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COMPOSITION AND METHOD FOR RENDERING SILVER SURFACES TARNISH RESISTANT

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ABSTRACT OF THE DISCLOSURE

Elemental sulfur in finely divided form in a silver polish renders a silver surface to which the polish is applied resistant to tarnishing.

DISCLOSURE

This invention relates to rendering silver surfaces tarnish resistant, and more particularly to a silver polish for both cleaning and polishing tarnished silver surfaces and rendering them tarnish resistant.

Polishes for removing tarnish from silver surfaces are widely employed. They are usually in the form of a paste or a liquid suspension, both comprising essentially a liquid carrier, and an abrasive powder in such finely divided form and of such hardness that it will not scratch a silver surface. Hence, when the composition is applied to and rubbed over the silver surface, the tarnish is removed by the abrasive. Suitable emulsifying and protecting agents, and organic solvents may also be employed in the polish, as is exemplified in the U.S. patents to Avedikian 2,691,593, Murphy Re. 24,819, and Aler et al. 3,117,012. These patents also disclose as antitarnish or tarnish resistant agents incorporation of long chain organic sulfur compounds in the polish, such as thioureas and thiols.

It has been found pursuant to this invention that elemental sulfur, namely free sulfur, possesses superior tarnish resistant properties in precluding tarnishing of a silver surface which has been cleaned or polished, for example, by a silver polish composition. Moreover, the inorganic sulfur is odorless and much less costly than the organic sulfur compounds of the aforementioned type which have an obnoxious odor, particularly the thiols, and can be employed effectively in much smaller quantities, in the order of a few hundredths of a percent by weight of the composition.

Summarizing this invention, the elemental sulfur can be in any one of various well known forms, such as finely divided or powdered crystalline sulfur, amorphous sulfur in the form of a fine powder, colloidal sulfur which is inherently formed finely divided, flowers of sulfur which is sublimed sulfur also inherently in fine powder form, milk of sulfur also known as precipitated or colloidal sulfur or the so-called "water-wettable" sulfur of commerce.

On the polished silver surface, the elemental sulfur evidently reacts with the silver to form a very thin transparent substantially monomolecular film or layer of silver sulfide (Ag_2S) which is substantially non-volatile, in contradistinction to the volatility of organic sulfur compounds. Because of such non-volatility, the film remains intact over a protracted period thus protecting the silver against tarnishing throughout such protracted period. At the same time, because of the thinness and transparency of the film, the lustre of the polished silver will be visible therethrough.

The elemental sulfur need only be uniformly incorporated in any type of silver polish. When such silver polish is applied to a tarnished silver surface, the abrasive removes the tarnish film, and the elemental sulfur forms the protective film. After the polishing with the silver polish, the silver may be wiped dry or washed or rinsed in the usual manner with water, usually warm water, but the silver sulfide film will remain to protect the silver against tarnishing over a protracted period.

If a silver surface has been polished by a polish not containing the inorganic sulfur hereof, an aqueous or solvent solution or suspension of such sulfur can be applied over the polished surface, and it will form the tarnish resistant protective film. Addition of wax to the composition apparently has a synergistic effect with the sulfur because when wax is employed in the composition, tests have established that the film protection against tarnishing lasts for an even longer period as a result of wax in the film.

From the preceding, it is seen that the invention has as its objects, among others, the provision of an improved silver polish composition containing elemental sulfur as the essential component in providing a tarnish resistant film on the silver surface after polishing thereof, which is substantially non-volatile and odorless in the composition, and can be used effectively in small amounts, and the provision of an improved method for rendering a polished silver surface resistant to tarnish. Other objects of the invention will become apparent from the following more detailed description.

The silver polish can be of any suitable formulation comprising as essential components a fine silver non-scratching abrasive powder, and a liquid carrier in which the elemental sulfur is dissolved or uniformly suspended. Desirably, the composition hereof also contains an organic solvent immiscible with water as part of the liquid carrier, an emulsifying agent, and a protective colloid or suspending agent to minimize separation of the components. Wax is advantageously included in the composition as wax has been found to enhance the tarnish resistant effect, but wax may be omitted. The proportions of a suitable silver polish containing elemental sulfur may be as follows in percent by weight:

	Percent by weight
Liquid carrier	45–85
Protective colloid	0.01–0.3
Emulsifying agent	1.5–5
Abrasive powder	8–30
Wax	0–5
Elemental sulfur	0.01–10

A minor proportion of carrier, which is essentially aqueous, may include an organic solvent.

With respect to the elemental sulfur, it will be noted that even a relatively small amount of at least 0.01 percent will serve to form a tarnish resistant film. The maximum amount is relatively immaterial but amounts in excess of 10 percent by weight of the composition will serve no useful purpose and hence are not preferred. The most effective range of elemental sulfur in the composition is about 0.01 to 0.20 percent by weight; and as previously related, the elemental sulfur can be in any of its various forms.

When an organic solvent is employed to supplant some of the water, any suitable solvent may be utilized, desirably liquid hydrocarbon type solvents, such as odorless kerosene, naphtha, gasoline, odorless paint thinner or non-flammable solvents, such as chlorinated hydrocarbons, in the boiling range from about 200° F. to 525° F. Such solvent is desirable when wax is in the composition as it dissolves the wax, leaving a waxy film when the liquid evaporates. Generally, about 10 to 40 percent of the liquid carrier can be solvent.

As the protective colloid, any suitable suspending agent such as natural gums, for example, gum tragacanth or gum arabic, may be employed. Synthetic gums, such as sodium carboxy methyl cellulose, ethoxy cellulose gum or a hydroxyalkyl cellulose product may be employed, and also any suitable aliginate thickening agent. As the wax, any suitable type can be employed, such as microcrystalline wax, paraffin wax, vegetable wax, and mineral wax. Suitable emulsifying agents are desirably non-ionic such as non-ionic detergents, or anionic, such as fatty acid soaps, or alkyl aryl sulfonates.

As the abrasive, the more finely divided the abrasive is, the better. Any of the well known abrasives may be employed in finely divided powder form so that it is non-scratching, such as fine charcoal, diatomaceous earth, precipitated chalk, or jeweler's rouge, or mixtures of these components. Diatomaceous earth is the preferred abrasive of the following particle size:

Microns:	Percent
Over 40	Zero
22–40	Trace
10–20	0.5
6–10	1.5
3–6	12
Less than 3	86

In formulating the composition, it is immaterial how the elemental sulfur is introduced into the composition as long as it is uniformly dispersed. The following is a typical formulation (and preferred range variation) of a suitable composition containing flowers of sulfur.

EXAMPLE I

	Percent by weight	Range in percent by weight
Essentially aqueous carrier	82.90	70–85
Composed of—		
Water (60.9)		(50–70)
Odorless kerosene (22.0)		(10–30)
Protective colloid (sodium carboxy methyl cellulose)	0.09	0.05–0.3
Emulsifying agent (potassium oleate)	3.89	1.5–5.0
Abrasive powder (above diatomaceous earth)	9.57	8.0–20.00
Wax (paraffin wax, melting point 134° F.)	3.53	1.0–5.00
Elemental sulfur (flowers of sulfur)	0.02	0.01–0.20
Total	100.00	

In making the composition, it is preferable first to disperse the small amount of flowers of sulfur by stirring it in the odorless kerosene at a temperature of about 70° C. to 90° C., add the wax which dissolves in the kerosene upon continued stirring, then add this to warm water (about 70° C. to 90° C.) containing the protective colloid and emulsifying agent dissolved or suspended therein, and agitate the components by stirrring to form a stable emulsion; and while the stirring is continued, adding the abrasive gradually. The order of mixing is, however, not critical. The product is then allowed to cool to room temperature for filling in suitable containers.

The above polish may be applied to clean a silver surface in a conventional manner; and after cleaning of such surface the article is rinsed with warm water, leaving a waxy film of silver sulfide which is substantially non-volatile thus protecting the surface against tarnishing for a protected period.

The elemental sulfur can be formed in situ while the composition is being formulated by precipitating the same in the composition in any suitable manner, such as by precipitation from a thiosulfate by an acid.

The following example is typical of a substantially similar formulation and the manner of making the same wherein the elemental sulfur is formed in situ from the following components in percent by weight:

EXAMPLE II

	Percent by weight	Range in percent by weight
Essentially aqueous carrier	81.95	70–85
Composed of—		
Water (60.21)		(50–70)
Kerosene, as above (21.74)		(10–30)
Protective colloid (sodium carboxy methyl cellulose)	0.09	0.05–0.3
Emulsifying agent (potassium oleate)	3.83	1.5–5.00
Abrasive powder (above diatomaceous earth)	9.46	8.0–20.00
Wax (paraffin wax, melting point 134° F.)	3.47	1.0–5.00
Colloidal sulfur (estimated 0.15%) formed by precipitation from:		
Sodium thiosulfate ($Na_2S_2O_3.5H_2O$)	1.19	1.0–2.0
Sulfuric acid (H_2SO_4)	0.01	0.01–0.02
Total	100.00	

In the above formulation, the precipitated or colloidal sulfur is prepared in situ by precipitation from sodium thiosulfate by the acid. In formulating the above composition, the order of mixing is not critical. However, it is preferred that the solvent in which wax is dissolved be added to the essentialy aqueous carrier containing the other components after the colloidal sulfur has been formed therein. The sulfur is desirably precipitated in the presence of the protective colloid in the water as this enhances dispersion and stability.

Thus, the sodium thiosulfate and concentrated sulfuric acid are added with agitation to the water containing the protective colloid at a temperature of about 70° to 90° C. at which temperature the formation of the precipitated sulfur is accelerated. After such precipitation, the emulsifying agent is added. The wax dissolved in the solvent, is then added with agitation to the aqueous colloidal sulfur dispersion, and finally, the abrasive powder is added gradually under agitation after which the composition is allowed to cool to room temperature and is filled into suitable containers. The composition can be employed in the same manner as described for Example I.

As previously related, although wax is advantageous, it need not be employed, and the solvent need not be employed because the sulfur can be precipitated from sodium thiosulfate with acid in situ in water at room temperature. The following is a typical example of such composition which is formulated without application of heat:

EXAMPLE III

	Percent by weight	Range in percent by weight
Essentially aqueous carrier (all water)	74.77	70–85
Protective colloid (sodium carboxy methyl cellulose)	0.14	0.05–0.3
Emulsifying agent (potassium oleate)	3.89	1.5–5.0
Abrasive powder (above diatomaceous earth)	20.00	8.0–20.00
Colloidal sulfur (estimated 0.15%) formed by precipitation from:		
Sodium thiosulfate ($Na_2S_2O_3.5H_2O$)	1.19	1.0–2.0
Sulfuric acid (H_2SO_4)	0.01	0.01–0.02
Total	100.00	

The protective colloid is dissolved in the water at room temperature, and then the sodium thiosulfate is added to the water and dissolved at room temperature. After complete solution, the concentrated sulfuric acid is added thus effecting formation of colloidal sulfur; the reaction taking place slowly at room temperature under stirring. The emulsifying agent is then added with stirring, after which the abrasive is gradually added under stirring. Finally, the composition is filled in suitable containers and used in the manner described. The order of mixing is not, however, critical.

Tests have established that the above compositions containing the elemental sulfur in even minute amounts, will resist tarnishing of a freshly polished silver surface at

least twice as long as a popular silver polish now on the market containing thiol compounds. Also, the compositions hereof are easy to apply, and will not damage the silver surface polished, and are odorless in contrast to volatile organic thiols which have a marked unpleasant odor.

We claim:

1. The method of rendering a polished silver surface resistant to tarnishing which comprises forming a substantially non-volatile transparent film on said surface by applying to said silver surface a composition containing free, elemental sulfur in finely divided form in an essentially aqueous carrier for the sulfur.

2. The method of rendering a polished silver surface resistant to tarnishing which comprises forming a substantially non-volatile transparent film on said surface by applying to said polished silver surface an essentially aqueous composition containing wax and free, elemental sulfur in finely divided form, the amount of said free, elemental sulfur in said composition constituting at least 0.01% by weight thereof.

3. The method of rendering a polished silver surface tarnish-resistant, which comprises forming a substantially non-volatile transparent tarnish-resistant film on said surface by applying thereto a composition comprising the following components in approximately the following percentages by weight:

	Percent by weight
Essentially aqueous carrier	45–85
Protective colloid	0.01–0.3
Emulsifying agent	1.5–5
Wax	0–5
Silver non-scratching finely divided abrasive powder	8–30
Elemental sulfur	0.01–10.0

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