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COMPOSITION AND METHOD FOR CLEANING
AND STRIPPING METALS

John W. Stilwell, 4255 E. 36th St., Indianapolis, Ind.

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This invention relates to a composition of matter which, when dissolved in water, provides an acid cleaner for ferrous and non-ferrous metals and alloys. The subject cleaner is unique in that it will remove oxides, welding flux, carbonaceous materials, general shop soils and certain plated metals (electrodeposited, peened or dip-coated) without any significant attack, etching, or discoloration of the base metal. The cleaning action provided by a solution of this composition is a thorough and rapid solvent action on the soil, scale or plate being removed.

In particular, this material has application where acid pickling would ordinarily be considered necessary for the removal of oxides or other substances, but where hydrogen embrittlement is a problem, as is the case in connection with many carburized or high carbon steel parts.

Many high strength steels used in the military as well as in industry, in general, are subject to very stringent controls to avoid or eliminate hydrogen embrittlement in the manufacture. The use of the present composition on such steels, under conditions specified below, results in parts with no detectable amount of hydrogen embrittlement.

The inhibitive properties incorporated in this product make possible the use of plain, low carbon steel containers and associated equipment for handling the composition in use, either in dry form or in aqueous solution.

Prior to my invention, the one method most preferred in industry for the removal of oxides, welding flux, and many other types of soils has been acid pickling. In order to clarify the present disclosure, the following definitions are offered for "acid pickling," "hydrogen embrittlement" and "acid pickling inhibitors," as those terms are used herein.

(1) *Acid pickling*.—A method of removing oxides from iron and steel wherein the metal is held in an acid solution for a period of time necessary to remove the oxides. The acids usually preferred in the arts are sulfuric, muriatic, or one of the stronger acid salts such as sodium bisulfate or sulfamic acid. The concentration of the acid used in water solution will vary depending on facilities available and the type and thickness of the oxides to be removed. The iron or steel to be cleaned is usually contained in some type of high alloy steel barrel or basket, or suspended by a cable or hook. The work is lowered into the acid solution and remains until the material is free of oxides. The acid solution is usually contained in a tank lined with an acid resistant material such as lead or neoprene.

The action by which acid pickling proceeds is through a corrosive attack upon, and dissolution of, the base metal (iron or steel) under the oxides to be removed. When sufficient base metal has been removed, the oxide or soil falls free.

(2) *Acid pickling inhibitors*.—Acid pickling inhibitors are agents which, when added to an acid pickling bath, retard the acid attack on the base metal below the soil to be removed. Since the physio-chemical occurrences involved in acid pickling constitute the dissolution of base metal below the soil, the rate of removal of such soil is reduced by the addition of inhibitors. Inhibitors also diminish the severity of hydrogen embrittlement in the base metal.

(3) *Hydrogen embrittlement*.—Hydrogen embrittlement is a phenomenon which occurs during the process

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of acid pickling of iron or steel. This condition proceeds as the acid pickling releases iron to the acid solution (oxidation) and the water breaks down, releasing hydrogen (reduction). The hydrogen, at the instant it is produced, is in the atomic form and may enter the iron or steel. Molecular hydrogen or, as some contend, hydrocarbons are formed from this interstitial element and the carbon in the steel, which leaves the iron or steel in an embrittled state unless relieved.

Hydrogen embrittlement may be relieved by bringing the iron or steel to a certain temperature for a period of time (usually 375° F. for two hours within a period of four hours after the embrittled condition has been effected). There is, however, published evidence to show that such treatment may not alleviate the embrittled condition but that, under certain conditions, the embrittlement may even be increased.

There are many objectionable features to acid pickling as a means of removal of oxides or other soils from metals.

(1) The large amount of metal loss results in poor control of metal size, over-etching, discoloration, and rapid metal build-up in the solution (which decreases the activity of the acid solution) and consequent sludge formation with certain acids.

(2) Severe corrosion problems in handling, in storage, and in the utilization of the acid in solution necessitate expensive resistant material for tank lining, piping, cranes and hooks used in transporting the metal to and from the acid solution.

(3) Extreme conditions of hydrogen embrittlement, resulting from acid pickling, preclude the use of this method of cleaning for certain types of metal and alloys where such a condition would be deleterious to a finished part.

(4) Immediate and thorough rinsing and neutralization must follow any acid pickling operation of iron or steel, in order to avoid the occurrence of severe rusting. Even when extreme care is exercised, some quantity of rust will always form during the transfer of the iron or steel from the acid solution to the rinse.

(5) Acid pickling using inhibitors results in the saving of base metal and acid solution; however, control of the inhibitive properties of the pickling solution is difficult due to the breakdown of most inhibitors with time and temperature.

Electrolytic cleaning is a second method used to remove smut and light oxides from metals. The electrolytic process employs a highly alkaline solution contained in an insulated tank equipped with electrodes (usually steel) and an insulated tumbling barrel or rack to hold the metal parts to be cleaned. A direct electric current source is attached to the electrodes and to the barrel or racks containing the parts.

The electrolytic cleaning action, in the removal of smut or other soils foreign to the base metal, is a mechanical agitation (gas evolution) on the surface of the part being cleaned resulting from the electrodecomposition of the water in the alkaline cleaning solution. The parts to be cleaned are either made anodic (anodic electrocleaning) or cathodic (cathodic electrocleaning) depending on the type of soil to be removed.

For the effective removal of oxides from iron or steel, the parts to be cleaned by this electrolytic process must be made cathodic (cathodic electrocleaning) in order that reducing conditions shall exist on the surface of the metal.

Smut and non-metallic soils are removed from iron or steel most efficiently by anodic electrocleaning.

There are objectionable features to electrolytic methods of cleaning as a means of removal of oxides or other soils from metals.

(1) Anodic electrocleaning will not remove oxides

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from metals such as iron or steel and under certain conditions (high concentration of alkaline cleaner, high temperature, and high current densities) may even add to the oxide layer.

(2) Cathodic electrocleaning offers a serious disadvantage, in the removal from iron or steel, of soils such as smut or other non-metallic materials since there is a tendency to deposit, on the parts being cleaned, quantities of impurities, especially of a metallic nature. Also, hydrogen embrittlement will most certainly occur in parts cleaned by this method.

(3) There is a comparatively large expense involved not only in the initial set-up and maintenance of electrocleaning equipment but also in the high cost of operation (electrical power and cost of alkaline electrolytic cleaner).

The primary object of my invention is to overcome the defects and disadvantages of previously-known substances and procedures for cleaning metal parts by providing a dry composition which, when dissolved in water, will produce a strongly acidic cleaner for ferrous and non-ferrous metals and alloys, which will not attack, etch or discolor any of the base metals, or components thereof, but will attack or dissolve only the oxides or other soils ordinarily encountered in industry.

A further object of my invention is to provide, for the purposes outlined, a dry composition composed essentially of an acid (organic or inorganic) or acid salt such as sodium bisulfate, sulfamic acid, monosodium acid phosphate or disodium acid phosphate (96% to 87%) or one of the fluorated organic acids, plus a ditertiary acetylenic glycol (0.25% to 1.0%), calcium silicate (0.4% to 1.0%), an alkylaryl sulfonate (3.0% to 10.0%) and thiocarbamide (0.25% to 1.0%) which when dissolved in water, will attack and remove from a surface substantially any coating or soil which is itself soluble in sulfuric acid. Of the mentioned acids and acid-formers, sodium bisulfate and sulfamic acid are presently believed to be most practical.

A further object of my invention is to provide a highly acidic solution for the removal of plated metals (namely, zinc, cadmium and chromium), either electrodeposited, peeled or dip-coated, from ferrous metals and alloys, which solution produces no attack, etch or discoloration of said base metal or alloys.

Still another object of the invention is to produce a composition which, when dissolved in water, will remove carbon smut from ferrous metals and alloys (deposited through heat treatment or rolling operations) with no attack, etch or discoloration to the base metal.

A further object of the invention is to provide a dry composition which, in itself, is non-corrosive so that it may be shipped, stored and handled in metal or fibre drums, with or without a moisture-repellent liner, which produces a highly-acidic solution when dissolved in water, but which includes inhibitive components of such character that such a solution may be used in plain carbon steel tanks and handling equipment without attacking such tanks and/or equipment.

A still further object of the invention is to provide methods of cleaning metal parts of various types, through the properly-controlled use of solutions of my novel composition.

Still further objects of the invention will appear as the description proceeds.

To the accomplishment of the above and related objects, my invention may be embodied in the assembly of the ingredients or their equivalents and in the steps described in the following specification, attention being called to the fact, however, that the specific composition and the specific procedures described are by way of illustration only and that changes may be made therein, so long as the scope of the appended claims is not violated.

According to the present invention, the above-listed objections and disadvantages of known procedures are overcome through the use, in a manner to be described, of

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a compound whose optimum formula is as follows: Sodium bisulfate 87% to 96%, ditertiary acetylenic glycol 0.25% to 1.0%, calcium silicate 0.4% to 1.0%, an alkyl aryl sulfonate 3.0% to 10.0%, and thiocarbamide 0.25% to 1.0%.

The percent of ditertiary acetylenic glycol and of thiocarbamide may be used in excess of the range indicated but to no advantage since inhibition is complete below the maximum limits indicated. Percentages of either below the minimum limits will result in a mixture not completely inhibited against attack. These two materials may also be used to inhibit other acids (organic and inorganic) and acid salt mixtures such as sulfamic acid (H_2NHSO_3), monosodium acid phosphate (NaH_2PO_4) and disodium acid phosphate (Na_2HPO_4).

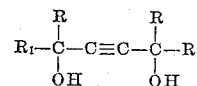
A typical formula and the one that I prefer is as follows; each component being available, commercially, in the form as indicated.

Item No.	Material	Percent by Weight
1-----	Sodium bisulfate (NaHSO_4) anhydrous—prilled	94.5
2-----	Ditertiary acetylenic glycol	0.5
3-----	Calcium silicate ($\text{Ca}(\text{SiO}_3)$) anhydrous—fine powder	0.5
4-----	An alkyl aryl sulfonate	4.0
5-----	Thiocarbamide ($\text{CS}(\text{NH}_2)_2$)	0.5

Item No.—

(1) The crystalline form of sodium bisulfate monohydrate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$) may be used. However, the anhydrous prilled form is preferred to effect a more homogeneous free flowing mixture. It constitutes, of course, the acid-former of the composition.

(2) The ditertiary acetylenic glycol performs an inhibitive function in the composition and may be any one of the several available to the art having the following general structure:



R and R₁ may be any of the alkyl groups such as methyl, ethyl, propyl, butyl, iso-propyl, iso-butyl, tertiary butyl, or combinations thereof i.e., 3,6-dimethyl-4-octyne-3,6-diol.

(3) Calcium silicate, $\text{Ca}(\text{SiO}_3)$, anhydrous, is in a very fine powder form and is incorporated as a compounding aid and desiccant. The glycol is a wax-like substance; and in order that it may be used in the composition without damaging the free-flowing characteristics thereof, it should be dissolved in a volatile solvent from which, as the solvent evaporates, it emerges as waxy balls or beads. The powdery calcium silicate coats these balls or beads to destroy the inherent tackiness of the bead surfaces.

(4) The alkyl aryl sulfonate is the wetting agent. There are several varieties available commercially but the one preferred is the 40% active. The physical form is a fine flake or pellet.

(5) Thiocarbamide (thiourea), H_2NCSNH_2 , is preferred over any of the 1,3 substituted compounds such as 1,3-diethyl or 1,3-di-iso-propyl. The physical form is a fine crystal. This ingredient also performs an inhibitive function in the composition.

The actual mechanism of inhibitor action is in considerable disagreement. Undoubtedly, all materials possessing inhibitive properties, in an acid bath, function in the same general manner but not all because of the same attributes. Since coordination bonding is involved, only those metals of the periodic table which are capable of forming the more stable coordination complexes are likely

to be affected, in an acid bath, by materials called ligands with certain attributes which contribute to the formation of the aforementioned coordination complexes. The stability of the predominately covalent bonding character of such complexes is determined by such attributes of the ligand as charge, dipole moment, size, polarizability, electronic configuration and structure. Since ligands are the donor atoms of the electrons shared covalently with the central atom (Cu, Fe, Co, Ni etc.), elements such as nitrogen, oxygen, and sulfur contained in the ligand are the components of the molecule responsible for the formation of such complexes. This is the reason most inhibitors (in an acid solution), for such materials as iron, contain one or more of these last-named elements as part of their structural configuration.

Thiocarbamide and the ditertiary acetylenic glycol both fall in the class of materials described above as ligand formers. Neither of them alone, however, in whatever concentration, will produce complete inhibitive protection for the metal to be cleaned. When used in the presence of each other, these two substances, even in the relatively minute quantities suggested above, enter into a mutual coaction which does result in such complete inhibitive protection. I presently believe that this effect can be explained upon the following theory.

The part of the inhibitive properties contributed by the thiocarbamide (thiourea), or any of the substituted higher molecular weight compounds of that family, is due to the formation of a coordination compound with the unoxidized iron (or other base metal) under the oxidized surface layer. This compound may exist as a polymer, monomolecular in thickness, but quite uniformly distributed over the entire surface of clean, unoxidized metal. This surface condition is semi-impervious to the acid (within a certain temperature range) since the outermost atoms of the metal are not at all times free to react with the acid.

The ditertiary acetylenic glycols, also, are capable of forming coordination bonds. These are formed with the metal atoms not bonded by the thiocarbamide. These glycols, being relatively large molecules, now fill openings in the previously mentioned monomolecular layer on the clean metal. The inhibition is now complete on the unoxidized metal, leaving only the oxides or other coatings to be attacked by the acid solution. Inhibitors will not combine with the oxidation products of the metal because of electrostatic repulsion.

This inhibited protective surface condition will remain on the metal part until it is rinsed thoroughly in hot water. This may be demonstrated by exposing a steel sample, cleaned in my novel composition but not rinsed, to a humidity corrosion test. The specimen will withstand extended exposure with no evidence of corrosion, even with the heavy coating of acid salt from the cleaning solution adhering to the surface.

Optimum equipment for compounding my novel composition is the common powder type mixer, such as a "ribbon" type, with a means for loading and unloading. Adequate ventilation should be provided to remove vapor and dust as the mixer is operating.

The sodium bisulfate is first introduced into the mixer and the machine is operated to break up all lumps and provide a free flowing form. The ditertiary acetylenic glycol is dissolved in a minimum amount of trichloroethylene or similar solvent. This saturated solution is added to the sodium bisulfate in the mixer and mixing is continued until all the bisulfate is coated with the ditertiary acetylenic glycol and the solvent has been evaporated. The anhydrous calcium silicate is then added to effect a dry, free flowing mixture. Next, the wetting agent (an alkyl aryl sulfonate) is added and the thiocarbamide is added last. The mixer is operated until substantial homogeneity is attained. The product is packaged in fibre or steel drums, with a polyethylene liner if desired to protect the composition against moisture.

Examples

The following applications of my novel composition have been successfully demonstrated in the laboratory and the results substantiated by industrial usage over a period of time sufficient to establish commercial uniformity and excellence of results. These applications are many and varied but, in general, they may be grouped as follows.

(1) This product may be used for the removal, from ferrous metals and alloys, of oxides of all types, carbon smut, drawing compounds, many dyes and stains, phosphate coatings, and plated metals (electrodeposited, dip-coated or peened). The plates most successfully removed are zinc, cadmium and chromium.

The metal parts may be suspended in the solution, with or without agitation, until the soil is removed; or they may be contained in a perforated type barrel which is rotated in the cleaning solution.

The requirements of concentration and temperature are factors which will vary depending on the amount and type of soil to be removed. In general, however, the concentration and temperature ranges found to be adequate are as follows.

Concentration—8 to 48 ounces of composition per gallon of aqueous solution.

Temperature—room to 165° Fahrenheit.

Most of the ingredients of my composition are readily soluble in water at the temperatures herein specified; but, when this composition is mixed with water in the concentrations and at the temperatures herein described, the inhibitors exist in a state of molecular hydration which would be more accurately described as a dispersion or colloidal suspension. The term "solution," as used in the present specification and in the claims appended hereto, is intended to include such a partial solution and partial dispersion or suspension as has just been explained.

A solution of any concentration is totally inhibited to attack on any ferrous metal or alloy below a temperature of 165° F. At these low temperatures, the acid solution dissolves the oxide or other unwanted coating; but when the base metal surface is exposed to the solution, the above-described protective film is instantaneously formed thereon to prevent acid attack upon the base metal. At temperatures significantly above 165° F., some slight etching of the base metal surface will occur.

(2) My composition may be used as a descaling medium for bright barrel finishing of ferrous metals and alloys employing natural or bonded stones or chips.

Concentration—2 to 16 ounces of composition per gallon of aqueous solution.

Temperature—room to 160° Fahrenheit.

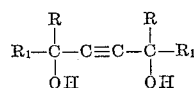
(3) Anodized coatings, dyed or chromate sealed, on aluminum and aluminum alloys are removed by simple immersion in a solution of my composition.

Concentration—16 to 32 ounces of dry composition per gallon of aqueous solution.

Temperature—160°–180° Fahrenheit.

I claim as my invention:

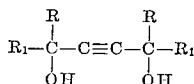
1. A composition of matter for surface-cleaning metals, comprising an acid which is normally corrosive to the metal to be cleaned, a first inhibitor consisting of a ditertiary acetylenic glycol having the general structure:



in which R and R₁ are alkyl groups selected from the group consisting of methyl, ethyl, propyl, butyl, isopropyl, isobutyl, tertiary butyl and combinations thereof, and which, in a solution of such acid and in the presence of the metal to be cleaned, produces one type of coordina-

tion complex adherent to the metal to be cleaned as a thin film resistant to such acid, a second inhibitor selected from the group consisting of thiocarbamide, 1,3-diethyl thiocarbamide and 1,3-diisopropyl thiocarbamide; and which, in a solution of such acid and in the presence of the metal to be cleaned, produces a different type of coordination complex adherent to the metal to be cleaned as a thin film resistant to such acid, and a desiccant.

2. A composition of matter for surface-cleaning metals, comprising a dry and substantially homogeneous, free-flowing mixture consisting essentially of an acid-forming solid which, when dissolved in water, is corrosive to the metal to be cleaned, a first solid inhibitor consisting of a ditertiary acetylenic glycol having the general structure:



in which R and R₁ are alkyl groups selected from the group consisting of methyl, ethyl, propyl, butyl, isopropyl, isobutyl, tertiary butyl and combinations thereof, and which, in such a solution and in the presence of the metal to be cleaned, produces one type of coordination complex adherent to the metal to be cleaned as a thin film resistant to such acid, a second inhibitor selected from the group consisting of thiocarbamide, 1,3-diethyl thiocarbamide and 1,3-diisopropyl thiocarbamide and which, in such a solution and in the presence of the metal to be cleaned, produces a different type of coordination complex adherent to the metal to be cleaned as a thin film resistant to such acid, and a dry desiccant.

3. A composition of matter for surface-cleaning metals, comprising a dry and substantially homogeneous, free-flowing mixture consisting essentially of an acidic substance selected from the group consisting of sodium bisulfate, sulfamic acid, monosodium acid phosphate, disodium acid phosphate and the dry fluorinated organic acids; together with a ditertiary acetylenic glycol, thiocarbamide, calcium silicate and an alkyl aryl sulfonate.

4. A composition of matter for surface-cleaning metals, comprising a dry and substantially homogeneous, free-flowing mixture consisting essentially of sodium bisulfate, a ditertiary acetylenic glycol, thiocarbamide, calcium silicate and an alkyl aryl sulfonate.

5. A composition of matter for surface-cleaning metals, comprising a dry and substantially homogeneous, free-flowing mixture consisting essentially of sodium bisulfate 96% to 87%, a ditertiary acetylenic glycol 0.25% to 1.0%, thiocarbamide 0.25% to 1.0%, calcium silicate 0.4% to 1.0% and an alkyl aryl sulfonate 3.0% to 10.0%.

6. A composition of matter for surface-cleaning metals, comprising a dry and substantially homogeneous, free-flowing mixture consisting essentially of sodium bisulfate 94.5%, a ditertiary acetylenic glycol 0.5%, thiocarbamide 0.5%, calcium silicate 0.5% and an alkyl aryl sulfonate 4.0%.

7. A cleaning bath for dip-cleaning of oxides, coating metals, shop soils and the like from ferrous metals and alloys, comprising an aqueous solution of the composition of claim 1 in a concentration of 8 to 48 ounces of composition per gallon of solution.

8. A cleaning bath for dip-cleaning of oxides, coating metals, shop soils and the like from ferrous metals and alloys, comprising an aqueous solution of the composition of claim 3 in a concentration of 8 to 48 ounces of composition per gallon of solution.

9. A cleaning bath for dip-cleaning of oxides, coating metals, shop soils and the like from ferrous metals and alloys, comprising an aqueous solution of the composition of claim 5 in a concentration of 8 to 48 ounces of composition per gallon of solution.

10. A cleaning bath for dip-cleaning of oxides, coating metals, shop soils and the like from ferrous metals and alloys, comprising an aqueous solution of the composi-

tion of claim 6 in a concentration of 8 to 48 ounces of composition per gallon of solution.

11. A cleaning bath for use as a descaling medium for bright barrel finishing of ferrous metals and alloys employing stones or chips as the abrasive medium, comprising an aqueous solution of the composition of claim 1 in a concentration of 2 to 16 ounces of composition per gallon of solution.

12. A cleaning bath for use as a descaling medium for bright barrel finishing of ferrous metals and alloys employing stones or chips as the abrasive medium, comprising an aqueous solution of the composition of claim 3 in a concentration of 2 to 16 ounces of composition per gallon of solution.

13. A cleaning bath for use as a descaling medium for bright barrel finishing of ferrous metals and alloys employing stones or chips as the abrasive medium, comprising an aqueous solution of the composition of claim 5 in a concentration of 2 to 16 ounces of composition per gallon of solution.

14. A cleaning bath for use as a descaling medium for bright barrel finishing of ferrous metals and alloys employing stones or chips as the abrasive medium, comprising an aqueous solution of the composition of claim 6 in a concentration of 2 to 16 ounces of composition per gallon of solution.

15. A cleaning bath for dip-cleaning of anodized coatings from aluminum and aluminum alloys, comprising an aqueous solution of the composition of claim 1 in a concentration of 16 to 32 ounces of composition per gallon of solution.

16. A cleaning bath for dip-cleaning of anodized coatings from aluminum and aluminum alloys, comprising an aqueous solution of the composition of claim 5 in a concentration of 16 to 32 ounces of composition per gallon of solution.

17. A cleaning bath for dip-cleaning of anodized coatings from aluminum and aluminum alloys, comprising an aqueous solution of the composition of claim 6 in a concentration of 16 to 32 ounces of composition per gallon of solution.

18. The method of dip-cleaning oxides, coating metals, shop soils and the like from ferrous metals and alloys without etching of the base metal, which comprises the steps of immersing the piece to be cleaned in an aqueous solution of the composition of claim 6 in a concentration of 8 to 48 ounces of composition per gallon of solution, while maintaining the temperature of the solution within the range between room temperature and 165° F., removing the piece from the solution after cleaning is complete, and rinsing the piece thoroughly with hot water.

19. The method of descaling ferrous metals and alloys for bright barrel finishing thereof without etching of the base metal, which comprises the steps of tumbling the piece to be cleaned, in contact with stones or chips, while immersed in an aqueous solution of the composition of claim 6 in a concentration of 2 to 16 ounces of composition per gallon of solution, while maintaining the temperature of the solution within the range between room temperature and 160° F.

20. The method of cleaning anodized coatings from aluminum and aluminum alloy pieces without significantly etching the base metal, which comprises the steps of immersing the piece to be cleaned in an aqueous solution of the composition of claim 6 in a concentration of 16 to 32 ounces of composition per gallon of solution, while maintaining the temperature of the solution within the range between 160° F. and 180° F., removing the piece from the solution after cleaning is complete, and rinsing the piece thoroughly with hot water.

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