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3,365,312

METAL CLEANER, ARTICLE AND METHOD
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9 Claims. (Cl. 106—3)

ABSTRACT OF THE DISCLOSURE

A tarnish-resisting agent for use in metal polishes is described consisting of alkyl benzyl thiol. Tarnish-resisting cleaning and polishing compositions containing alkyl benzyl thiol are also described, including methods for preventing the formation of tarnish on metals through the use of such compositions.

This invention relates to tarnish resisting metal cleaners and more particularly to cleaning and polishing compositions which are especially suited for use on noble and other metals.

A major disadvantage in the use of cleaning and polishing compositions of the type that employ abrasives for removing soil and tarnish from metallic surfaces is the lack of permanence of the luster they produce. Fresh metal is exposed during the polishing operation which is highly reactive. This fresh surface therefore tarnishes quickly. For example, copper cooking wear which has been carefully polished, hazes quickly with tarnish when stored near gas ranges and the like. This is also true with the more reactive polished silver. Unless these surfaces are protected against corrosive agents they quickly tend to lose their brilliance, discolor and tarnish heavily.

Attempts to protect these polished surfaces from tarnishing have involved coating the surface with various plastics and lacquers. These methods while successful for some purposes are not well suited for use on metallic surfaces which are frequently used, such as silver serving dishes and the like. An additional disadvantage of these previous methods is their difficulty of removal. It is desirable to provide a protective coating for freshly polished metal surfaces which is applied simultaneously with the cleaning composition and which can be easily reviewed by subsequent applications of that same composition.

Compositions of this latter type have been tried but thus far have been somewhat limited in their application.

Compositions which adequately protect against tarnish forming on freshly polished silver for example, have little effect on copper. The reverse is also true.

It is therefore an object of this invention to provide a cleaning composition, which when used on various metals renders the metal resistant to subsequent tarnishing.

It is also an object of this invention to provide tarnish resisting cleaning compositions which simultaneously clean various metals and apply a protective film on the surface of the metal which film is renewed by subsequent application of the composition.

Further objects of this invention are providing cleaning compositions having the above properties which do not need to employ odor masking agents, do not have to be removed from the metal by washing, are non-toxic and compounded of materials which make the composition easier to work when cleaning various metals.

The above and additional objects and advantages of this novel invention will become apparent from its further description.

This invention derives its unique advantage from the use of certain organic mercaptans.

This invention achieves its tarnish resistant nature by the use of various alkyl aryl mercaptans where preferably

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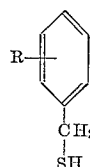
the major portion of the alkyl groups present are branched chain hydrocarbons containing from 12 to 16 carbon atoms, and the aryl group chosen is the benzyl radical.

A variety of mercaptans useful for achieving the objects of this invention may be economically obtained as the reaction product obtained from the reaction of their corresponding alkyl benzyl chlorides with thio urea.

Alkyl benzyl halides are commercially available today containing an alkyl radical which is primarily a branched chain hydrocarbon containing from 12 to 16 carbon atoms. The alkyl radical of the chloride for purposes of economy may contain minor amounts of hydrocarbon branched chains having as low as 8 and as high as 20 carbon atoms without departing from the advantages obtained from this invention.

An alkyl benzyl mercaptan useful in the practice of this invention may be obtained by mixing stoichiometric amounts of a corresponding alkyl benzyl chloride together with thio urea in a suitable organic media, such as isopropanol, and refluxing for a sufficient time to allow for a complete addition reaction. Aqueous sodium hydroxide is then added to the reaction mixture to cleave the addition product to obtain the sodium salt of the alkyl benzyl thio. The addition at this point of dilute sulphuric acid to the mixture will enhance the formation and separation of the thiol. The thiol product forms a separate oily layer on the aqueous mixture. The reaction can be considered complete when the aqueous mixture has been rendered acidic by the addition of the acid. The oily layer of alkyl benzyl thiol product is then separated for use in a variety of tarnish resisting cleaning compositions prepared according to this invention.

An alkyl benzyl thiol having the general formula:



where R is a branched chain hydrocarbon having from 8 to 20 carbon atoms, can readily be formed by this reaction.

In preparing a preferred tarnish resisting cleaning composition from among those contemplated, the most successful have been prepared by utilizing alkyl benzyl thiols where the major alkyl constituent present in the composition is a branched chain hydrocarbon containing about 12 to 16 carbon atoms.

Typical formulations of tarnish resisting compositions should preferably contain about 1% to 10% alkyl benzyl thiol; about 5% to 99% abrasive; about 0 to 5% gelling, suspending stabilizing and emulsifying agents; about 0 to 10% chelating agent and about 0 to 10% additional anti-tarnishing agents with the balance being water or a suitable alcohol or mixture of both.

Superior results can be obtained in individual formulations by utilizing other anti-tarnishing compounds in combination with the alkyl benzyl thiol described above. For example, alkyl disulfides are known tarnish resisting agents which are uniquely successful when used in combination with these alkyl benzyl thiols.

In addition, chelating agents can be employed in various formulations making the composition thus formed more suitable for use on specific metal surfaces. It has been learned for example, that compositions formulated with citric acid and ammonium chloride present in small amounts are particularly well suited for cleaning copper and brass.

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Example 1

A tarnish resistant cleaning composition with the following constituents and proportions has been shown to be superior for silver and silver alloys.

Ingredients:	Approx. percentage by wt.
Bentonite	2-10
Diatomaceous earth (1-2 microns)	2-10
Dodecyl benzyl thiol	0.25-40
Nonyl phenoxy polyoxy ethanol (approximately 10 ethylene oxides)	0.25-5
Isopropanol	2-40
Balance to make 100%; water, dye and deodorizer if desired.	

Nonyl phenoxy polyoxy ethanol is used in the above composition as an emulsifying agent and is known in the trade by the registered trade name "Triton N-101."

Various abrasives are suitable for use in the tarnish resisting compositions of this invention. Finely divided polishing agents are commercially available in a wide variety of particle sizes. A selection of a suitable abrasive is a matter of choice to a person skilled in the art. Exemplary of such abrasives are diatomaceous earth, which is available in porous form, alumina, silica and chalk.

After this composition has been worked onto a metal surface to clean it and then allowed to dry, the dried cleaner and removed tarnish is simply wiped away leaving a brilliant tarnish resistant surface.

Another example of a composition suitable for silver is:

Example 2

Ingredients:	Approx. percentage by wt.
Bentonite	2-10
Diatomaceous earth (1-2 microns)	2-10
Hexadecylbenzyl thiol	0.25-40
Nonyl phenoxy ethanol (approximately 10 ethylene oxides)	0.25-5
Isopropanol	2-40
Balance to make 100%; water, dye and deodorizer if desired.	

As previously mentioned the compositions prepared according to this invention are capable of cleaning and protecting a metal surface without requiring rinsing the composition from the surface after working it on. The dried used abrasives, emulsifying agents and the like can simply be dusted or wiped from the surface carrying with them the soil and tarnish. The tarnish resisting properties of the composition are provided by the retention of the alkylbenzyl thiol by the metal surface. This capture of the thiol is probably caused by chemical bonding between the freshly exposed surface metal and the sulfur of the thiol. The remaining alkyl benzyl portion of the molecule then forms a colorless waxy film over the surface previously covered by the cleaner composition. This film effectively prevents further attack of the covered metal by tarnish agents for the life of the film.

An outstanding characteristic of this film is its resistance to normal household detergent solutions at elevated temperature. This permits a prepared article to be repeatedly washed without impairing its tarnish resistant properties. The chemically inert nature of the film also permits its use on materials which contact various foods. It is also strong enough to withstand the hard usage given to articles such as silverware. The film, in addition, is non-toxic, resistant to attack by dilute acids and bases and various solvent solutions.

The advantages of this protective film can be utilized on other metal surfaces such as copper, brass and the like. Typical formulations effective for such use are shown in the following example.

Example 3

Ingredients:	Approx. percentage by wt.
Dodecyl benzyl mercaptan	0.25-40

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Diatomaceous earth (2-3 microns)	5-50
Citric Acid	1-30
Ammonium chloride	0.8-25
Gelling agent (colloidal silica)	1-5.
Emulsifying agents:	
Nonyl phenoxy polyoxy ethanol (approximately 10 ethylene oxides)	0.5-5.0
Tertiary octyl pehnnoxy polyoxy ethanol	0.25-2.5
Balance water to make 100%.	

Tertiary octyl phenoxy polyoxy ethanol is used above as an emulsifying agent and as an aid in providing good working characteristics for the cleaner. It is commercially available and known in the trade by the registered trade name "Triton X-45."

Example 4

Ingredients:	Approx. percentage by wt.
Bentonite	2-10
Diatomaceous earth (1-2 microns)	2-10
Hexadecyl benzyl mercaptan	2-40
Nonyl pehnnoxy polyoxy ethanol (approximately 10 ethylene oxides)	0.25-5
Isopropanol	2-40
Balance to make 100%; water, dye and deodorizer if desired.	

Example 5

Ingredients:	Approx. percentage by wt.
Bentonite	2-10
Diatomaceous earth (1-2 microns)	2-40
Dodecyl benzyl thiol	0.25-40
Hexadecyldisulfide	0.25-5
Nonyl pehnnoxy polyoxy ethanol (approximately 10 ethylene oxides)	0.25-5
Isopropanol	2-40
Balance to make 100%; water, dye and deodorizer if desired.	

Example 6

Ingredients:	Approx. percentage by wt.
Bentonite	2-10
Diatomaceous earth (1-2 microns)	2-40
Hexadecyl benzyl thiol	0.25-40
Nonyl pehnnoxy polyoxy ethanol (approximately 10 ethylene oxides)	0.25-5
Hexadecyldisulfide	0.25-5
Isopropanol	2-40
Balance to make 100%; water, dye and deodorizer if desired.	

The general composition works well in resisting tarnish and corrosion on a wide variety of metal surfaces.

The alkyl aryl thiols preferred for use in this invention have been particularly disclosed. It is of course possible to obtain the benefits of this invention by employing derivatives of the disclosed compounds. However, the addition of functional groups to either the alkyl (R) or aryl (R') portion of the molecule should be avoided where water solubility of the compound would be increased or where the addition would impair adversely the bonding ability of the R-R'S- to the freshly cleaned metal surface.

As previously pointed out one of the advantages of the composition according to this invention is the ability of the cleaners and the like of the composition to be removed from the metal surface without the necessity of rinsing with water or other solvents. To this end it is preferable that the composition be formulated without phosphorous containing compounds. The specific examples of formulations indicate the wide latitude possible when utilizing the benefits of this invention. Changes may be made in these specific examples to modify the compositions for particular uses. For example, it is preferable to adjust the pH of compositions used for silver polishing into a range of from about 5 to 7 while compositions for cleaning and protecting copper and brass may be adjusted in pH to

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about 2 or 3. In addition, other tarnish resisting agents such as various alkyl disulfides may be added for improved results, and cleaning agents other than abrasives types may be added or substituted to tailor the formulation for a particular purpose without departing from the spirit of the invention as described herein or from the scope of the appended claims.

What is claimed is:

1. A metal polish for resisting tarnish consisting essentially of about 5% to about 50% abrasive in combination with about 1% to about 10% of a mixture of alkyl benzyl thiols wherein the major portion of the alkyl radicals in the mixture consists of branched chain hydrocarbons containing from 8 to 16 carbon atoms and a liquid carrier.

2. A tarnish resisting cleaning composition for application to metallic surfaces consisting essentially of a liquid carrier, about 5% to about 50% abrasive grit in the carrier effective for cleaning tarnish from metal, and dodecyl benzyl thiol present in the carrier in an amount from about 1% to about 10%.

3. A tarnish resisting cleaning composition for application to metallic surfaces consisting essentially of a liquid carrier, about 5% to about 50% abrasive grit in the carrier effective for cleaning tarnish from metal and about 1% to about 10% of alkyl benzyl thiol, having its alkyl radical selected from the group consisting of octyl, nonyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl and octadecyl alkyls, present in the carrier in an amount sufficient to protect a metal surface from tarnishing when the carrier has been removed.

4. A metal cleaner consisting essentially of a volatile liquid carrier about 5% to about 50% abrasive grit contained in the carrier having a particle size of from about 1 to about 4 microns and an alkyl benzyl thiol, whose alkyl radical consists essentially of a hydrocarbon radical with 12 to 16 carbon atoms, in the carrier in an amount from about 1% to about 10% sufficient for its retention on the cleaned metal surface for protecting the metal surface from soil and tarnish after removal of the carrier.

5. A tarnish resistant silver polish comprising the following by weight percent:

about 5 to 50% of an abrasive having a particle size of from about 1 to 2 microns;

about 0.25 to 40% of a liquid alkyl benzyl thiol in which the alkyl radical contains from 8 to 16 carbon atoms;

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about 0.5 to 10% of emulsifying and gelling agents; the balance to make 100%; comprising water and an alcohol.

6. A copper and brass tarnish resisting polish comprising the following by weight percent:

about 5 to 50% of an abrasive having a particle size of from about 1 to 4 microns;

about 1 to 10% of a liquid alkyl benzyl thiol in which the alkyl radical contains from 8 to 16 carbon atoms;

about 0.5 to 5% of a liquid alkyl disulfide;

about 0.5 to 30% of citric acid and ammonium chloride in combination;

about 0.5 to 10% of emulsifying and gelling agents the balance to make 100%; comprising water and an alcohol.

7. A method of preventing the formation of tarnish on metals selected from the group consisting of silver, silver alloys, copper and copper alloys comprising the steps of rubbing the surface to be protected with a composition consisting essentially of about 5% to about 50% abrasive in combination with about 1% to about 10% or an alkyl benzyl thiol in a liquid carrier, allowing the composition to dry to a powder, removing the dried powder thereby leaving a substantial portion of the alkyl benzyl thiol bonded to the through thiol to metal bonds and metal forming a protective tarnish-inhibiting film on the metal.

8. An article having a metallic surface substantially resistant to tarnish by having chemically bonded thereon by thiol to metal bonds a protective film containing an alkyl benzyl thiol.

9. The article of claim 8 wherein the surface metal is selected from the group consisting of silver, silver alloys, copper and copper alloys.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 24, for "thio" read -- thiol --; column 3, line 70, for "Typicl" read -- Typical --; column 4, lines 8, 21, 33 and 44, for "pehnoxy", each occurrence, read -- phenoxy --; column 6, line 25, strike out "bonded to the through thiol to metal bonds and metal" and insert instead -- bonded to the metal through thiol to metal bonds and --.

Signed and sealed this 4th day of March 1969.

(SEAL)

Attest:

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Commissioner of Patents