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# PREVENTION OF FERRIC ION CORROSION USING ACID CLEANING SOLUTION CONTAINING HYDROGEN SULFIDE AND AN ALDEHYDE CORROSION INHIBITOR

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## ABSTRACT OF THE DISCLOSURE

This patent relates to a method of treating ferrous metal surfaces to remove iron oxide encrustations which comprises contacting the surface with an aqueous solution comprising an acid, a hydrogen sulfide liberating material and an aldehyde-containing corrosion inhibitor.

## BACKGROUND OF THE INVENTION

Ferric oxide encrustations, commonly known as rust, frequently form on ferrous metal surfaces. Various methods of removing the ferric oxide encrustations have been devised, a common one being to contact the ferrous surface with an acid such as hydrochloric acid to thereby dissolve the ferric oxide and thus remove the rust encrustations from the surface. As a result of this operation, an iron salt is formed, the specific ferric salt depending upon the acid used. When hydrochloric acid is used, ferric chloride is formed. As a result of the ferric ion formation, severe corrosion problems may be experienced during acid cleaning of ferrous surfaces.

Ferric chloride is formed as follows:

(1) $$Fe_2O_3+6HCl\rightarrow 2FeCl_3+3H_2O$$

Ferric chloride is rapidly and quantitatively reduced to ferrous chloride by iron or copper in acid solutions. The reduction of ferric chloride by iron is shown in the following equation:

(2) $$2FeCl_3+Fe\rightarrow 3FeCl_2$$
$$E=1.21 \text{ volts}$$

This stoichiometric reaction is known as ferric ion corrosion. It is because ferric chloride attacks copper that it is used as an etchant in preparing printed circuits in electronic equipment. In chemical cleaning, ferric chloride produces corrosion of the ferrous equipment being cleaned as well as pumps and transfer lines to and from the equipment. It can be calculated that for every thousand pounds of ferric chloride formed there will be an attendant metal loss of 173 pounds of steel. Of course, it is customary to carry out the acid cleaning of ferrous surfaces in the presence of a corrosion inhibitor to prevent the corrosion which would normally occur in the presence of an acid. However, these ordinary inhibitors have been of no value in preventing ferric ion corrosion.

## SUMMARY

Briefly, this invention relates to a method of removing ferric oxide encrustations from metal surfaces. In the normal cleaning methods involving, e.g., hydrochloric acid, ferric ion corrosion presents a severe problem. According to this invention, ferric ion corrosion is almost entirely eliminated by incorporating into the cleaning acid solution a source of hydrogen sulfide and a corrosion inhibitor containing an aldehyde, and preferably containing an aldehyde together with an amine or an acetylenic compound.

It is thus an object of the present invention to provide a method and composition for the treating of ferrous metal surfaces to remove iron oxide encrustations.

It is a further object of this invention to provide a corrosion inhibitor composition for acid solutions used in metal cleaning.

A further object is to provide a composition which will reduce ferric ion corrosion.

These and further objects of this invention will become apparent from the specification and claims which follow.



## DESCRIPTION OF PREFERRED EMBODIMENTS

In general, the present invention involves the process of rust removal from ferrous surfaces by treating with an acid. However, rather than merely treating with an aqueous acid, the present process involves the use of a solution of acid which also contains hydrogen sulfide or a hydrogen sulfide source and an aldehyde-containing corrosion inhibitor.

Normally, hydrogen sulfide is considered very corrosive to ferrous surfaces and great pains are taken to avoid contacting the ferrous surfaces with the hydrogen sulfide. However, we have surprisingly found that in the presence of an acid, hydrogen sulfide and a corrosion inhibitor containing an aldehyde, the hydrogen sulfide has no deleterious effects and the rate of corrosion due to the ferric ion is greatly reduced.

The hydrogen sulfide and aldehyde-containing corrosion inhibitor should be incorporated into the acid cleaning solution at the time it contacts the metal surface or very readily thereafter. Clearly, ferric ion corrosion will result if they are not added before ferric ions are formed.

The hydrogen sulfide may be added by any convenient method. Thus, hydrogen sulfide gas may be bubbled into the hydrochloric acid solution prior to treatment or during treatment of the ferrous surface. Additionally, various materials which liberate hydrogen sulfide, e.g., any acid soluble sulfide, may be used. Ferrous sulfide will react in a hydrochloric acid solution to produce hydrogen sulfide. Additionally, thioacetamide will also react in a hydrochloric acid solution to produce hydrogen sulfide. Thus, the hydrogen sulfide may be present as such or as a hydrogen sulfide source.

The invention will work satisfactorily with a hydrogen sulfide concentration over a fairly large range. Thus, from about 0.1% to about 5% hydrogen sulfide may be present in the solution. In general, it is desired that the molar concentration of hydrogen sulfide be at least equal to the number of moles of ferric chloride produced during the acid treating operation. It can be seen that the hydrogen sulfide concentration will thus vary depending upon the amounts of ferric ion present. In general, a hydrogen sulfide concentration of about 1% by weight results in satisfactory inhibition.

Along with the hydrogen sulfide or hydrogen sulfide source, an aldehyde-containing inhibitor must be present. The combination of the hydrogen sulfide and corrosion inhibitor which contains an aldehyde will result in a decreased rate of corrosion rather than an increased rate of corrosion as is the case when hydrogen sulfide alone is present. Although the corrosion inhibitor may comprise an aldehyde alone, it is preferred that it comprise an aldehyde in combination with an acetylenic compound or a nitrogen containing compound.

The preferred inhibitor comprises an aldehyde and a material selected from the group consisting of a nitrogen containing organic compound, an acetylenic compound and mixtures thereof.

In general, any aldehyde may be used in this invention. Thus, suitable aldehydes include alkyl aldehydes, aryl aldehydes and alkylaryl aldehydes. The aldehydes may be substituted with nondeleterious substituents such as a hy-

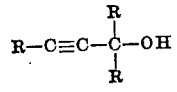
droxyl group and may be saturated or unsaturated. Suitable aldehydes include formaldehyde, benzaldehyde, butyraldehyde, β-hydroxy butyraldehyde (aldol), propionaldehyde, and glyoxal. The aldehyde may be used alone or in a suitable solvent such as alcohol.

A convenient method of using formaldehyde is the use of a solution of formaldehyde in alcohol. For example, formaldehyde may be dissolved in an approximately equal amount of methanol. Other alcohols such as ethyl alcohol, propyl alcohol, butyl alcohol, and isobutyl alcohol may also be used. Solutions of formaldehyde in alcohol such as Methyl Formcel (formaldehyde in methanol) are readily available commercially from the Celanese Chemical Company. Another convenient form of formaldehyde is paraformaldehyde, a solid polymer of formaldehyde.

The nitrogen bearing organic compounds of this invention include amines, quaternary ammonium salts, amides, imines, imidazolines, etc. The amines may be primary, secondary or tertiary and contain alkyl, aryl, or alkaryl substituents. Suitable amines include mono, di and trialkyl amines and N-heterocyclic amines. This includes such amines as ethylamine, diethylamine, triethylamine, proplyamine, dipropylamine, tripropylamine, mono, di, and tributylamine, mono, di and tripentylamine, mono, di and trihexylamine and isomers of these such as isopropylamine, tertiarybutylamine, aniline, etc. Any of the amines which are well-known in the corrosion inhibitor art may be used in this invention. Examples of such amines are rosin amine, dehydroabiethylamine, pyridine and alkyl pryidines such as alkyl pyridines having from 1 to 5 nuclear alkyl substituents per pyridine moiety, said alkyl substituents having from 1 to 12 carbon atoms and preferably those having an average of 6 carbon atoms per pyridine moiety, such as a mixture of high-boiling tertiary-nitrogen-heterocyclic compounds such as HAP (High Alkyl Pyridines), Reilly 10–20 base and Alkyl Pyridines HB, primary alkyl amines containing 12 to 14 carbon atoms known commercially as Primene 81 R and sold by Rohn and Haas, aniline, etc.

The acetylenic compounds of this invention may be alkyl and aryl hydrocarbons. They may be substituted such as with hydroxyl groups and other nondeleterious substituents, e.g., acetylenic amines, ketones, aldehydes, halogens, esters, acids, etc. Examples of suitable acetylenic compounds include hexynol, dimethyl hexynol, dimethyl hexynediol, diethyl hexynediol, dimethyl octynediol, methyl butynol, methyl pentynol, ethynyl cyclohexanol, 2-ethyl hexynol, phenyl butynol, dodecyclaminopropyne and ditertiary acetylenic glycol.

Other acetylenic compounds which can be employed in accordance with the present invention are for example methylbutynol, ethyl octynol, methylpentynol, butynediol, 1-ethynylcyclohexanol, 3-methyl-1-nonyn-3-ol, 2-methyl-3-butyn-2-ol, also 1-propyn-3-ol, 1-butyn-3-ol, 1-pentyn-3-ol, 1-heptyn-3-ol, 1-octyn-3-ol, 1-nonyl-3-ol, 1-decyn-3-ol, 1-(2,4,6-trimethyl-3-cyclohexenyl)-3-propyne-1-ol, and in general acetylenic compounds having the general formula



wherein R is —H, alkyl, phenyl, substituted phenyl or hydroxyalkyl radical, and the alpha R's may be joined together to form a cyclohexyl ring.

Acetylenic sulfides having the general formula HC≡C—R—S—R—C≡CH can also be employed in the present invention in lieu of the acetylenic alcohol. Examples of these are dipropargyl sulfide, bis(1-methyl-2-propynyl) sulfide and bis(2-ethylnyl-2-propyl) sulfide.

The aldehyde may be combined with either the nitrogen bearing organic compound alone, with the acetylenic compound alone, or with a combination of the two. The relative proportion of aldehyde and inhibitor may vary



over a wide range. Furthermore, it has been found that the concentration of aldehyde and the concentration of the organic nitrogen compound or acetylenic compound are not interdependent and thus significant improvement in corrosion protection can be obtained by varying the concentration of one of the components in the corrosive medium without varying that of the other. In general, the aldehyde concentration in the corrosive medium may vary from about 0.003 to 10%. However, lower or higher concentrations will still be effective although the effect of a lower concentration will be small and the amount of improvement obtained by adding more than 10% will generally be negligible. The concentration of the nitrogen bearing organic inhibitor in aqueous acid solution may vary from about 0.05 to 10% while the acetylenic inhibitor concentration will normally vary between 0.05 and 10% by volume. Once again, concentrations outside this range may be used, the exact concentration often being dictated by the economics of the situation.

The aldehyde and inhibitor component may be premixed before being added to a corrosive environment. However, if desired, they may also be added separately. Thus, an inhibitor component such as a nitrogen bearing organic compound may first be added to a corrosive environment and later the aldehyde may be added. However, to obtain the most effective protection, it is generally desirable to add the aldehyde at the same time as the other components.

A particularly effective inhibitor comprises a mixture of an acetylenic alcohol, a nitrogen compound, and an aldehyde dissolved in an alcohol. On a basis of a volume 100%, this composition is comprised as follows:

| | Percent |
|---|---|
| Acetylenic compound | 41–92 |
| Nitrogen or ammonia base compound | 3–9 |
| Aldehyde | 5–50 |

Another effective composition is the combination of an aldehyde, e.g., Methyl Formcel, with a composition comprising 41%–92% of an acetylenic compound, 3%–9% of a nitrogen compound and 5%-50% of a nonacetylenic alcohol. Since Methyl Formcel contains methanol, it also adds to the nonacetylenic alcohol concentration. Suitable nonacetylenic alcohols include those having the general formula ROH, wherein R is either an alkyl group or a ketone group. Some examples of these alcohols are diacetone alcohol, normal propanol, isopropanol, ethanol, methanol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, hexylene glycol, and 1,5-pentanediol.

The amount of inhibitor used may vary from about 0.1% to about 10%. However, it has been found that a concentration of about 0.1% to 1% will normally be sufficient for most uses. Of course, the amount of inhibitor will depend at least in part on the amount of hydrogen sulfide present, larger inhibitor concentrations being required for larger sulfide concentrations.

The acid used in removing the ferric oxide encrustations should be a strong mineral acid capable of rapidly removing the rust. In general, hydrochloric acid is used.

The invention can be more fully understood by reference to the following examples.

## EXAMPLE I

This example illustrates the necessity of having both the hydrogen sulfide and the aldehyde-containing inhibitor present to reduce corrosion.

The following procedure was used in making corrosion determinations. The acid solutions were mixed by diluting 20° Bé HCl with water to the desired concentrations. The acid solutions were then titrated with a standard base solution to ascertain the exact acid concentration. The various acid solutions were prepared in advance in sufficient quantities to complete an entire series of tests with the same batch of acid.

Corrosion coupons of the metal tested were ordered

in sufficient quantities to complete a series of tests on the same batch of coupons. The coupons were cleaned as follows: pickled in an uninhibited 10% HCl acid solution for 10 minutes, neutralized in a 10% solution of sodium bicarbonate, scrubbed by hand with a fine wire brush and a detergent containing a pumice, rinsed, dipped in acetone to remove the excess water and then dipped in alcohol and allowed to dry. They were then weighed to the nearest milligram and stored in a desiccator until time for use.

The acid solution was poured into glass bottles in sufficient quantity to approximate the specific acid volume to coupon surface area ratio that was desired. The quantity of acid used was dependent upon the surface area of the coupon to be tested. In most of the tests, a 25 cc./in.$^2$ acid volume to coupon surface area ratio was used.

After the desired amount of acid was poured into the bottles, the inhibitor was added with a hypodermic syringe and the resulting solution was stirred with a glass rod. The inhibited acid solution was then placed in a water bath which had been set at a predetermined temperature and allowed to preheat for 20 minutes, after which time, the coupons were placed in the preheated inhibited acid solutions. The coupons were left in the acid solutions for the specified test time, then removed, neutralized, recleaned, rinsed, dipped in acetone then alcohol, allowed to dry, then reweighed.

The loss in weight in grams was multiplied times a calculated factor to convert the loss in weight to lbs./ft.$^2$/24 hrs. The factor was calculated as follows:

$$\frac{144\frac{\text{in}^2}{\text{ft}^2}}{454\text{g}\times\text{Surface Area of Coupon}-\text{in}^2\times\frac{1\text{ day}}{24\text{ hrs}}}=\text{Factor}$$

Example: Test time, 6 hours, Surface Area of Coupon, 4.0 in$^2$, then $\frac{144}{454\times4.0\times6/24}=\frac{144\times4}{454\times4.0}=0.317$

The inhibitors used in this invention were Rodine 213, an inhibitor containing the reaction product of rosin amine, formaldehyde and a ketone, and two inhibitors designated as Blend 1 and Blend 2, the compositions of which are set forth below.

BLEND 1

| Chemical: | Percent by vol. |
|---|---|
| Pure propargyl alcohol | 33.94 |
| Crude propargyl alcohol | 11.31 |
| Ethyl octynol | 16.97 |
| Alkyl pyridines | 3.85 |
| Diacetone alcohol | 33.94 |

BLEND 2

| Chemical: | Percent by vol. |
|---|---|
| Pure propargyl alcohol | 33.94 |
| Crude propargyl alcohol | 11.31 |
| Ethyl octynol | 16.97 |
| Reilly high alkyl pyridines | 3.85 |
| Formaldehyde (55%) in methanol | 33.94 |

The tests were conducted at 175° F. for 6 hours in 10% hydrochloric acid. The ferrous metal tested was AISI-1010 carbon steel with an acid volume to surface area ratio of 22 cc./in.$^2$. The results are set forth in Table 1 below.

TABLE I

| Inhibitor | Concentration, percent | Contaminant | Corrosion Rate in lbs./ft.$^2$/day |
|---|---|---|---|
| Blend 1 | 0.3 | None | 0.002 |
| Do | 0.3 | 1.0% $FeCl_3$ | 0.037 |
| Do | 0.3 | 1.0% $FeCl_3$+1.0% FeS | 0.074 |
| Blend 2 | 0.3 | None | 0.003 |
| Do | 0.3 | 1.0% $FeCl_3$ | 0.039 |
| Do | 0.3 | 1.0% $FeCl_3$+1.0% FeS | 0.011 |
| Rodine-213 | 0.3 | None | 0.005 |
| Do | 0.3 | 1.0% $FeCl_3$ | 0.043 |
| Do | 0.3 | 1.0% $FeCl_3$+1.0% FeS | 0.025 |



## EXAMPLE II

This example describes the effect of using various concentrations of inhibitors with different types of metals.

The test procedure used in Example I was followed. However, the test temperature was 150° F. and the test time was 6 hours. In all cases, a corrodent containing 5% hydrochloric acid was used.

The inhibitor contained 3.4 parts of Methyl Formcel and 6.6 parts of Blend 1 set forth in Example I.

The results are set forth in Table 2.

TABLE 2

| Metal Type | Corrodent | Additive | Inkibitor concentration, percent | Corrosion rate in lbs./ft.$^2$/24 hours |
|---|---|---|---|---|
| 416 SS | 5% HCl | None | 0.2 | 0.421 |
| 416 SS | 5% HCl | 0.5% FeS | 0.2 | 0.008 |
| 416 SS | 5% HCl | 1.0% $FeCl_3$ | 0.2 | 0.814 |
| 416 SS | 5% HCl | 0.5% FeS+1.0% $FeCl_3$ | 0.2 | 0.018 |
| 416 SS | 5% HCl | None | 0.3 | 0.089 |
| 416 SS | 5% HCl | 1.0% $FeCl_3$ | 0.3 | 0.099 |
| 416 SS | 5% HCl | None | 0.4 | 0.019 |
| 416 SS | 5% HCl | 1.0% $FeCl_3$ | 0.4 | 0.054 |
| Cast iron | 5% HCl | None | 0.2 | 0.87 |
| Do | 5% HCl | 0.5% FeS | 0.2 | 0.058 |
| Do | 5% HCl | 1.0% $FeCl_3$ | 0.2 | 0.90 |
| Do | 5% HCl | 0.5% FeS+1.0% $FeCl_3$. | 0.2 | 0.10 |
| Do | 5% HCl | 0.5% FeS+1.0% $FeCl_3$. | 0.3 | 0.032 |
| Do | 5% HCl | None | 0.3 | 0.176 |
| Do | 5% HCl | 1.0% $FeCl_3$ | 0.3 | 0.185 |
| Do | 5% HCl | None | 0.4 | 0.118 |
| Do | 5% HCl | 1.0% $FeCl_3$ | 0.4 | 0.112 |

It can be seen from the foregoing examples that the ferrous containing metal corrodes at a rapid rate in the presence of hydrochloric acid and ferric chloride even in the presence of the inhibitor. However, in the presence of both the aldehyde-containing inhibitor and the hydrogen sulfide or hydrogen sulfide source, the corrosion rate is reduced to a very low level.

It should be understood that the foregoing examples are merely illustrative and should not be considered to limit the scope of the invention. Indeed, the scope of the invention is to be limited only by the legal scope of the appended claims.

It can readily be seen to one skilled in the art that many variations in the present invention may be used. In general, any method of treatment of a ferrous surface with hydrochloric acid or any acid which will produce a ferric ion capable of resulting in ferric ion corrosion may be used. Furthermore, any suitable method of providing hydrogen sulfide and an aldehyde-containing inhibitor may be used. In addition, it can readily be seen that wide variations in the concentrations of hydrogen sulfide and inhibitor may be used depending upon the conditions of concentration, temperature, etc., under which the treatment of the ferrous metal occurs.

We claim:

1. A method of treating metal ferrous surfaces to remove iron oxide encrustations comprising treating the surface with an aqueous solution comprising an hydrochloric acid, hydrogen sulfide and an aldehyde-containing corrosion inhibitor.

2. The method of claim 1 wherein the hydrogen sulfide is obtained from ferrous sulfide provided in said solution.

3. The method of claim 1 wherein the hydrogen sulfide is obtained from thioacetamide provided in said solution.

4. The method of claim 1 wherein hydrogen sulfide gas is bubbled through said solution.

5. The method of claim 1 wherein the inhibitor is a composition comprising an aldehyde and a material selected from the group consisting of nitrogen bearing organic compounds, acetylenic compounds and mixtures thereof.

6. The method of claim 5 wherein the nitrogen bearing compound is an amine.

7. The method of claim 5 wherein the acetylenic compound is propargyl alcohol.

8. The method of claim 6 wherein the aldehyde is selected from the group consisting of formaldehyde, crotonaldehyde, benzaldehyde, butyraldehyde, propionaldehyde, glyoxal, aldol and mixtures thereof.

9. The method of claim 8 wherein the aldehyde is formaldehyde.

10. The method of claim 9 wherein the aldehyde is present in the form of an alcohol solution.

11. The method of claim 10 wherein the concentration of said inhibitor is from about 0.1% to 10%.

12. The process of claim 10 wherein the hydrogen sulfide concentration is from about 0.1% to 5% by weight.

13. A method of treating metal ferrous surfaces to remove iron oxide encrustations comprising treating the



surface with an aqueous solution comprising an hydrochloric acid, material capable of producing hydrogen sulfide in acid solution and an aldehyde-containing corrosion inhibitor.

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