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# METAL CLEANING AND ANTITARNISH COMPOSITIONS

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## ABSTRACT OF THE DISCLOSURE

This invention relates to the provision of compositions useful as metal cleaning and antitarnish agents. It relates further to metal surfaces which are coated with a thin layer of an organic trivalent phosphorous compound which imparts tarnish resistance to the surface of the metal. It relates further to compositions containing a phosphine which is generally water or alcohol soluble, and a water and/or alcoholic solvent therefor, said composition containing an amount of phosphine which is capable of imparting tarnish resistance to a metal surface to which it is applied.

Generally stated, the subject matter of the present invention relates to a metal cleaning and tarnish inhibiting composition. More particularly, the invention relates to a metal cleaning and tarnish inhibiting composition which contains a trivalent organophosphorous compound.

Metal cleaning compositions are employed to remove tarnish and dirt from metals, and contain as a basic component an abrasive substance. In addition, the composition may also contain soaps and emulsified fatty acids which act to both maintain the abrasive substance in uniform suspension, as well as aid in the removal of tarnish and dirt. The abrasive substance is selected relative to the hardness of the metal, utilizing as the criterion of selection, maximum abrasion without deleterious scratching of the metal surface. Among the various abrasive substances used, either alone or in combination are chalk, collodial clay, diatomite, magnesium oxide, pumice, red iron oxide and the like. Metal cleaning therefore, constitutes an abrading action, and even though the abrasive substance is chosen relative to the hardness of the metal there is a gradual diminution of the metal as a consequence to the abrading action.

With regard to tarnish inhibition, effective inhibiting has for the most part, with minor exceptions, been nonexistent. The expedient usually resorted to requires the use of an oil, such as pine oil or oleic acid, the oil leaving a thin film on the metal surface to act as a protective against tarnishing. Recently, particular mercaptans have been used as tarnish inhibitors for silver; however, an effective silver cleaning and tarnish inhibiting composition still requires the use of an abrasive substance along with the mercaptan.

Attempts to obviate the inherent disadvantages of the traditional abrading metal cleaning compositions resulted in the development of the electrolytic and chemical processes for cleaning metals; however, as a consequence to the inherent disadvantages of both processes they have not been broadly adopted in either industrial, or consumer metal cleaning. The electrolytic process in many instances, results in the removal of metal to the extent of several thousandths of an inch, and requires the use of materials such as concentrated sulfuric acid and cyanide, among others. Whereas, the chemical process requires the use of a composition comprising an acid, having a pH in the range of 1 to 5, and thiourea. Furthermore, the process requires the addition of water to the aforementioned composition prior to its use; the amount being



directly dependent on the character of the impurities to be removed from the metal surface. Lastly, effective cleaning necessitates immersion of the article to be cleaned in the aforementioned aqueous solution.

The present invention represents the culmination of a series of investigations conducted largely by the inventors and their associates in the problems of metal cleaning, utilizing purely chemical means and attempting to obviate the inherent disadvantages of the traditional abrading metal cleaning composition. The inventive concept upon which the present invention is based resides in the discovery that trivalent organophosphorous compounds are effective metal cleaners, in that tarnish and dirt are removed from a metal surface without the inherent disadvantages of the traditional abrading metal cleaning compositions, and the aforementioned chemical process.

Furthermore, the inventive concept resides in the added discovery that the trivalent organophosphorous compounds are capable of effectively inhibiting the tarnishing of metal. This unexpected result is presumably due to the residual bonding of the trivalent phosphorous moities to the metal surface in the form of a tightly adherent, transparent barrier film.

Therefore, the invention relates to a metal cleaning and tarnish inhibiting composition comprising a suitable carrier having admixed therein at least 0.1% by weight of a member selected from the group consisting of a water soluble trivalent organophosphorous compound, an alcohol soluble trivalent organophosphorous compound and mixtures thereof.

The advantages which inure to the art as a consequence to the advent of the present invention should be readily apparent from the foregoing. Primarily, the disadvantage of gradual diminution of the metal as a consequence to the traditional abrading action of metal cleaning has been obviated. Furthermore, effective tarnish inhibition can be achieved by a tightly adherent, transparent barrier film formed on the metal surface, said film not materially impairing the brilliance of a cleaned metal surface.

The following compounds are typical of the trivalent organophosphorous compounds of the present invention:

(3-hydroxypropyl)phosphine,
[2-(ethoxycarbonyl)ethyl]phosphine,
[3-(trimethylammonium)propyl]phosphine chloride,
disodium bis(2-carboxyethyl)phosphine,
bis(3-hydroxypropyl)phosphine,
bis(3-sulfamoylpropyl)phosphine,
tris(hydroxymethyl)phosphine,
tris(3-hydroxypropyl)phosphine,
disodium bis(3-carboxypropyl)ethylphosphine,
tris(2-hydroxyethoxymethyl)phosphine,
tris(1-hydroxyethyl)phosphine,
tris(1-hydroxy 1-methylethyl)phosphine,
hexyl bis(hydroxymethyl)phosphine,
(3-aminopropyl)bis(3-hydroxypropyl)phosphine,
sodium dimethyl (3-sulfopropyl)phosphine,
(3,5-dihydroxyphenyl)bis(hydroxymethyl)phosphine,
trisodium tris(p-carboxyphenyl)phosphine,
tris(2-carbamoylethyl)phosphine,
tris(2,3-dihydroxypropyl)phosphine,
2-hydroxyethyl dipropylphosphinite,
ethyl dimethylphosphinathioite, N-2-hydroxyethyl-p,p-diisobutylphosphinous amide,
p,p-bis(2-hydroxyethyl)-N,N-dimethylphosphinous amide,
dimethyl(3-hydroxypropyl)phosphonite,
bis(2-hydroxyethyl)[2-(ethoxycarbonyl)ethyl]phosphonite,
bis(p-hydroxybenzyl) methylphosphonodithioite,
p-isobutyl-N,N,N',N'-tetramethylphosphonous diamide,
(2-hydroxyethyl)dimorpholinophosphine,
triethyl phosphite,
trimethyl phosphorotrithioite,

tris(2-hydroxyethyl)phosphite,
hexamethylphosphorous triamide,
hexakis(2-hydroxyethyl)phosphorous triamide,
ethyl N-(2-hydroxyethyl)-p-methylphosphonamidite,
methyl p-ethyl-N,N-dimethylphosphonamidothioite,
diethyl morpholinophosphonite,
dimethyl dimethylphosphoramidodithioite,
2-(2-hydroxyethoxy)ethyl N,N'-(2-hydroxyethyl) phosphorodiamidite,
trimethylenebis[bis(hydroxymethyl)phosphine],
tetrasodium ethylene-bis[bis(2-carboxyethyl)phosphine],
p-phenylenebis[bis(hydroxymethyl)phosphine],
bis(2-hydroxyethyl)trimethylenebis[ethylphosphinite],
ethylene tetrakis(2-hydroxyethyl)diphosphite,
oxydiethylene tetraisobutyldiphosphinite,
ethylene 2-hydroxyethyl phosphite,
1-(hydroxymethyl)phosphorinane,
5-(hydroxymethyl)2-,4,6-triisopropyl-1,3,5-dioxaphosphorinane.

Generally, the trivalent organophosphorous compounds utilized in the novel composition of the present invention have the facility to act as a metal cleaner, as well as a tarnish inhibitor; however, the efficiency of the compounds, as either a metal cleaner or tarnish inhibitor, is directly related to the number, and nature of substituents. For example, a primary phosphine is an effective metal cleaner; however, greater metal cleaning efficiency is achieved by utilizing the tertiary phosphine.

With regard to the nature of the substituents, it has been observed that here again the nature, that is molecular weight, extent of hydrocarbon character, as well as the hydrophilic nature of the substituents, is directly related to the efficiency of the compound as either a metal cleaner or tarnish inhibitor. For example, a tertiary phosphine having substituents containing 1 to 8 carbon atoms, as well as water solubilizing groups, possesses greater efficiency as a metal cleaner than a tertiary phosphine of hydrocarbon character containing substituents of 12 to 20 carbon atoms. Whereas, a tertiary phosphine of hydrocarbon character containing substituents of 12 to 20 carbon atoms possesses greater efficiency as a tarnish inhibitor. Therefore, it is conceivable that a metal cleaning and tarnish inhibiting composition of the present invention would contain more than one trivalent organophosphorous compound.

The trivalent organophosphorous compounds utilized in the novel compositions of the present invention should possess either water or alcohol solubility. It is preferred to use as an alcoholic solvent a lower alkyl alcohol, that is an alcohol containing 1 to 5 carbon atoms. No theory is offered as to the mechanism of activity of the trivalent organophosphorous compounds of the present invention, nor is it intended that the present invention be so limited to any theoretical considerations of the mechanism of activity.

With regard to the concentration of trivalent organophosphorous compounds present in the novel composition of the present invention, 0.1% represents a concentration at which the trivalent organophosphorous compounds will act both as a metal cleaner, as well as a tarnish inhibitor; however, the efficiency of the trivalent organophosphorous compounds as metal cleaners is directly related to concentration. The factors of concentration and time, that is the time required to accomplish effective removal of tarnish and dirt from a metal surface, are indirectly proportional, in that as the concentration increases the time necessary to effectively remove the tarnish and dirt from a metal surface decreases. However, a point is reached at which an increase in concentration will not appreciably effect the factor of time. For example, the trivalent organophosphorous compounds are effective as metal cleaners in a pure state, that is 100%, and when so used the decrease in time is not significant when contrasted to a concentration of 20%. Concerning the effect of concentration on tarnish inhibition, the efficiency of the trivalent organophosphorous compounds is not appreciably effected by concentration, since only a monomolecular layer is necessary to achieve effective tarnish inhibition. Therefore, a preferred concentration which will satisfactorily achieve effective metal cleaning, as well as tarnish inhibition is from about 5% to 20%.

The novel composition of the present invention is operable at conditions of normal room temperature, pressure and humidity, as well as either acidic or alkaline conditions. However, the presence of moisture, as well as conditions of temperature and pH are directly related to the efficiency of the compounds. With regard to the presence of moisture and temperature, the efficiency is directly proportional to same, since an increase in either temperature, or the amount of water present increases the efficiency of the compounds. Lastly, the preferred pH may be defined as the ambient pH of the particular trivalent organophosphorous compound utilized, that is the pH of the solution, either aqueous or alcoholic, in which the compound is dissolved. Since the trivalent organophosphorous compounds tend to have an ambient pH which is usually alkaline, the preferred pH would in most instances be alkaline. However, this should not be construed as a limitation to the invention, since the compounds are operable in an acidic environment. For example, an aqueous solution of the compound tris(hydroxymethyl)phosphine, has a pH of 8, which is the preferred pH at which maximum efficiency is achieved, however, the compound is operable at both a higher and lower pH.

As presently used the term suitable carrier may be defined to mean that carrier which is compatible with the trivalent organophosphorous compounds of the present invention, as well as with the ultimate end use of the composition, that is the metal to which the composition is to be applied. In addition, the carrier may constitute the solvent in which the trivalent organophosphorous compound is dissolved.

Since the trivalent organophosphorous compounds are readily oxidized, it is preferred to formulate the novel metal cleaning and tarnish inhibiting composition of the present invention with an inert propellant under pressure, to be dispensed as an aerosol foam, cream or the like. The novel composition of the present invention may also include an antioxidant to stabilize the composition such as hydroquinone, monoethylether of hydroquinone, 2,2' - ditertiarybutyl-4-methylene-6,6'-dimethyl bisphenol, sulfites and bisulfites among others. Furthermore, additional buffing and polishing agents may be added to the novel composition of the present invention, an well as a silver tarnish inhibiting mercaptan, or thioglycolate. Lastly, the composition may also include reducing agents, which aid in the cleaning of a metal surface such as sodium hydrophosphite, sodium hyposulfite, hydrazine and the like.

The trivalent organophosphorous compounds utilized in the novel composition of the present invention may be prepared in situ; for example, a tertiary phosphine may be prepared from the corresponding phosphonium salt by the addition of a basic substance to a solution of the phosphonium salt.

The novel compositions of the present invention may be utilized with those metals which are subject to tarnishing, that is those metals which are capable of forming a surface film of contrasting color, formed on an exposed surface of a metal, and usually consisting of the oxide or sulfide of said metal. Illustrative of the metals which fall within this category are such metals as copper, brass, aluminum, nickel, cobalt, silver, ferrous metal objects and the like.

A preferred embodiment of the novel metal cleaning and tarnish inhibiting composition of the present invention would, therefore, contain 10 percent by weight of tris(hydroxymethyl)phosphine, 1 percent by weight of octadecyl bis(hydroxymethyl)phosphine, and a sufficient

quantity of a hydroalcoholic solution, containing equal parts of isopropanol and water, to bring the volume to 100 percent. This solution is then admixed with a halogenated hydrocarbon propellant in the ratio of solution to propellant of 9:1.

The following examples are provided for illustrative purposes and may include particular features of the invention, however, the examples should not be construed as limiting the invention, many variations of which are possible without departing from the spirit or scope thereof.

## EXAMPLE I

### Utilization of a primary phosphine in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a primary phosphine with metallic silver.

A composition consisting of the following ingredients was prepared:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.22 |
| Methyl salicylate | 1.11 |
| (3-hydroxypropyl)phosphine | 11.11 |
| Denatured alcohol | 58.36 |
| Water up to 100. | |

The stearyl cetyl ethoxylate was melted in a suitable container on a steam bath. The denatured alcohol and a small amount of water were then added to the melted stearyl cetyl ethoxylate with stirring until a homogeneous mixture was obtained. The mixture was then cooled to room temperature, placed under a nitrogen blanket and the balance of ingredients were then added. The resulting solution was then admixed with a halogenated hydrocarbon propellant, in the ratio of solution to propellant of 9:1. The halogenated hydrocarbon propellant consisted of a mixture of dichlorodifluoromethane and dichlorotetrafluoroethane in the ratio of 2:3 respectively.

Sterling silver strips measuring 4" by 2", and referred to as "silver coupons," were cleaned with a traditional silver cleaning composition and finally rinsed to dryness in acetone. The coupons were placed in a desiccator and subjected to an atmosphere containing hydrogen sulfide for 2 days, at which time the strips possessed a heavy coating of tarnish.

A silver strip prepared in the above manner was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criteria of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criteria of performance.

A metal cleaning composition incorporating a primary phosphine was prepared in the manner hereinabove set forth, substituting for (3 - hydroxypropyl)phosphine, [2 - (ethoxycarbonyl)ethyl]phosphine, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE II

### Utilization of a secondary phosphine in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a secondary phosphine with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.22 |
| Bis(3-hydroxypropyl)phosphine | 10.5 |
| Denatured alcohol | 58.36 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criteria of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a secondary phosphine was prepared in the manner hereinabove set forth, substituting for bis(3-hydroxypropyl)phosphine, disodium bis(2-carboxyethyl)phosphine, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE III

### Utilization of tertiary phosphines in the novel composition of the present invention

This example demonstrates the metal cleaning facility of tertiary phosphines with metallic silver.

A composition consisting of the following ingredients was prepared:

| | Percent by wt. |
|---|---|
| Nonyl phenol ethoxylate | 0.20 |
| Tris(hydroxymethyl)phosphine) | 10.00 |
| Hexylene glycol | 5.00 |
| Water up to 100. | |

The nonyl phenol ethoxylate and the hexylene glycol were added to a small amount of water, this mixture was then placed under a nitrogen blanket and the tris-(hydroxymethyl)phosphine and the remaining water were added. The resulting solution was then admixed with a halogenated hydrocarbon propellant in the ratio of solution to propellant of 7:3. The halogenated hydrocarbon propellant consisted of a mixture of dichlorodifluoromethane and dichlorotetrafluoroethane in the ratio of 1:4, respectively.

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criteria of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating tertiary phosphines was prepared in the manner hereinabove set forth, substituting for tris(hydroxymethyl)phosphine, tris-(3-hydroxypropyl)phosphine, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE IV

### Utilization of a phosphinite ester in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphinite ester with metallic silver.

A composition consisting of the following ingredients was prepared:

| | Percent by wt. |
|---|---|
| Dioctyl sodium sulfosuccinate | 0.10 |
| 2-hydroxyethyl dipropylphosphinite | 15.00 |
| Denatured alcohol | 10.00 |
| Water up to 100. | |

The dioctyl sodium sulfosuccinate and the 2-hydroxyethyl dipropylphosphinite were added to the denatured alcohol under a nitrogen blanket. The water was then added to the above admixture. The resulting solution was then admixed with an isobutane propellant in the ratio of solution to propellant of 4:1.

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphinite ester was prepared in the manner hereinabove set forth, substituting for 2-hydroxyethyl dipropylphosphinite, ethyl dimethylphosphinothioite, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE V

Utilization of a phosphinamide in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphinamide with metallic silver.

A composition consisting of the following ingredients was prepared:

| | Percent by wt. |
|---|---|
| Octodecyl thioglycolate | 0.50 |
| Stearyl cetyl ethoxylate | 2.00 |
| Methyl salicylate | 0.50 |
| N-2-hydroxyethyl-p,p-diisobutylphosphinous amide | 10.00 |
| Denatured alcohol | 58.36 |
| Water up to 100. | |

The stearyl cetyl ethoxylate was melted in a suitable container on a steam bath. The denatured alcohol, in which the octadecyl thioglycolate had been dissolved, and a small amount of water were then added to the melted stearyl cetyl ethoxylate with stirring until a homogeneous mixture was obtained. The mixture was then cooled to room temperature, placed under a nitrogen blanket, and the balance of ingredients were then added. The resulting solution was then admixed with a halogenated hydrocarbon propellant, in the ratio of solution to propellant of 9:1. The halogenated hydrocarbon propellant consisted of a mixture of dichlorodifluoromethane and dichlorotetrafluoroethane in the ratio of 2:3 respectively.

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphinamide was prepared in the manner hereinabove set forth, substituting for N-2-hydroxyethyl-p,p-diisobutylphosphinous amide, p,p,-bis(2-hydroxyethyl)-N,N-dimethylphosphinous amide, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE VI

Utilization of a phosphonite ester in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphonite ester with metallic silver.

A composition consisting of the following ingredients was prepared:

| | Percent by wt. |
|---|---|
| Silicone oil | 0.1 |
| Dimethyl(3-hydroxypropyl)phosphonite | 12.00 |
| Denatured alcohol | 25.00 |
| Water up to 100. | |

The silicone oil was added to the denatured alcohol, and the resulting mixture was placed under a nitrogen blanket. The dimethyl(3-hydroxypropyl)phosphonite was then added to the above mixture along with the water. The resulting solution was then admixed with a hologenated hydrocarbon propellant, in the ratio of solution to propellant of 9:1. The halogenated hydrocarbon propellant consisted of a mixture of dichlorodifluoromethane and dichlorotetrafluoroethane in the ratio of 2:3 respectively.

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphinite ester was prepared in the manner hereinabove set forth, substituting for dimethyl(3-hydroxypropyl)phosphonite, bis(2-hydroxyethyl)[2-(ethoxycarbonyl)ethyl]phosphonite, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE VII

Utilization of a phosphonamide in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphonamide with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.22 |
| Methyl salicylate | 0.50 |
| P-Isobutyl-N,N,N',N'-tetramethylphosphonous diamide | 10.5 |
| Denatured alcohol | 58.36 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphoamide was prepared in the manner hereinabove set forth, substituting for p-isobutyl-N,N,N',N'-tetramethylphosphonous diamide, (2-hydroxymethyl)dimorpholinophosphine, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE VIII

Utilization of tertiary phosphite in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a tertiary phosphite with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.22 |
| Methyl salicylate | 0.75 |
| Triethylphosphite | 12.00 |
| Denatured alcohol | 58.36 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a tertiary phosphite was prepared in the manner hereinabove set forth, substituting for triethylphosphite, trimethylphosphorotrithioite, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE IX

Utilization of a phosphorous triamide in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphorous triamide with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.22 |
| Methyl salicylate | 1.11 |
| Hexamethylphosphorous triamide | 11.11 |
| Denatured alcohol | 58.36 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphorous triamide was prepared in the manner hereinabove set forth, substituting for hexamethylphosphorous triamide, hexakis(2-hydroxyethyl)phosphorous triamide, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE X

Utilization of a phosphinite ester amide in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphinite amide with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.22 |
| Methyl salicylate | 0.5 |
| Ethyl N-(2-hydroxyethyl)-p-methylphosphonamidite | 15 |
| Denatured alcohol | 60 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphinite ester amide was prepared in the manner hereinabove set forth, substituting for ethyl N-(2-hydroxyethyl)-p-methylphosphonamidite, methyl p-ethyl-N,N-dimethylphosphonamidothioite, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE XI

Utilization of a phosphorous amide ester in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphorous amide ester with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2 |
| Methyl salicylate | 0.25 |
| Diethyl morpholinophosphonite | 15 |
| Denatured alcohol | 55 |
| Water up to 100. | |



A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphorous amide ester was prepared in the manner hereinabove set forth, substituting for diethyl morpholinophosphonite, dimethyl dimethylphosphoramidodithioite, the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE XII

Utilization of a diphosphine in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a diphosphine with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 3 |
| Methyl salicylate | 1.5 |
| Trimethylene bis[bis(hydroxymethyl)phosphine] | 14 |
| Denatured alcohol | 60 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a diphosphine was prepared in the manner hereinabove set forth, substituting for trimethylene bis[bis(hydroxymethyl)phosphine], tetrasodium ethylene bis[bis(carboxyethyl)phosphine], the composition achieving the same effect as hereinabove demonstrated.

## EXAMPLE XIII

Utilization of a phosphorous heterocycle in the novel composition of the present invention

This example demonstrates the metal cleaning facility of a phosphorous heterocycle with metallic silver.

A composition consisting of the following ingredients was prepared in the manner set forth in Example I:

| | Percent by wt. |
|---|---|
| Stearyl cetyl ethoxylate | 2.5 |
| Methyl salicylate | 1.25 |
| Ethylene 2-hydroxyethyl phosphine | 12 |
| Denatured alcohol | 50 |
| Water up to 100. | |

A silver strip, prepared in the manner set forth in Example I, was subjected to an application of the composition hereinabove prepared and a visual judgment was made as to performance. The criterion of performance was whether an appreciable brightness of the coupon would be observed in 30 seconds of application. The aforementioned composition demonstrated effective cleaning and satisfied the criterion of performance.

A metal cleaning composition incorporating a phosphorous heterocycle was prepared in the manner hereinabove set forth, substituting for ethylene 2-hydroxyethyl phosphite, 1-(hydroxymethyl)phosphorinane, the composition achieving the same effect as heerinabove demonstrated.

EXAMPLE XIV

Illustration of the tarnish inhibiting effect of the novel compositions of the present invention

This example demonstrates the tarnish inhibiting effect of tertiary phosphines on metallic silver.

Three coupons prepared in the manner set forth in Example I were cleaned utilizing in the first instance a traditional silver cleaning composition in which chalk was the abrasive substance, this coupon was designated Sample A. The second coupon was cleaned with the composition of Example III, and designated Sample B. The third coupon was cleaned with the following composition, and was designated Sample C.

| | Percent by wt. |
|---|---|
| Tris(hydroxymethyl)phosphine | 11.1 |
| Octadecyl bis(hydroxymethyl)phosphine | 1 |
| Isopropanol | 70 |
| Water up to 100. | |

The composition was prepared by simply dissolving the tris(hydroxymethyl)phosphine and the octadecyl bis(hydroxymethyl)phosphine in the isopropanol under a nitrogen blanket and adding the remainder of water.

Each of the coupons were placed in the same desiccator and subjected to an atmosphere containing dydrogen sulfide, after 3 days the following visual observations were made. Sample A was heavily coated with tarnish and for the most part was substantially black in color. Sample B was tarnished, however, to a lesser degree than Sample A, and gave a brownish appearance. Sample C did not appear to have tarnished appreciably and gave the appearance of having a slight yellow cast.

EXAMPLE XV

In situ preparation of tris(hydroxymethyl)phosphine

This example demonstrates the in situ preparation of tris(hydroxymethyl)phosphine from its corresponding phosphonium salt.

A composition comprising the following ingredients was prepared:

| | Percent by wt. |
|---|---|
| Tetrakis(hydroxymethyl)phosphonium chloride | 48.8 |
| Sodium methoxide | 10.8 |
| Denatured alcohol up to 100. | |

The sodium methoxide was dissolved in a portion of the denatured alcohol. The resulting solution was placed under a nitrogen blanket and the tetrakis(hydroxymethyl)phosphonium chloride was dissolved in the remaining alcohol with agitation. Upon the addition of the tetrakis(hydroxymethyl)phosphonium chloride solution there was precipitation of sodium chloride. The sodium chloride was then filtered leaving a solution of tris(hydroxymethyl)phosphine and formaldehyde in denatured alcohol. The resulting solution was then vacuum distilled removing the denatured alcohol and the formaldehyde.

Although the invention has been described and illustrated by reference to particular embodiments thereof, it will be understood that in its broadest aspects the invention is not limited to such embodiments, and that variations and substitution of such equivalents may be resorted to within the scope of the appended claims.

We claim:

1. The method of cleaning metal surfaces and imparting tarnish resistance thereto which comprises treating said surface with an effective amount of an organic phosphine in water or a lower alkanol.

2. The method of claim 1 wherein the metal is copper or a copper alloy.

3. An article comprising a normally tarnishing metal surface having applied thereto as a tarnish inhibiting barrier in a carrier comprising water or a lower alcohol, a water or alcohol soluble oganic phosphine, said phosphine barrier being resistant to dissolution and removal upon contact with water.

4. The article of claim 3 in which the metal is composed at least in part of copper.

5. A metal cleaning and tarnish inhibiting composition comprising 0.1 to 20% of an organic phosphine which is generally soluble in water or in alcohol of 1–5 carbon atoms; and a liquid carrier, comprising water or a lower alkanol or mixtures thereof.

6. The composition of claim 5 wherein the liquid carrier contains denatured alcohol.

7. The composition of claim 5 wherein the liquid carrier contains water.

8. The composition of claim 5 wherein the liquid carrier is isopropyl alcohol.

9. A composition containing (a) at least 0.1% of an organic phosphine which is soluble in an alcohol of 1–5 carbon atoms or in water, (b) a liquid aqueous or alcoholic carrier, and (c) an antioxidant which stabilizes said organic phosphine against oxidative deterioration; said composition being capable of forming a tarnish protective barrier when applied to a normally tarnishing metal.

10. A composition suitable for application to a metal surface from a propellant container and capable of applying a tarnish protective barrier to said metal surface, comprising (a) at least 0.1% of an organic phosphine which is soluble in water or an alcohol of 1-5 carbon atoms, (b) an aqueous or alcoholic solvent for said phosphine, and (c) an inert halogenated hydrocarbon propellant wherein the ratio of (a) plus (b) to propellant is 7:3 to 9:1.

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