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3,410,703

SILVER AND COPPER TARNISH PREVENTATIVES

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ABSTRACT OF THE DISCLOSURE

Copper, and silver, and alloy polish formulated with high molecular weight alkane mercaptides of heavy metals in solid and liquid carriers.

This invention relates to compositions characterized by their containing chemical agents which produce tarnish and corrosion resistant surfaces on silver, silver alloys, copper and copper alloys.

A second object of this invention is to provide such tarnish protective chemical compositions containing abrasives.

These compositions, when used to polish a tarnished silver or silver alloy surface, clean the metal and at the same time produce an invisible protective film against further tarnishing. The abrasive containing chemical compositions can also be used to polish copper, brass and other copper alloys to produce a lustrous tarnish resistant finish.

Unightly tarnish on silver or silver alloys is undesirable for esthetic and technical reasons. The brilliance and beauty of silver are utilized in decorative and useful articles found in the home. However, the maintenance of the lustrous quality of the metal is a tedious chore and becomes more difficult due to the ever increasing concentrations of corrosive chemicals which pollute our atmosphere.

In electrical circuits, silver is used extensively in contacts and connectors. The utility of the metal for this application lies in its low resistivity. This electrical property is adversely affected when the metal surface becomes tarnished. To protect the silver against corrosion, it may be plated with a more noble metal such as gold. This procedure is expensive and does not completely protect against tarnish since silver can migrate through a porous gold film deposited electrolytically and a mottled tarnish develops.

Copper and copper alloys are also tarnished readily. This is especially true in manufacturing areas where corrosive fumes pollute the atmosphere. Thus, in plants where copper and copper alloys are being fabricated into useful articles, a corrosion or tarnishing of the metal or alloy may result and in many instances is the cause of substandard quality and rejects. Such conditions are encountered in the jewelry industry, manufacture of copper printed circuit boards, plastics laminated with copper foil and in other articles of manufacture based on copper and copper alloys.

It is the purpose of this invention to provide compositions of matter which can prevent the tarnishing of silver, silver alloys, copper and copper alloys. This is accomplished by treating the metal surface with a chemical composition capable of forming an invisible film which acts as an impervious barrier to the corrosive elements in the atmosphere.

In U.S. Patent 2,841,501, James G. Murphy, July 1, 1958, which later appeared as Reissue Patent #24,819, May 3, 1960, there was disclosed the use of high molecular weight normal alkane primary mercaptans for producing antitarnish finishes on silver.

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In a copending application Ser. No. 378,993 now Patent No. 3,330,672 Harry Kroll, one of the inventors herein, alkyl thioglycollate esters and mercaptans mixed with high molecular weight amine salts of organic acids are described as useful to protect silver against atmospheric corrosion.

The formation of a protective film on the silver and copper has been interpreted to be a chemisorptive process in which the thiol group of the mercaptan forms a metal mercaptide with positively charged silver or copper on the metal surface. This reaction produces a close packed, highly orientated monolayer of metal mercaptide. The metal-sulfur bond of the mercaptide is very stable, so that the hydrophobic film is firmly bound to the metal surface and is not readily removed by physical treatment. Further, the metal mercaptide is insoluble in water and many organic solvents so that the removal of the film by ordinary cleaning processes is rendered difficult. These properties of the film impart to the silver a protection which prevents the formation of the tarnish.

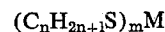
The use of high molecular weight mercaptans in formulations for treating silver or copper is replete with difficulties. Organic thiols are unstable in solution or dispersion; they undergo autoxidation to disulfides thereby decreasing their usefulness as antitarnish agents. They are also oxidized catalytically by iron salts in the presence of air or oxygen. Another undesirable feature of the n-alkane thiols is their unpleasant odor, which seriously reduces the household and industrial usefulness of the chemical in antitarnish formulations.

So it is, accordingly, a fundamental object of this invention to provide a silver cleaning and polishing composition, suitable for removing tarnish from such surfaces and deposition, at the same time, a monomolecular barrier layer which materially delays the formation of additional tarnish, the composition being characterized by its content of polyvalent metal mercaptides which are capable of forming the said monomolecular barrier layer.

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

The composition can be any small effective amount of the metal mercaptide, up to 100% thereof. Generally, it is preferred for use with a diluent such as diatomaceous earth, rouge, pumice, calcium carbonate, etc. (which also serves as an abrasive), it being understood that any abrasive used must be fine enough not to scratch and spoil the surface to be polished. Liquid dispersants may be oils, alcohols and water. The proportion of mercaptide is preferably related to the manner of use. Generally, about a 10–20% concentration on the surface being polished is desired. Hence this is a useful figure preferred for formulations. When it is desired to impregnate a cloth for ultimate use in cleaning and polishing silver surfaces, similar proportionation for impregnating the cloth is used.

We have found that certain metal mercaptides of high molecular weight normal alkane mercaptans may be used to produce highly effective antitarnish finishes on silver and copper. The useful mercaptides are those identified by the formula:

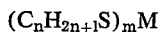


in which $m=2, 3$ or 4 , and $n=12$ to 20 , and M is a metal cation having valences of $2, 3$ or 4 as the case may be. Useful M metals are calcium, magnesium, zinc, stannic tin, lead, cadmium, titanium, zirconium. Economy indicates the preference for the more familiar metals, such as calcium, tin, zinc.

This discovery was unexpected since most metal mercaptides are highly stable and do not readily dissociate to yield the parent thiol compound. It was also found that the protective film on the silver surfaces treated with

the metal mercaptide contains both organic sulfur and metal ion. From these data, it was evident that the protective film on the silver or copper contained the added metal mercaptide.

The process of preparing metal mercaptides in its broad aspects comprises admixing a primary normal alkane mercaptan with a metal acetate, or other salt, in an inert solvent such as isopropanol. After mixing at temperatures varying from room temperature to the boiling point of the solvent, the metal mercaptide precipitates as a solid and is removed by filtration. Mercaptides, useful for purposes of the invention, prepared by this procedure have the formula:



where $m=2, 3$ or 4 and $n=12$ to 20 and M is a metal cation. Typical metals which we have used in preparing the mercaptides for carrying out this invention are magnesium, zinc, stannic tin, nickel, lead, and cadmium. Other di-, tri- and tetravalent metals are useful for the purpose, but are limited by their availability or on an economic basis.

In carrying out the invention in one form, the metal mercaptide is dissolved in an inert carrier such as pine oil, an ester of a higher fatty acid, or a nonionic surface active agent. This composition, which can vary in physical form from a gel to a free-flowing liquid, is mixed with selected surfactants and dispersed in water to yield a stable dispersion of the metal mercaptide. Clean silver articles immersed into this dispersion develop the antitarnish barrier film which is the feature of this invention. The incorporation of mild abrasives such as diatomaceous earth or pumice into the aqueous dispersion results in a composition which can be used for polishing silver, i.e., removing tarnish, and protecting the metal against subsequent atmospheric corrosion.

If desired, the metal mercaptide can be dissolved in organic solvents such as trichloroethylene, butyl Cellosolve, butyl Carbitol or various combinations of organic solvents. Silver or copper articles immersed in these solutions for several seconds up to ten or more minutes acquire a barrier film which protects the metal against atmospheric tarnish.

An alternative method for producing a tarnish resistant surface on silver is to impregnate a soft cloth, flannel or cotton, with a solution of the metal mercaptide in a volatile solvent such as trichloroethylene. The cloth is squeezed free of excess solution and then dried in a current of warm air. The amount of metal mercaptide impregnated on the cloth can be determined by the gain in weight of the material. Generally, using 20% solution it will leave in the cloth about 5% by weight of mercaptide. Clean silver surfaces when thoroughly wiped or gently buffed with a cloth treated in the above solution resists tarnishing for several months when exposed to atmospheric conditions. Untreated silver tarnishes in 1 to 3 weeks under the same exposure.

The invention will be further illustrated in more detail by the following examples, but it is not intended to be limited by the scope of these disclosures.

Example I.—Magnesium di(cetyl mercaptide) complex

To 350 milliliters of isopropyl alcohol was added 129 grams of cetyl mercaptan and 33 grams of 85% potassium hydroxide. The mixture was warmed to 60° C. This solution was added to a solution of 51 grams of magnesium chloride hexahydrate in 750 milliliters of isopropyl alcohol. An immediate precipitate formed. The mixture was stirred until the temperature dropped to 25° C. The white precipitate was removed by filtration, washed with isopropyl alcohol and dried in vacuum at 60° C. The yield was 110 grams.

The product had no melting point but decomposed on heating. A sodium nitroprusside test for uncombined mercaptan was negative. Elementary analysis showed the presence of magnesium, sulfur, chlorine, carbon and hy-

drogen. The infrared spectrum of the magnesium-cetyl mercaptan complex differed from the spectrum of cetyl mercaptan.

Example II.—Zinc di(cetyl mercaptide)

Cetyl mercaptan, 129 grams, was dissolved in 600 milliliters of isopropyl alcohol at 45° C. Zinc acetate dihydrate, 55 grams, was dissolved in 150 milliliters of water. The zinc acetate solution was added slowly to the agitated alcoholic mercaptan solution. A precipitate formed on mixing. The reaction mixture was filtered without cooling, and the filter cake washed with warm isopropyl alcohol. The white solid was dried in vacuum at 60° C. The dried product was a white powder, melting at 147–150° C. Elementary analysis gave good agreement for zinc cetyl mercaptide.

Example III.—Nickel di(cetyl mercaptide)

The method of Example II was used except that 45 grams of nickel acetate was substituted for the zinc acetate. Nickel cetyl mercaptide was isolated as a brown, waxy solid.

Example IV.—Lead di(cetyl mercaptide)

Cetyl mercaptan, 129 grams, was dissolved in 600 milliliters of isopropyl alcohol at 45° C. Lead acetate, 82 grams, dissolved in 150 milliliters of water at 60° C., was poured slowly into the alcoholic solution of cetyl mercaptan. A bright yellow precipitate formed immediately. The product, a yellow waxy solid was dried in a vacuum dryer.

Example V.—Stannic tetra(cetyl mercaptide)

Cetyl mercaptan, 129 grams, was dissolved in 600 milliliters of isopropyl alcohol. Stannic chloride dihydrate, 45 grams, was dissolved in 500 milliliters of isopropyl alcohol. The stannic chloride solution was added to the mercaptan solution with agitation. The clear solution, which resulted, was evaporated on a steam bath to remove the isopropyl alcohol. The residual oil was filtered and cooled to yield a solid having a melting point of 49–51° C.

Example VI.—Preparation of tarnish preventative polish containing magnesium mercaptide

To 40 grams of magnesium di(cetyl mercaptide) was added 40 grams of Alfonic 1218–6 (Continental Oil Company) and the mixture liquified by heating at 60° C. (Part A.)

Methocel DGS (Dow Chemical Company), 7.5 grams, was dissolved in 870 grams of water at room temperature. The temperature was raised to 60° C., and Part A was dispersed into the aqueous medium. The mixture was cooled to 25° C. Snow Floss (a diatomaceous earth, Johns-Manville), 40 grams, was added to the above mixture and agitated until homogeneous. A smooth grey dispersion was obtained.

A 2" x 2" silver plated panel was immersed into 0.3% solution of potassium sulfide. After 30 seconds, a uniform brown tarnish was produced on the silver surface. The panel was removed and rinsed in running water. The preparation containing magnesium di(cetyl mercaptide) was poured onto the tarnished surface which was then polished with a moist soft flannel cloth. The tarnish was removed rapidly. The panel was rinsed in warm water and polished with a soft clean cloth. The metal surface was bright and lustrous. The panel was reimmersed into the potassium sulfide solution. The silver panel showed no signs of tarnishing after 15 minutes' immersion.

A 2" x 2" copper panel was polished with the composition described in this example. The polished panel was immersed in the potassium sulfide solution. No tarnish formed on the copper after five minutes' exposure. A control panel was tarnished instantaneously.

Example VII.—Preparation of tarnish preventative polish containing zinc di(cetyl mercaptide)

Zinc cetyl mercaptide, 40 grams, was mixed with 40 grams of methyl oleate and 40 grams of Span 85 (Atlas Chemical Company) and the mixture heated to 80–90° C. until uniform. When solution was complete, the liquid was poured in a fine stream into 750 milliliters of water which was vigorously agitated. To the resulting dispersion was added 40 grams of Super Floss (a diatomaceous earth, Johns-Manville). The mixture was agitated until cooled to 20° C.

A tarnished sterling silver spoon was polished with the product and then placed in a laboratory fume hood. The spoon did not tarnish for two weeks. A control tarnished within 48 hours.

Example VIII.—Tarnish preventative emulsion containing zinc di(cetyl mercaptide)

To a mixture of 40 grams of zinc di(cetyl mercaptide) and 40 grams of Alfonic 1218–6 (Continental Oil Company) was added 920 grams of perchloroethylene. The solution was diluted 1:1 with water to form a milky emulsion.

Several hundred silver plated connectors used in the production of coaxial cables were placed in a stainless steel wire basket. The basket was immersed in the zinc di(cetyl mercaptide) emulsion for three minutes and then rinsed in running water.

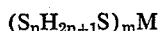
The silver plated connectors were dried in a current of warm air. The treated connectors passed the antitarnish test described in Federal Specification QQS–365a, Apr. 6, 1957, Sec. 4.5.5.1.

Example IX.—Tarnish preventative solution containing stannic tetra(cetyl mercaptide)

To 1000 grams of trichloroethylene was added 40 grams of stannic tetra(cetyl mercaptide). Two sets of 4" x 2" copper and brass panels were immersed in the solution for five minutes. The panels were removed and rinsed in clean trichloroethylene and air dried. The treated panels and untreated controls were placed in a chamber which had an environment of 100% humidity at a temperature of 120° F. After one day, the control panels exhibited tarnish whereas the treated copper and brass panels showed no visible tarnish.

What is claimed is:

1. A tarnish preventative for the surface of silver and copper and their alloys, comprising an effective amount of a metal mercaptide having a formula given by the following



where n is 12 to 20, inclusive,
 m equals 2, 3, or 4, and

M is a metal cation of valence greater than 1, capable of forming organic mercaptides, in at least a small effective amount in a carrier.

2. A polish and tarnish preventative for the surface of silver and copper and their alloys consisting essentially of an abrasive powder carrier and a metal mercaptide having a structure defined in claim 1.

3. A polish and tarnish preventative for silver and copper and their alloys in accordance with claim 1 wherein the mercaptide is magnesium di(cetyl mercaptide) and an abrasive powder as a carrier.

4. A polish and tarnish preventative for silver and copper and their alloys in accordance with claim 1 consisting essentially of zinc di(cetyl mercaptide) and an abrasive powder.

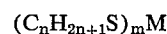
5. A polish and tarnish preventative for silver and copper and their alloys in accordance with claim 1, consisting essentially of stannic tetra(cetyl mercaptide) and an abrasive powder.

6. A tarnish preventative for silver and copper and their alloys in accordance with claim 1, consisting essentially of magnesium di(cetyl mercaptide) in a liquid diluent.

7. A tarnish preventative for silver and copper and their alloys consisting essentially of zinc di(cetyl mercaptide) in a liquid diluent, in effective amount to produce a tarnish resistant surface on a metal treated.

8. A tarnish preventative for silver and copper and their alloys consisting essentially of stannic tetra(cetyl mercaptide) in a liquid diluent, in effective amount to produce a tarnish resistant surface on a metal treated.

9. A polished tarnish resistant surface containing a metal from the group consisting of silver and copper and their alloys having thereon a metal mercaptide layer having the structure:



where

n is 12 to 20, inclusive,

m equals 2, 3, or 4, and

M is a polyvalent metal ion capable of forming organic mercaptides.

10. A surface in accordance with claim 9 containing a metal selected from the group consisting of silver and copper and their alloys having thereon a mercaptide layer containing magnesium di(cetyl mercaptide).

11. A surface in accordance with claim 9 containing a metal selected from the group consisting of silver and copper and their alloys having thereon a mercaptide layer containing zinc di(cetyl mercaptide).

12. A surface in accordance with claim 9 containing a metal selected from the group consisting of silver and copper and their alloys having thereon a mercaptide layer containing stannic tetra(cetyl mercaptide).

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