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3,595,800

COMPOSITION AND PROCESS FOR CLEANING NONFERROUS METALS AND THEIR ALLOYS

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ABSTRACT OF THE DISCLOSURE

Cleaning of metal surfaces and especially the surfaces of nonferrous metals and their alloys, as exemplified by the surfaces of zinc base die castings, to remove difficulty removable foreign deposits therefrom such as, for example, buffing compound residues and other soils, e.g. grease and oil, without any substantial corrosion and discoloration of the metal surface. The ready-to-use liquid cleaning composition comprises one or more soaps from the group of the amine and alkanolamine salts of fatty and rosin acids, an effective amount, sufficient to inhibit corrosion of the metal surface by the cleaning composition, of elemental sulfur, one or more solubilizers for the sulfur, and an aqueous liquid, usually water. Cleaner concentrate compositions adapted to be mixed together with the aqueous liquid to form such ready-to-use cleaning composition, also constitute the present invention.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to cleaning of metal surfaces and more particularly to new and improved compositions and a process for cleaning metal surfaces, especially the surfaces of nonferrous metals and their alloys as exemplified by the surfaces of zinc base die castings, to remove therefrom difficulty removable soils, for example buffing compound deposits, without any substantial corrosion and discoloration of the metal surface. Additionally this invention relates to concentrate compositions adapted to be added to an aqueous liquid, usually water, to form ready-to-use cleaner compositions, and to corrosion inhibitor additive compositions for addition to the cleaner compositions.

(2) Description of the prior art

Zinc base die castings frequently have a coating applied to their metal surfaces either for decorative or protective purposes. The coating can be applied by electroplating, painting, chromating or by another procedure. It is necessary that the casting metal surface or surfaces to be coated be free of soils of all kinds as the presence of the soil interferes with and prevents uniform adherence of the coating to the metal surface. Buffing compounds utilized for buffing zinc base die are especially difficult to remove. However, unless all or virtually all of the buffing compound is removed from the casting surface, inferior electroplating of the casting surface will result which tends to lead to blistering of the plating.

Cleaner compositions heretofore employed for removal of buffing compound deposits from the surfaces of zinc base die castings, were not especially satisfactory for the reason they corroded or discolored lustrous metal surfaces of the buffed casting. I found this corrosion and discoloration including tarnishing of the buffed zinc surface to occur with prior liquid cleaner compositions containing amine and alkanolamine soaps, with the corroded portions of the metal surface frequently being depressed or sunken to a certain extent. Further the discolored and tarnished portions of the metal surface had the appearance of clouds or haze in the buffed metal surface. The subsequent electroplating of the cleaned but corroded die

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casting surface was unsatisfactory as the electroplate showed the corroded and discolored appearance of the underlying surface. And this was the situation even when a levelling nickel electroplating bath was utilized with a chrome electroplate over the nickel plate.

In the past, silicates and pyrophosphates have been utilized in metal cleaner compositions for inhibiting corrosion of the metal by the cleaner. Although cleaner compositions containing such materials are satisfactory as metal cleaners in many respects, it was found that these silicate- and pyrophosphate-containing cleaner compositions still corrosively attacked the buffed surfaces of the zinc base die casting causing discoloration of the high luster surface in portions of the metal surface.

Organic sulfur-containing compounds having in their molecular structure a heterocyclic ring of from 5 to 6 members and wherein the chemically combined sulfur is either directly linked to the heterocyclic ring or is a member of such ring, are known in the prior art as inhibitors of discoloration of various metals and alloys, such as copper, brass and German silver by detergent compounds. Exemplary of such heterocyclic-ring containing organic sulfur-containing compounds are phenylene thiourea, ethylene thiourea, N,N'-trimethylene thiourea, thiourazole, benzoylene thiourea, 6-propyl thiouracil, thioparabanic acid, 1-phenyl imidazothione (2), 1-methyl imidazothione (2), monophenyl-thioparabanic acid, 5-benzal-2-thiohydantoin, 3-mercapto-1, 2,4-triazole, 1-methyl-2-mercapto-imidazole, thioammeline, 4,5-dihydroglyoxaline-2-thio-glycolic acid, S-methyl-mercaptatetrazole, 2-(benzyl-mercapto)-imidazole, 2-aminothiazole, 2-amino-benzothiazole, pseudothiohydantoin, 2-amino-4-ketodihydrothiazine, 2-amino - 5 - carboxymethyl thiazolone and 2-(allylamino)-benzothiazole; and such compounds are disclosed as discoloration inhibitors in detergent compositions in U.S. Pat. 2,618,603. Alkyl benzyl thiols are also reported in the prior art as tarnish preventatives in metal cleaners of the type having abrasive grit as an ingredient. Although these complex organic sulfur compounds may give good results as metal discoloration and tarnish inhibitors and preventatives, they have the drawback of being critical with respect to concentrations employed, i.e. being operable in only relatively narrow proportions ranges, making their use awkward in typical industrial applications. In addition, they also have the drawback of being expensive compounds.

SUMMARY OF THE INVENTION

In accordance with the present invention, I have found that soils including difficulty removable soils such as buffing compound residues, as well as greases and oils are effectively removed from metal surfaces, for instance zinc base die casting surfaces, without any substantial corrosion or discoloration of the metal surface by having present in the aqueous liquid cleaning composition utilized to clean the metal surface elemental sulfur. The liquid cleaning compositions of this invention contain, in addition to the elemental sulfur, a solubilizer for the sulfur, a soap which is an amine or alkanolamine salt of a fatty or rosin acid, or a mixture of such salts, and an inert aqueous liquid, usually water. Other ingredients herein-after disclosed may also be present in the aqueous cleaning composition. As a result of the cleaning, a metal surface is obtained which is well suited for subsequent plating, and this invention is especially well suited for cleaning buffed zinc base die castings in preparation for electroplating. The relatively inexpensive elemental sulfur is operable in the cleaning compositions of this invention over a relatively wide proportion range thereof, as contrasted with the narrow proportion ranges required for use of the prior complex organic sulfur compounds.

The cleaning process herein is usually a soak or tank cleaning procedure wherein the soiled metal article to be cleaned is immersed in the liquid aqueous cleaner, until the soil is removed from its surface. The soiled metal article to be cleaned, for instance the soiled zinc base die casting, can be immersed in the liquid cleaner in a stationary state or it can be moved slowly through the liquid cleaner, for instance on a conveyor, until the soil is removed from its surface. The application of ultrasonic wave energy to the soil articles immersed in the liquid cleaner composition can also be employed, if desired, and may be especially desirable in the fine cleaning of small parts or articles, for instance such parts of the electronics industry.

This invention also comprehends concentrate compositions adapted to be added to water to produce the liquid cleaner compositions. The concentrate composition comprises a soap from the group of the amine and alkanolamine salts of fatty and rosin acids, and mixtures thereof, elemental sulfur present in an effective amount sufficient to inhibit corrosion of the metal surface by the ultimate liquid cleaner composition, one or more solubilizers for the elemental sulfur, and water.

In another embodiment of the invention, additive compositions are provided for addition to cleaning compositions, especially the amine and/or alkanolamine soap-containing cleaning compositions, to inhibit corrosion and staining or discoloration of the metal surface to be cleaned by the cleaning composition. The additive composition herein comprises a mixture of one or more amines, for instance straight chain lower aliphatic hydrocarbon polyamines, one or more alkanolamines, for instance mono- and polyalkanolmonoamines, and the elemental sulfur. A solubilizer for the sulfur such as, for example, one or more of the solubilizers hereinafter disclosed may also be an ingredient of such additive composition. If the solubilizer for the elemental sulfur is to be an excess of such amine and/or alkanolamine as hereinafter disclosed, then it is unnecessary to include as an ingredient another material or compound as solubilizer although this can be done if desired. The proportions of the ingredients of such additive compositions are not especially critical and can be varied over wide ranges. Typical proportions of the amine and/or alkanolamine and sulfur ingredients are from about 25% to about 85% of the total amine and/or alkanolamine and from about 15% to about 75% of elemental sulfur, the percentages being by weight and based on the product additive composition. An inert diluent may also be an ingredient of such additive compositions and can be an inert liquid diluent, e.g. water.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The elemental sulfur is present in the cleaner concentrates herein in an effective amount, sufficient to inhibit corrosion of the metal surface being cleaned, preferably from about 0.05% to about 15% by weight, more preferably from about 0.2% to about 15% by weight. Such minor amount of elemental sulfur is also sufficient to inhibit discoloration of the metal surface. The amine and/or alkanolamine soaps are present in the cleaner concentrates in amount preferably from about 5% to about 60% by weight, the solubilizer for the sulfur in amount preferably from about 1% to about 40% by weight, and the water in amount preferably from about 5% to about 65% by weight, all percentages based on total concentrate composition.

The cleaner concentrate is mixed together with an aqueous liquid, usually water, to form the ready-to-use alkaline liquid cleaning composition usually by adding the concentrate composition to the aqueous liquid, preferably in the proportions of about 2 to about 25 fluid ounces of the concentrate composition per gallon of water, more preferably about 3.5 to about 17 fluid ounces per gallon.

The liquid alkaline cleaning compositions or bath herein usually have a pH in the range 8-12. The concentrate compositions herein are also alkaline and have a pH usually in the range 9.5-12.5.

Amines utilizable for forming the amine soaps are, for example, the straight chain lower aliphatic hydrocarbon polyamines, for instances such lower aliphatic-tri- amines, e.g. diethylenetriamine and triethylenetriamine, ethylene diamine and propylene diamine and such lower aliphatic pentamines, e.g. tetraethylenepentamine. Alkanolamines suitable for forming the soaps are, for example, the mono- and polyalkanolmonoamines wherein each of the alkanol chains has from 2 to 3 carbon atoms inclusive, e.g. monoethanolamine, diethanolamine, and triethanolamine.

The fatty acids that are reacted with the amines and alkanol amines to form the soaps are those having from 8 to 25 carbon atoms inclusive per molecule, e.g. caprylic, lauric, palmitic, stearic, oleic, linoleic, ricinoleic, abietic and other fatty acids having a total number of carbons within this range and/or mixtures of such fatty acids. Tall oil is by-product of the paper industry and contains principally the tall oil fatty acids oleic and linoleic acids, and also rosin acids.

The soap or soaps can be prepared either prior to being admixed with the other ingredients to form the cleaner concentrate, or it can be formed during the preparation of the cleaner concentrate or in situ therein by reaction of the amine and/or alkanol amine with the fatty acids or fatty and rosin acids.

The cleaning process herein to remove the soils from the metal article surfaces can be carried out at a cleaning composition liquid temperature of room temperature to about 200° F., preferably about 160° F. to about 180° F. The pH of the alkaline cleaning composition liquid or bath is typically in the range 8-12 during the cleaning. The time of immersion of the metal article being cleaned in the cleaning composition is until the soil is removed from the metal surface or surfaces, and is typically 2-10 minutes immersion time for a buffed zinc die cast part or article to remove buffing compound deposits therefrom.

The cleaner concentrate compositions of this invention are prepared by supplying the amine or alkanolamine, for instance monoethanolamine, to the mixing tank, and also supplying the fatty or rosin acid, for instance tall oil fatty acids, to the tank, and mixing the ingredients at room temperature. If the amine which is not an alkanolamine, for instance diethylenetriamine, is also to be utilized, such amine is then added to the ingredients while continuing to mix the ingredients. The elemental sulfur, for instance flowers of sulfur, is then added and permitted to dissolve completely in the liquid, which occurs in about 5-10 minutes. If a solubilizer for the elemental sulfur other than or in addition to the amine and/or alkanolamine is to be utilized, it is added at the time of adding the elemental sulfur. The mixture is then further mixed and water at normal temperature is added thereto in the specified amount. While continuing to mix the ingredients, other ingredients, e.g. sodium glucoheptonate and/or glucose, can be added to the mixture, with mixing continued for about 5 minutes.

The elemental sulfur can be included as an ingredient of the cleaner concentrate during its preparation, or the sulfur can be added either as such or as an ingredient of an additive composition hereinafter disclosed to the already prepared cleaner concentrates or cleaning composition.

The mechanism involved in the inhibition of corrosion and discoloration of the metal by the elemental sulfur is not known with certainty. One explanation advanced is that the formation of insoluble metal sulfides on the surface of the object being cleaned once organic contaminants such as buffing compound residues have been removed, prevents corrosive attack on such surfaces by the cleaner, such attack being generally caused by dissolu-

tion of the metal through formation of a soluble metal complex or chelate by the constituents of the cleaner.

The solubilizer or solubilizing agent for the elemental sulfur can be, for example, one or more of the amines and/or alkanolamines previously disclosed herein for forming the amine soap. When this is the case, the amine and/or alkanolamine is present in amount in sufficient excess over the amount thereof required to react with the fatty and/or rosin acid to form the soap, so as to provide sufficient amine and/or alkanolamine to serve as the solubilizer. Such amines are, for example, the straight chain lower aliphatic hydrocarbon polyamines, e.g., diethylenetriamine, ethylene diamine, propylene diamine and tetraethylenepentamine. Such alkanolamines are, for example, the mono- and polyalkanolmonoamines wherein each of the alkanol chains has from 2-3 carbon atoms inclusive, e.g. monoethanolamine, diethanolamine and triethanolamine. Other solubilizers for the elemental sulfur utilizable herein are, for example, carbon disulfide. Any solubilizer capable of imparting appreciable water solubility to the sulfur and compatible in the ready-to-use cleaning solution and concentrate composition for forming same can be utilized here. The amine and/or alkanolamine form a chemical complex with the sulphur and the carbon disulfide also forms a complex with the sulfur. The solubilizer is utilized in the concentrate composition and the ready-to-use liquid cleaning composition herein in an effective amount sufficient to impart appreciable or substantial water or cleaner solution solubility to the sulfur. A preferred amount of the solubilizer in the concentrate composition herein is an effective water-solubilizing amount in the range, by weight, from about 1%-40%. The solubilizer is present as either a single compound or material or a mixture of compounds or materials.

The following Examples I-III of the table further illustrate the invention with respect to the ready-to-use liquid cleaning compositions thereof. The proportions of the ingredients in the examples of the table are in grams per liter.

Example.....	I	II	III
Sodium carbonate.....			10
Sodium glucoheptonate.....		4	2
Monoethanolamine.....	1/2	15	8
Diethylenetriamine.....	2	5	3
Aminomethylpropanol.....	30		10
Tall oil.....		10	
Palmitic acid.....	2		3
Cottonseed oil, distilled.....	2		4
Dextrose.....	1	6	4
Flowers of sulfur.....	1/2	1/2	1/2

Excess monoethanolamine and diethylenetriamine serves as the solubilizer for the elemental sulfur, i.e. flowers of sulfur, in Examples I-III of the foregoing table. Monoethanolamine and diethylenetriamine salts or soaps of fatty acids were present in the aqueous liquid cleaning compositions of Examples I-III of the table due to reaction in situ of these amines with the fatty acids (tall oil fatty acid in Example II). Such amine soaps were present in the cleaner composition of Example I in total amount of about 0.65%, in the cleaner composition of Example II in total amount of about 37%, and in the cleaning composition of Example III in total amount of about 31%.

The purpose of the sodium glucoheptonate present in the cleaning solutions of foregoing Examples II and III is to chelate metal oxides present on the metal surfaces being cleaned, for instance zinc oxide on zinc and zinc base alloy surfaces. The function of the dextrose in the cleaning solutions of foregoing Examples I-III is to inhibit or prevent re-oxidation of the cleaned metal surface. The aminomethylpropanol of Examples I and III functions to dissolve buffing compound residues from the metal surface.

The fatty acids contained in the distilled cottonseed oil present in the cleaning solutions of Examples I and

III are reported to comprise about 9% caprylic acid, 10% capric acid, 45% lauric acid and 20% myristic acid.

The following examples further illustrate the concentrate compositions of this invention:

EXAMPLE 4

	Percent by weight
Monoethanolamine	0.7
Diethylenetriamine	2.6
Aminomethyl propanol	39.4
Palmitic acid	2.6
Cottonseed oil	2.6
Dextrose	1.3
Flowers of sulfur	0.7
Water	50.1

Monoethanolamine and diethylenetriamine salts or soaps of fatty acids are formed in situ in the foregoing concentrate by reaction of the amines with the fatty acids. Such amine and alkanolamine soaps are present in the cleaner concentrate in total amount of about 8.5 weight percent. Excess monoethanolamine and diethylenetriamine present in the composition of Example 4 functions as solubilizer for the sulfur.

The liquid cleaner concentrate of Example 4 is added to water to form the ready-to-use liquid cleaning composition in the proportion of 6-10 fl. oz. of the concentrate composition per gallon of water.

EXAMPLE 5

	Percent by weight
Sodium glucoheptonate	4.9
Monoethanolamine	18.5
Diethylenetriamine	6.2
Tall oil	12.3
Dextrose	7.4
Flowers of sulfur	0.25
Water	50.45

Amine and alkanolamine salts or soaps of fatty acids are formed in situ in the foregoing concentrate by reaction of amines with the fatty acids. Such amine and alkanolamine soaps are present in the cleaner concentrate in total amount about 42 weight percent. Excess monoethanolamine and diethyleneamine present in the composition of this Example 5 functions as solubilizer for the sulfur.

The liquid cleaner concentrate of Example 5 is added to water to form the ready-to-use liquid cleaning composition in the proportion of 6-10 fl. oz. of the concentrate composition per gallon of water.

EXAMPLE 6

	Percent by weight
Sodium carbonate	11.3
Sodium glucoheptonate	2.3
Monoethanolamine	9.0
Diethylenetriamine	3.4
Aminomethylpropanol	11.3
Palmitic acid	3.4
Cottonseed oil	4.5
Dextrose	4.5
Flowers of sulfur	0.56
Water	49.74

Amine and alkanolamine salts or soaps or fatty acids are formed in situ in the concentrate of this Example 6 by reaction of the amines with the fatty acids. Such amine and alkanolamine soaps are present in the cleaner concentrate in total amount of about 20.5 weight percent. Excess monoethanolamine and diethylenetriamine present in the composition of this Example 6 serves as solubilizer for the sulfur.

The liquid cleaner concentrate of Example 6 is added to water to form the ready-to-use liquid cleaning composition in the proportion of 6-10 fl. oz. of the concentrate composition per gallon of water.

The proportions of the ingredients in the additive compositions are not especially critical and can be varied

over wide ranges. One additive composition herein preferably contains a mixture, by weight, between about 20% and about 40% of the lower aliphatic hydrocarbon polyamine, e.g. diethylenetriamine, between about 40% and about 60% of the mono- or polyalkanolmonoamine, e.g. monoethanolamine, and between about 10% and about 30% of the elemental sulfur.

The cleaner concentrate composition of this invention, prior to the reaction in situ of the amine and/or alkanolamine and the fatty acid and/or rosin acid to form the soap comprises a mixture of the amine and/or alkanolamine per se, for example one or more of the straight chain lower aliphatic hydrocarbon polyamines previously disclosed herein and/or one or more of the mono- and polyalkanolmonoamines wherein each of the alkanol chains has from 2 to 3 carbon atoms inclusive, one or more of the fatty acids having from 8 to 25 carbon atoms inclusive per molecule, the elemental sulfur, e.g. flowers of sulfur, present in effective amount, sufficient to inhibit corrosion of the metal surface by the ultimate cleaner composition, a solubilizer for the elemental sulfur such as, for example, one or more of the solubilizers previously disclosed herein present in an effective amount, sufficient to impart water solubility to the sulfur, and water. The amine and/or alkanolamine as such is present in the cleaner concentrate, prior to the reaction of the amine and/or alkanolamine with the fatty and/or rosin acid, in total amount preferably from about 3% to about 40% by weight, the fatty and/or rosin acid is present in such cleaner concentrate in total amount preferably from about 2% to about 20% by weight, the elemental sulfur in amount preferably from about 0.05% to about 15% by weight, more preferably from about 0.2% to about 15% by weight, the solubilizer in amount preferably from about 1% to about 40% by weight, and the water preferably from about 5% to about 65% by weight.

The testing of aqueous liquid cleaning compositions of this invention containing a mixture of amine and alkanolamine salts of fatty acids, flowers of sulfur, a solubilizer for the elemental sulfur, and water for cleaning high luster zinc base die casting alloy having buffing compound residues thereon yielded excellent results in removing the buffing compound residues without corroding and discoloring the metal surfaces. The high luster of the buffed zinc alloy surfaces was fully preserved, with no sign of corrosive attack or discoloration.

What is claimed is:

1. A cleaning concentrate adapted to be mixed together with water to form a cleaner composition for use on surfaces of nonferrous metals and their alloys, said concentrate consisting essentially of:

(a) from about 5% to about 60% by weight of an amine soap selected from the group consisting of straight chain lower aliphatic hydrocarbon polyamine and mono- and poly-lower alkanolamine salts of fatty acids having 8 to 25 carbon atoms per molecule and rosin acids, and mixtures thereof;

(b) from about 0.05% to about 15% by weight of elemental sulfur;

(c) from about 1% to about 40% by weight of a solubilizer for the elemental sulfur; and

(d) from about 5% to about 65% by weight of water; said cleaning concentrate having an alkaline pH.

2. The concentrate composition of claim 1 wherein the elemental sulfur is present therein in amount from about 0.2% to about 15% by weight.

3. The concentrate composition of claim 1 wherein the sulfur is flowers of sulfur, the soap is a mixture of the monoethanolamine and diethylenetriamine salts of fatty acids having from 8 to 25 carbon atoms per molecule, the solubilizer is monoethanolamine and diethylenetriamine, and further characterized by containing, by weight, from about 2.0% to about 10.0% of sodium glucoheptanate and from about 2.0% to about 12.0% of dextrose.

4. An aqueous liquid cleaning composition comprising the concentrate composition of claim 1 mixed together with sufficient additional water to form the cleaning composition.

5. An aqueous liquid cleaning composition comprising the concentrate composition of claim 1 mixed together with water in the proportions of about 2 to about 25 fluid ounces of the concentrate composition per gallon of water.

6. A process of cleaning a soiled nonferrous metal surface to remove the soil therefrom, which comprises immersing the soiled metal surface in an alkaline aqueous liquid cleaning composition of claim 4 until the soil is removed from the metal surface.

7. The process of claim 6 wherein the liquid cleaning composition is at a temperature between about 110° F. and about 200° F. and a pH of 8-12.

8. The process of claim 7 wherein the liquid cleaning composition is at a temperature between about 155° F. and about 185° F.

9. The process of claim 6 wherein the metal surface is of a metal from the group consisting of zinc and zinc base alloys.

10. The process of claim 6 wherein the metal surface is that of a zinc base die casting.

11. The process of claim 6 wherein ultrasonic wave energy is applied to the soiled metal surface during the immersing.

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