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NEUTRAL METAL CLEANING COMPOSITIONS CONTAINING HYDRAZINE AND A POLYCARBOXYLAMINO ACID

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This invention relates to chemical compositions and a process for the removal of corrosion products from metal surfaces. More particularly, this invention relates to substantially neutral chemical compositions and the process of employing them for the removal of oxide films from iron and ferrous alloys in inaccessible places.

Removal of oxide corrosion products from metal surfaces may be accomplished by several physical or chemical means. Scraping, sandblasting, pickling, and reduction are exemplary of a few of the well known cleaning methods which may be used. All of these methods may be easily employed with no particular problem when the metal surfaces are exposed and accessible. However, when corosion or crud removal from inaccessible metal interiors is necessary, application of phyical removal means is impossible and resort to chemical compositions must be taken.

In the past, the chemical compositions which were employed for crud and corrosion removal were either strongly acidic or strongly basic and required special precautionary measures for handling and application. Moreover, application of solutions in the extreme pH ranges etched highly finished metal surfaces so that previously close fitting tolerances were ruined, and even then, dissolution of all the objectionable oxides forming the crud was not always effected. Particularly resistant to dissolution was magnetic iron oxide.

Certain of the metal cleaning chemical compositions in the prior art contained sulfur compounds. These compositions, while acceptable for certain applications, were objectionable for apparatus constructed from expensive alloys which were subject to abnormal stresses. Sulfite embrittlement or crevice corrosion resulting from attack on the metal surfaces by the sulfur compounds produced equipment having unsatisfactory strength and reliability. Often, as a result of the use of these sulfur containing compositions, the cleaned product was structurally more unsatisfactory than the corroded metal.

The primary object of this invention, therefore, is to provide substantially neutral metal cleaning compositions which will remove all objectionable metallic oxide films without etching the surface.

A further object of this invention is to provide a safe, substantially neutral metal cleaning composition having a pH range of between 6.5 and 9.5.

An additional object of this invention is to provide neutral metal cleaning compositions which will effectively clean a wide variety of structural metals and alloys.

Further objects will become apparent to those skilled in the art from the following explanation and examples.

The foregoing objects are achieved according to this invention by formulating buffered aqueous solutions of hydrazine and a polycarboxylamine acid chelating agent. Chelating agents which contain 3 to 5 carboxyl groups appear to be roughly equivalent in this solution. Exemplary polycarboxylamine acids which are equivalent constitutents of these novel cleaning compositions are nitrolotriacetic acid, N-hydroxyethylethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and 1,2-diaminocyclohexanetetraacetic acid; however, ethylenediaminetetraacetic acid is preferred. No sulfur compounds or other constituents leading to sulfite embrittlement, crevice corrosion, or other mishap are present in the ingredients. The metal cleaning composition according to this invention is non-corrosive to all ferrous metals and alloys.

Hydrazine, alone, or the metal salts of the polycarboxylamino acids in the absence of hydrazine have no appreciable effect upon certain mixed metal oxides, that is, oxides of iron, cobalt, nickel, and manganese. A synergistic action, evidenced by the unexpected improved solubility of the metal axides, occurs when the two compounds are mixed in the proper proportions. This synergistic action dissolves metal oxides which were substantially immune to the separate ingredients.

Ethylenediaminetetraacetic acid (EDTA) is mixed with hydrazine in proportions which will result in a pH of from 6.5 to 9.5 and preferably in a range of 7 to 9. Ammonia may be substituted as a buffering agent for a portion of the hydrazine when it is necessary to adjust the pH of the resulting solution to bring it within the desired range. The proportions of hydrazine and ethylenediaminetetraacetic acid are not critical provided at least 0.1 molar concentration of hydrazine is used and the pH remains within the prescribed range. Generally, a ratio of 2 to 6 moles of hydrazine per mole of ethylenediaminetetraacetic acid will keep the cleaning solution within the prescribed pH range. However, if the proportions of the ingredients render the pH of the solution below the 6.5 to 9.5 range, ammonia may be added to make the necessary adjustments in the pH.

The minimum concentration of ethylenediaminetetaraaceti acid which is effectively used must be at least 0.08 molar; however, a concentration of 0.25 molar is preferred. The concentration of hydrazine used with the ethylenediaminetetraacetic acid has litle consequence on the effectiveness of the solution, provided the solution is at least 0.1 molar in hydrazine.

Dissolution of metal corrosion products is better effected the cleaning solution is employed at elevated temperatures. Dissolution of magnetic iron oxide (Fe_3O_4) may normally be achieved in approximately two hours with the solution at 95° to 100° C.; however, significant dissolution may be effected after a one hour application at temperatures between 80° and 100° C. Although dissolution has been detected at temperatures as low as 65° C., in order to maintain a rapid reaction, temperatures in the range of 90° to 100° C. are preferred.

EXAMPLE I

Several samples were prepared in which the hydrazine concentration in the cleaning solution was varied from 0.1 to 0.5 molar. Ammonia was added to the solution in amounts sufficient to bring the pH within the 6.5 to 9.5 range. A blue or greenish blue coloration upon the addition of bromthymol indicator denoted the proper pH of the solution.

Approximately 0.2 gram of magnetic iron oxide (Fe_3O_4) was added to each of the various concentrations and heated for two hours at 95° C. An examination of the various samples after completion of the treatment showed that the solutions 0.2 to 0.5 molar in hydrazine dissolved 99.9% of the magnetic iron oxide. The solution 0.1 molar in hydrazine dissolved 99.7% of the magnetic iron oxide.

Example II

Additional samples were prepared to determine the effect of the hydrazine-EDTA solution on oxides of mixed metals, particularly, oxides of iron, nickel, cobalt, and manganese. Separate samples of these mixed metal oxides were heated to 400° C. and to 600° C. The composition of the metals oxides was determined by X-ray fluorescent analysis to contain 76% Fe, 7.2% Ni, 8.4% Co, and

8.4% Mn. Samples of these mixed oxides were heated for two hours at 95° C. in a solution 0.1 molar in ethylenediaminetetraacetic acid and 0.5 molar in hydrazine. Approximately 91.8% of the mixed oxides which were heated to 400° C. were dissolved in the solution. The mixed metal oxides which were heated to 600° C. were slightly more resistant to dissolution in the same composition than the ones heated to 400° C. About 76.5% of the mixed metal oxides which were heated to 600° C. were dissolved in the solution. An analysis of the mixed metal oxide residue showed that approximately 95.0% of the iron oxide, 87% of the nickel oxide, 89% of the cobalt oxide, and 57% of the manganese oxide in the original sample were dissolved.

The test conditions under which this solution was tested were more severe than normally encountered. Normally, the corrosion products of metal alloys are not exposed to temperatures as high at 400° C. to 600° C. These conditions are far more severe than those in which the solution is normally applied.

Example III

Several more samples were prepared using a hydrazine-EDTA solution of the same formulation as in Example II. Radioactive oxide corrosion products scraped from a nuclear reactor fuel element were placed in the solution and heated at 95° for 4 hours. The results obtained from the test are summarized in the following table:

TABLE I

Constituent of Corrosion Product—Total	Weight of Constituent, mg.		Percent Removed
	Before Treatment	After Treatment	
Total	10	2	80
Fe oxide	4.2	1.1	73.8
Ni oxide	0.6	0.2	66.7
Co oxide	0.05	0.02	60.0
Cr oxide	0.1	0.1	0.0

Iron, nickel, and cobalt oxides showed satisfactory solubility while chromium remained unaffected by the solution.

Example IV

Other samples were prepared for the purpose of determining the solubility of magnetic iron oxide in a solution containing hydrazine and a different chelating agent. A solution containing hydrazine and nitrilotriacetic acid (NTA) was prepared. Weighted samples of magnetic iron oxide were placed in portions of the neutral solution and heated to 95° C. for 2 hours. The following table summarizes the results obtained for the test.

TABLE II

NTA (molar)	Hydrazine (molar)	pH Initially	pH Finally	Undissolved Residue, Percent
0.25	0.50	6.42	6.72	0.50
0.25	0.55	7.34	7.33	0.50
0.25	0.51	6.75	6.92	0.50
0.25	0.525	7.09	7.13	0.25

Similar results were obtained with solutions containing ammonia as partial replacement for hydrazine. Solutions in which the pH was adjusted by an ammonia buffer, meantime taking care to maintain at least an 0.3 molar concentration of hydrazine in the solution, had substantially no detrimental effect on the dissolving power of the solution, and residues comparable to those shown in Table II were produced.

Example V

The hydrazine-EDTA solution, according to this invention, was employed in the decontamination of a primary loop pressurizer in a pressurized water reactor cooling system. The initial dose rate in the pressurizer averaged approximately 1,000 to 1,200 milliroentgens per hour. One application of the hydrazine-EDTA solution produced a decontamination factor of from 2 to 5. The decontamination factor is defined as the initial dose rate divided by the final dose rate. Outstanding decontamination was achieved by an additional treatment with potassium permanganate followed by a second hydrazine-EDTA application. This three-step process reduced the initial average dose to an average of approximately 5 milliroentgens per hour, giving a decontamination factor range from 400 to 900. In order to appreciate the benefits and advantages o fthis neutral hydrazine-chelate solution, and the improvements which it makes over the prior art, comparisons were made between prior art compositions and the hydrazine-EDTA solution.

Example VI

Magnetic iron oxide (Fe_3O_4) pellets were placed in test solutions and all of the samples were heated for one hour at 95° C. Oxalic and citric acids and their salts were compared with hydrazine-EDTA, as shown in the following table.

TABLE III

Compounds	Molar	pH	Undissolved Residue, Percent
Oxalic acid	0.25	0.99	48.4
Citric acid	0.25	1.61	91.5
Diammonium citrate	0.20	4.75	81.3
EDTA	0.20		
Hydrazine and	0.50		
Ammonia	0.60	8.55	0.92

It is evident from an observation of the amount of the residues that salts of these carboxylic acids commonly used in descaling solutions were not nearly as effective as the hydrazine-EDTA solution.

From the afore-disclosed examples, it can be seen that the neutral hydrazine-EDTA solution according to this invention offers numerous advantages over the prior art cleaning compositions. The solution is, of course, attractive not only from the standpoint of being effective in the removal of corrosion products which are only partially dissolved or removed by prior art compositions, but also from the sandpoint of being completely safe with respect to the personnel handling the solution, due to its neutral or nearly neutral pH.

It is to be understood that certain changes and modifications can be performed on the composition disclosed herein without departing from the spirit and scope of the invention. Having thus described my invention, I claim:

1. A substantially neutral metal cleaning composition consisting essentially of an aqueous solution of hydrazine and a polycarboxylamino acid having 3 to 5 carboxyl groups in proportions yielding a solution having a pH between 6.5 to 9.5 and wherein the concentration of hydrazine is from 0.1 molar to 0.5 molar.

2. A substantially neutral metal cleaning composition according to claim **1** wherein the pH of the solution is 7 to 9.

3. A substantially neutral metal cleaning composition according to claim **1** wherein the polycarboxylamino acid is ethylenediaminetetraacetic acid.

4. A substantially neutral metal cleaning composition according to claim **1** wherein the polycarboxylamino acid is nitrilotriacetic acid.

5. A substantially neutral metal cleaning composition according to claim **1** wherein the polycarboxylamino acid is N-hydroxyethylethylenediaminetriacetic acid.

7. A substantially neutral metal cleaning composition according to claim 1 wherein the polycarboxylamino acid is 1,2-diaminocyclohexanetetraacetic acid.

8. A substantially neutral metal cleaning composition according to claim 1 wherein the proportions are 2 to 6 moles of hydrazine per mole of polycarboxylamino acid.

9. A substantially neutral metal cleaning composition according to claim 1 wherein the concentration of the polycarboxylamino acid is from 0.08 molar to 0.25 molar.

10. A substantially neutral metal cleaning composition according to claim 1 wherein a portion of the hydrazine is replaced by ammonia.

6. A substantially neutral metal cleaning composition according to claim 1 wherein the polycarboxylamino acid is diethylenetriaminepentaacetic acid.

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