 1 dissolved in a water insoluble organic solvent, said composition being capable of preventing silver and its alloys from tarnishing.

8. A composition of matter wherein active ingredients consist essentially of from 0.1% to 10% of stearyl thioglycolate and 0.1% to 10 stearyl dimethylamine acetate.

9. A composition of matter as defined in claim 1 wherein active ingredients consist essentially of from 0.1% to 10% of stearyl thioglycolate, 0.1% to 10% stearyl dimethylamine salt, and 0.1% to 20% of a mixture of diatomaceous earth and calcium carbonate.

10. A cotton cloth impregnated with a composition as defined in claim 1 wherein active ingredients consist essentially of 0.1% to 10% of stearyl thioglycolate, 0.1% to 10 % of stearyl dimethylamine salt, and 0.1% to 20% of finely divided polishing abrasive materials.

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ALEXANDER H. BRODMERKEL, *Primary Examiner.*

L. B. HAYES, *Assistant Examiner.*