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METAL TARNISH REMOVERS

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Int. Cl. C11d 3/28, 3/34
U.S. Cl. 252—542 10 Claims

ABSTRACT OF THE DISCLOSURE

A composition and method suitable for removal of tarnish from metal surfaces, such as copper, silver, tin, lead, zinc, cadmium, and alloys thereof. The composition comprises one or more mercaptoamides or mercaptoimides, optionally including an abrasive and/or diluent.

FIELD OF THE INVENTION

This invention relates to the treatment of metal surfaces. In another aspect, it relates to a composition suitable for the removal of tarnish from metal surfaces.

DESCRIPTION OF THE PRIOR ART

Many metals, either pure or as alloys, are known to tarnish rapidly. Tarnishing has been a problem as long as mankind has worked with metals. When freshly prepared and clean, many metal surfaces have an attractive bright shiny lustrous appearance. Such socially acceptable appearance soon dulls the luster vanishes, and unattractive discolorations appear, often rapidly, due to the gradual reaction of the surface with oxygen or with various sulfur containing compounds attributable to a variety of environmental factors.

Cleaning of tarnished surfaces generally is a laborious task at best. Tarnish removing compositions of various types have been suggested, such as grinding or polishing compounds containing abrasives, sometimes including a chemical additive, which has not necessarily assisted the cleaning process. For example, high molecular weight long chain alkyl mercaptans have been used in such formulations. Unfortunately, as chemical additives, these mercaptans tend to dull the luster of bright silver and its alloys and leave an objectionable greasy film on the surface of the metal.

Of course, the use of abrasives, generally, is undesirable. The metal surface must, perforce, be worn away to at least a slight extent, at each and every abrading. In time, this depreciates the value of the article, particularly plated articles. The abrading itself, exen with very finely divided abrasives, tends to increase the total surface area of the metal exposed to the tarnish-causing environment, by creating a myriad of criss-crossed fine scratches, and usually results in accelerated tarnishing rates for the articles.

OBJECTS OF THE INVENTION

An effective class of cleaning agents is certainly to be desired, tarnish removal agents to remove discoloration, surface oxidation, sulfurization, tarnish, and the like, from a variety of metal surfaces, with minimal efforts, and particularly with minimal undesirable effects to the metal surface itself.

It is an object of my invention to provide chemical agents suitable for cleaning metal surfaces.

Other aspects, objects, and the several advantages of my invention will be apparent to one skilled in the art to which my invention most nearly pertains from the following description and from my appended claims.

SUMMARY OF THE INVENTION

I have discovered the mercaptoamides and mercaptoimides to be unusually effective agents for the removal of tarnish and other discoloration from metal surfaces.

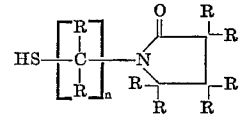
DETAILED DESCRIPTION OF THE INVENTION

Mercaptoamides and mercaptoimides are particularly effective, I have discovered, for the removal of tarnish from metal surfaces of the nonferro and nonalumino type metals and alloys in general. More specifically, for the removal of tarnish from such as copper, silver, tin, lead, zinc, cadmium, and the various and sundry alloys thereof. By alloys, I refer to those solid mixtures of two or more metals, or one or more metals with various nonmetallic elements, generally prepared by fusing of the components. I include those alloys containing one or more of tarnishable metals I have listed in the alloy, or such as two or more together such as copper with tin, or copper with zinc.

Mercaptoamides

The mercaptoamides useful within the context of my invention can be represented by the generalized formula

(I)



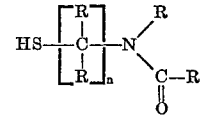
In this formula, R is hydrogen or an alkyl radical, including straight or branched chain alkyl, and cycloalkyl, and n is an integer of 1 to 5. The total number of carbon atoms in the mercaptoamide can vary widely, limited only by methods of application and formulations. The range for most purposes will be from 5 to 12. Examples of these mercaptoamides include:

N-1-mercaptoethyl-2-pyrrolidone
N-2-mercaptoethyl-2-pyrrolidone
N-3-mercaptopropyl-2-pyrrolidone
N-5-mercaptopentyl-2-(3,4-dimethyl)pyrrolidone
N-4-mercaptobutyl-2-(3,4-diethyl)pyrrolidone
N-5-mercaptopentyl-2-(4-isopropyl)pyrrolidone
N-mercaptomethyl-2-pyrrolidone

and the like.

Useful mercaptoamides also include those which can be represented by the general formula

(II)



where n is an integer of from 1 to 5, R is hydrogen or alkyl, including straight or branched chain and cycloalkyl. Again the total carbon number in the compound can range widely and is not limited as to operability of the compound. I believe for most applications that a carbon range per compound of from 2 to 12 to be suitable.

Examples of these types of mercaptoamides include:

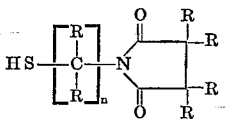
N-mercaptomethyl formamide,
N-mercaptomethylacetamide
N-3-mercaptopropyl-acetamide
N-4-mercaptobutyl-N-methyl formamide
N-3-mercaptopropyl formamide
N-4-mercaptobutyl-N-ethyl acetamide
N-2-mercaptoethyl acetamide
N-1-mercaptoethyl acetamide
N-2-mercaptoethyl formamide
N-1-mercaptoethyl formamide
N-3-mercaptopropyl-N-isobutyl valeramide
5-mercaptopentyl-N-methyl acetamide

and the like.

Mercaptoimides

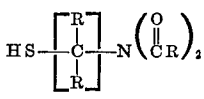
Mercaptoimides useful in the practice of my invention include those which can be represented by the general formula:

(III)



or

(IV)



wherein in R and *n* are as hereinbefore defined. The total number of carbon atoms per compound again is not limited by operability of the compound. A useful range of carbon atoms in each individual compound for most applications, I believe, is from 5 to 12 in the case of the Formula III above, or from 3 to 12 in the case of Formula IV. Examples of suitable mercaptoimides corresponding to the above formulas include:

N-mercaptomethyl diformamide
N-4-mercaptobutylsuccinimide
N-3-mercaptopropyl diacetamide
N-2-mercaptoethylsuccinimide
N-4-mercaptobutyl dipropionamide
N-1-mercaptoethylsuccinimide
N-2-mercaptoethyl divaleramide
N-mercaptomethylsuccinimide
N-6-mercaptohexyl diformamide
N-3-mercaptopropylsuccinimide
N-4-mercaptobutyl-tetramethylsuccinimide

and the like.

In the case of each type of mercaptoamide and mercaptoimide indicated, a general maximum total number of carbon atoms per individual compound upper limit is dictated primarily by upper feasible solubility limits of the individual compound in the applications and processes according to my invention.

The mercaptoamides can be prepared by any method of preparation known to the art. One method of preparing mercaptoamides and mercaptoimides is disclosed in United States Letters Patent No. 3,278,526, to Rector P. Louthan and Raymond L. Cobb, issued Oct. 11, 1966. Certainly, other methods known to the art for preparing mercaptoamides and mercaptoimides generally can be utilized.

PROCESS OF THE INVENTION

In the process of my invention, the tarnished metal object or surface can be cleaned by contacting the surface with at least one compound as I have described them above. The entire metal object itself where it is of a convenient size, or otherwise a tarnished surface of a metal or alloy or a metal coating or sheeting on some object or surface, is contacted by a solution or dispersion in a suitable solvent of the mercapto-compound or mixture of mercapto-compounds, such as an aqueous solution-dispersion.

A solution or dispersion of the mercapto-compounds can be used for purposes of economy, since it is certainly unnecessary to use large quantities of the effective agent itself for the cleaning of a tarnished metal surface.

The cleaning solution dispersion can be brushed on the object or surface, or sprayed onto the tarnished or discolored metallic surfaces such as by pressurized sprayer or aerosol, or the object itself can be wholly or partly dipped into the cleaning formulation.

After exposure to my cleaning formulation, the metal surface can be rinsed, such as with water, and wiped dry. For badly discolored surfaces, some mild pressure with a cleaning cloth can be applied to assist in brightening the surface.

The content of mercaptoamide or mercaptoimide in the cleaning solution-dispersion can range widely. I suggest from about 0.005 weight percent to 20 weight percent of total mercaptoamides and/or mercaptoimide compound or compounds, and a most convenient range of about 0.005 to 10 weight percent. The optimum range for the particular ingredient compounds chosen depends, at least in part, on the solubility of the particular species chosen, and the nature and depth of the metal tarnish being removed. For convenience, dispersions or solutions of relatively high strength can be prepared for stock or storage, and diluted further at time of usage. Commercial users may prefer a concentrated solution-dispersion, as opposed to more dilute formulations suitable for general resale and household usage.

The cleaning solution-dispersion formulation can be at any suitable pH range, but is most effective when at least slightly alkaline. Thus, for best results the cleaning solution-dispersion should show a pH range of above about 7, with a range of 8 to 12 being most effective.

The pH of the solution or formulation can be adjusted to the desired pH range in any conventional manner including use of ammonia, or of ammonium or an alkali metal hydroxide, or an organic amine, or a combination thereof, in such amount or amounts as are sufficient to provide or to assist in providing the desired pH range. Examples of suitable amines that can be used are those that have a reasonable water solubility or dispersability and exhibit an alkaline reaction in aqueous media. For this purpose, organic amines containing from 1 to 12 carbon atoms per amine molecule are more suitable, and include such as pyridine, morpholine, ethylamine, ethanolamine, di-n-propylamine, tributylamine, trimethylamine, diethanolamine, and the like.

Other alkaline substances can be utilized, such as the alkali metal carbonates, particularly where a moderately alkaline pH range is desired. The alkali metal compounds include those of lithium, sodium, potassium, rubidium, or cesium. Also, the ammonium or alkali metal phosphates can be utilized, particularly those which have an alkaline balance, i.e., on hydrolysis in water provide a suitable pH range, or thereby assist in providing a suitably buffered pH range. Some of these phosphates, such as the hexametaphosphates, trimetaphosphates, pyrophosphates, tripolyphosphates, and the like, additionally are useful in imparting properties to the cleaning formulation to assist in metal surface treatment, such as assisting in removing dirt and the like, or providing a mild detergent action for the removal of oily substances, such as fingerprints, and the like, so that the mercaptoamide and mercaptoimide can most effectively operate to remove the tarnish and discoloration.

While an aqueous media is presently preferred and convenient, it is also quite suitable to use varying proportions of one or more alcohols, such as 30 weight percent alcohol, along with the water, particularly using any of the lower alcohols of from about 1 to 4 carbon atoms per molecule, including methanol, ethanol, the propanols, or the butanols. Alcohols often are useful in assisting con-

ditioning of a metal surface to be cleaned by a wetting action so that the mercaptoamide or mercaptoimide compound itself can be most effective. Many of the amines hereinbefore mentioned also assist in this activity.

A stabilizing agent, particularly an antioxidant, can be added to the formulation in order to increase the storage or shelf life, and assist in avoiding oxidation of the mercaptoamide or mercaptoimide content of the formulation due to the activity of oxygen in the air.

Hydrosulfites (dithionites), sulfites, including the hydrogensulfite or bisulfite, as well as pyrosulfate or metabisulfite. Presently preferred are the sulfites, particularly the sodium sulfite, because of availability and economy. These stabilizers, as described, can be used alone or in admixtures of two or more thereof, and as either the anhydrous or hydrated form. Such stabilizers can be used in a broad range of concentration depending on the content of mercaptoamide or mercaptoimide. A range sufficient for most purposes is from about 1:10 to 5:1, preferably 1:1, weight ratio of total stabilizers to total mercapto content of the cleaning solution formulation.

When the stabilizer used itself is slightly alkaline, such as the alkali metal sulfites, the pH of the cleaning solution incorporating the mercaptoamide or mercaptoimide often can be wholly or partly adjusted by the resulting hydrolysis of the chosen stabilizer in aqueous solution. For example, sodium sulfite frequently produces a pH in the neighborhood of about 8.5, which provides a composition suitable for removal of many metal tarnishes. Where a higher pH is desired, an additional alkaline material can be added to the formulation.

The cleaning formulation can incorporate other ingredients frequently used in metal cleaning compositions, such as wetting agents, detergents, surface active agents, colorants, odorants, odor masking components, and the like, all of known type and usage to those skilled in the metal cleaning art. Certainly, tarnished surfaces which have thereon considerable amounts of dirt, grease, oily matter, and the like, should be treated for dirt and oil removal such as by washing with a suitable detergent before treating according to my invention.

EXAMPLES

To further illustrate my invention, tests were made on various metal strips. The materials used in the tests, both as to metal and illustrative mercaptoamide or mercaptoimide, should properly be considered as illustrative only, and not as limited as to particular components used, or the metals for which tarnish can be removed, and thus certainly not limitative of the reasonable scope of my invention.

A metal cleaning solution was prepared by dissolving 2 grams of N-2-mercaptoethyl-2-pyrrolidone in a mixture of 96 grams of water and 2 grams of sodium sulfite as stabilizer. The admixture was stirred at room temperature, becoming homogeneous and ready for use. A severely tarnished copper strip was dipped in the solution for approximately 10 seconds, removed, and found to be bright, shiny, and clean.

A solution was prepared of N-3-mercaptopropylsuccinimide by dissolving 2 grams of the mercaptoimide in 96 grams of water containing 2 grams of sodium sulfite as stabilizer. The solution was stirred at room temperature, and effected prompt homogeneous dispersion, ready for immediate use. Again, tarnished metal strips, for example copper strips, were immersed for approximately 10 seconds, removed, and found to be bright, shiny, tarnish-free, with good luster and appearance.

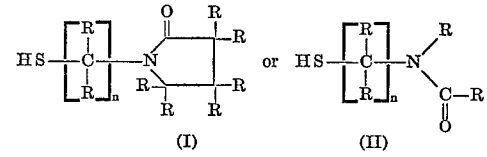
Such brief immersions rendered the badly tarnished strips bright and shiny. No abrasives were required or necessary. The strips were simply rinsed with water and remained bright for a considerable time.

Similarly, various samples of other discolored metals which I have described, also can be similarly treated, similarly cleaned, easily, simply, and effectively.

Certainly, reasonable variations and modifications are possible within the scope of my disclosure, yet without departing from the reasonable scope and certainly not from the intended spirit thereof, as shown both by the specification itself, including the claims here appended.

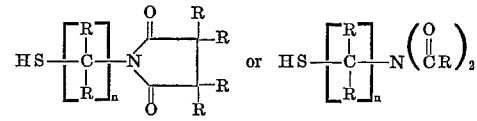
I claim:

1. A process for the removal of tarnish from nonferro and nonalumino metal surfaces which comprises bringing said tarnished metal surfaces into contact with an effective minor amount of at least one mercaptoamide, mercaptoimide, or mixtures thereof in a solvent selected from water or lower alcohols or mixtures thereof wherein said mercaptoamide can be represented by:



(I) (II)

and said mercaptoimide can be represented by:



(III) (IV)

wherein each *n* represents an integer of 1 to 5, and each R is individually selected from hydrogen or alkyl.

2. The process according to claim **1** wherein the total number of carbon atoms per individual mercaptoamide or mercaptoimide does not exceed 12.

3. The process according to claim **2** wherein the total number of carbon atoms per individual mercaptoamide per Formula I is 5 to 12, in Formula II 2 to 12; and in each mercaptoimide in Formula III is 5 to 12 and in Formula IV 3 to 12.

4. The process according to claim **3** wherein said metal surfaces are selected from copper, silver, tin, lead, zinc, cadmium and alloys thereof.

5. The process according to claim **4** wherein said mercaptoamide or mercaptoimide and solvent comprise a solution-dispersion containing from about 0.005 to 20 weight percent of said mercaptoamide or mercaptoimide based on the total weight of said solution-dispersion.

6. The process according to claim **5** wherein said solution-dispersion is an aqueous solution-disperison, and further lower alcohols containing 1 to 4 carbon atoms per molecule.

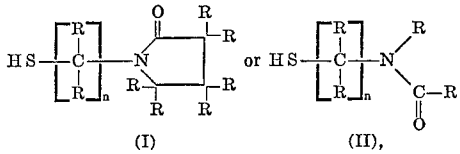
7. The process according to claim **6** containing a stabilizing agent selected from an ammonium or alkali metal hyposulfite, sulfite, or metabisulfite, said alkali metal is lithium, sodium, potassium, rubidium, or cesium, and said stabilizer is present in said solution-dispersion in the range of from 1:10 to 5:1 based on the weight ratio of said stabilizer to total mercaptoamide or mercaptoimide content of said solution-dispersion or an alkaline material present in an amount sufficient to adjust the pH of said solution-dispersion to within the range of from about 8 to 11.5, and selected from ammonia, ammonium or alkali metal hydroxides, phosphate, carbonate, or organic amine.

8. The process according to claim **7** wherein said solution-dispersion contains from about 0.005 to 10 weight percent of said at least one mercaptoamide or mercaptoimide.

9. The process according to claim **8** wherein said mercaptoimide is N-2-mercaptoethyl-2-pyrrolidone or N-3-mercaptopropylsuccinimide.

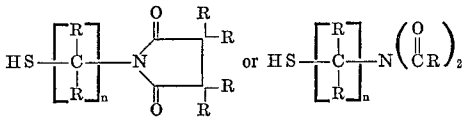
10. A metal treating formulation which comprises an effective minor amount of at least one mercaptoamide or mercaptoimide, water, and a sulfur containing inorganic

stabilizing agent, wherein said mercaptoamide can be represented by



(I) (II),

and said mercaptoimide can be represented by



(III) (IV),

wherein each *n* represents an integer of 1 to 5, and each R is hydrogen or alkyl, wherein at least one said mercaptoamide or mercaptoimide is present in said metal cleaning formulation in a concentration of about 0.005 to 20

weight percent based on the total weight of said cleaning solution-dispersion; and said stabilizer is an inorganic sulfur compound and is an ammonium or alkali metal hyposulfite, sulfite or metabisulfite, and is present in the range of from 1:10 to 5:1 weight ratio of stabilizer to mercaptoamide or mercaptoimide.

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U.S. Cl. X.R.

252—105, 153, 391, 394, 395, 402, 405, 406, 524, 526, 545; 134—2