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3,668,009

# CLEANING METHOD

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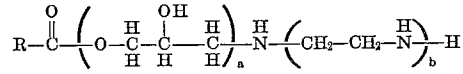
U.S. Cl. 134—2 7 Claims

## ABSTRACT OF THE DISCLOSURE

Improved method of cleaning a ferrous metal surface having a hardness deposit by contacting it with an aqueous alkaline cleaning solution containing about 0.1 to 40 weight percent of an ammoniated polycarboxylic acid complexing agent. The improvement involves including with the solution in an amount of from 0.0005 to 0.1 weight percent a corrosion inhibiting compound of the formula:



wherein R is an alkyl or alkenyl group containing from 12 to 18 carbon atoms, *a* is 1 or 2 and *b* is 1–5.

The use of aqueous alkaline solutions of ammoniated polycarboxylic acid complexing agents for the cleaning of closed ferrous metal systems, e.g. steam boilers, is known. Among the complexing agents which are useful in such a process are the mono or polysubstituted ammonium salts of ethylenediamine tetraacetic acid, diethylenetriaminepentacetic acid, nitrilotriacetic acid and citric acid.

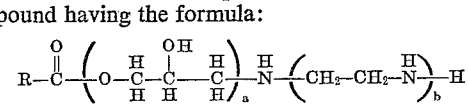
The cleaning operation is normally carried out at elevated temperatures, i.e. 90° to 400° F. and preferably at about 300° F., thus making the use of a corrosion inhibitor desirable.

It is an object of the present invention to provide a method for inhibiting corrosion in the above-described cleaning operation.

An additional object is to provide such a method which employs inhibitors which are stable to decomposition at temperatures of up to about 400° F. and above.

An additional object is to provide a method of inhibiting corrosion which does not interfere with the removal of hardness scale from the ferrous metal surface being cleaned.

The invention is based upon the discovery that an aqueous alkaline solution of an ammoniated polycarboxylic acid complexing agent is effectively inhibited against attack on a ferrous metal surface at temperatures of up to about 400° F. by incorporating into the solution from about 0.0005 to about 0.1 percent by weight an inhibitor compound having the formula:



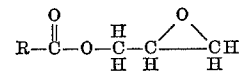
In the above formula R is alkyl or alkenyl containing from 12 to 18 carbon atoms, *a* is 1 or 2 and *b* is 1–5.

In carrying out cleaning with the present inhibited cleaning solution, the solution is adjusted to a preselected alkaline pH normally in the range of from about 7.3 to 9.3 and the system to be cleaned is filled or otherwise contacted with the cleaning solution. The solution is then heated to a temperature of at least about 90° F. and preferably to a temperature of from 250° to 300° F. Temperatures as high as about 400° F. may be used. The hot cleaning solution is then maintained in contact with the ferrous metal surface for the requisite period of time

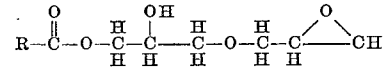


to dissolve the hardness deposit. Most any ferrous metal surface can be cleaned by the method, especially cast iron, ductile iron, mild steel and austenitic, martensitic or ferritic stainless steel.

In general, the inhibitor compounds are prepared by reacting a long chain fatty acid with epichlorohydrin or diglycidyl ether at moderately elevated temperatures to form the corresponding monoepoxyester. In this reaction, sufficient base is used to neutralize the byproduct HCl when epichlorohydrin is used and NaOH added to epoxidize the ester product. The intermediate monoepoxy ester will have the formula:

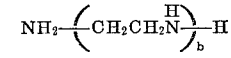


when epichlorohydrin is reacted and:



when diglycidyl ether is employed.

After preparation of the monoepoxyester any excess epichlorohydrin or diglycidyl ether is removed by distillation, extraction or other means to a residual level of less than 5 percent and the ester reacted with an ethylene polyamine of the formula:



where *b* is an integer from 1 to 5. This process is more fully described in U.S. Pat. 3,467,684.

The corrosion inhibtors are viscous liquids which can be dispersed in water or in the concentrated cleaning solution. The inhibitor is dispersed in an amount sufficent to provide from 0.0005 to 0.1 weight percent of the final solution with 0.001 to 0.005 weight percent being the preferred concentration range.

The inhibitors are effective when used alone. It has been discovered that a strong synergistic action is demonstrated when certain sulfur containing compounds, i.e. thioethylamine, sodium mercaptobenzthiazole, bisethylamine bisulfide or thiazolidine, are added to the inhibited cleaning solution. These compounds are normally employed in an amount sufficient to provide from 0.01 to 0.1 weight precent of the solution.

The invention is further illustrated by the following examples:

## EXAMPLE I

Inhibitor compounds were prepared as described above from the reactants set out in Table I. The usefulness of each inhibitor was determined by placing two polished, mild steel, 1" x 3" x 1/16" coupons along with a mill scaled (about .65 gm. $Fe_3O_4$) coupon in a beaker containing a 3.8% solution of ammoniated EDTA containing the amount of inhibitor indicated. The beakers were placed in a pressure vessel and heated to 250° F. for 16 hours. At the end of the heating period the coupons, which were weighed before being placed in the beaker, were reweighed and the corrosion rate determined by the weight loss. A control specimen was used with no inhibitor present upon which corrosion rates were determined intermittently during the 16 hour period. After the testing period all of the coupons were clean with no evidence of black deposits being observed.

Table I sets out the inhibitor, its concentration and the corrosion rate for each of 18 runs.

TABLE I

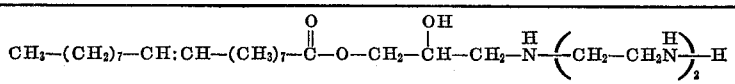
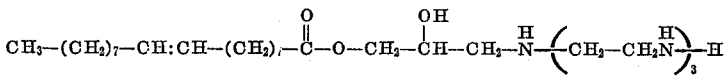
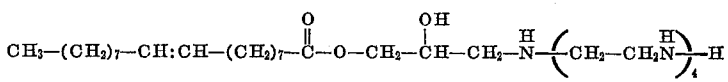
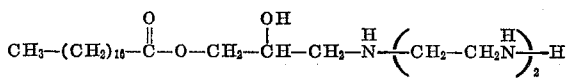
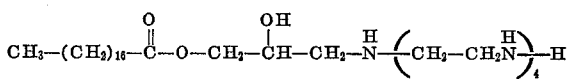
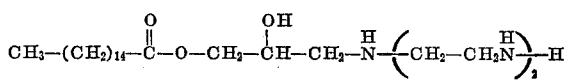
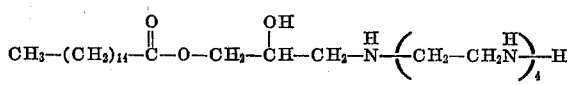
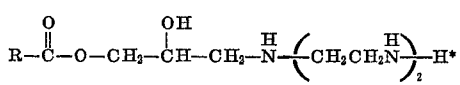
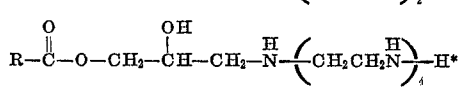
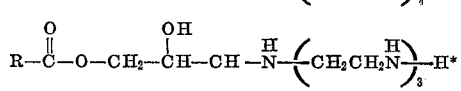
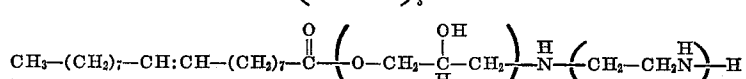
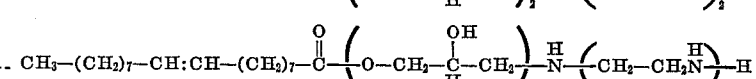
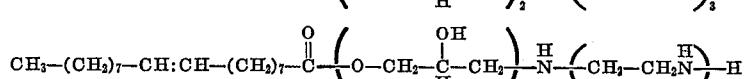
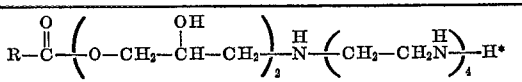
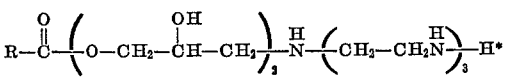
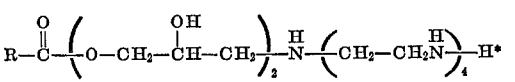
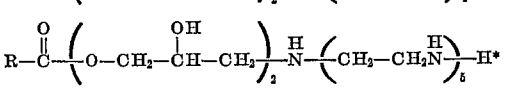
| Run No. | Inhibitor reactants | Inhibitor formula | Conc, wt, percent | Cor, rate, lbs./ft.²/day |
|---|---|---|---|---|
| 1 | Oleic acid plus epichlorohydrin plus diethylenetriamine |  | .002 | .0080 |
| 2 | Oleic acid plus epichlororhydrin plus triethylenetetramine |  | .002 | .0077 |
| 3 | Oleic acid plus epichlorohydrin plus tetraethylenepentamine |  | .002 | .0084 |
| 4 | Stearic acid plus epichlorohydrin plus diethylenetriamine |  | .002 | .0071 |
| 5 | Stearic acid plus epichlorohydrin plus tetraethylenepentamine |  | .002 | .0091 |
| 6 | Palmitic acid plus epichlorohydrin plus diethylenetriamine |  | .002 | .0087 |
| 7 | Palmitic acid plus epichlorohydrin plus tetraethylenepentamine |  | .005 | .0089 |
| 8 | Tall oil plus epichlorohydrin plus diethylenetriamine |  | .005 | .0062 |
| 9 | Tall oil plus epichlorohydrin plus tetraethylenepentamine |  | .002 | .0059 |
| 10 | Tal oil plus epichlorohydrin plus triethylenetetramine |  | .005 | .0060 |
| 11 | Oleic acid plus diglycidyl ether plus diethylenetriamine |  | .005 | .0077 |
| 12 | Oleic acid plus diglycidyl ether plus triethylenetetramine |  | .005 | .0079 |
| 13 | Oleic acid plus diglycidyl ether plus tetraethylenepentamine |  | .005 | .0082 |

TABLE I—Continued

| Run No. | Inhibitor reactants | Inhibitor formula | Conc, wt, percent | Cor, rate, lbs./ft.²/day |
|---|---|---|---|---|
| 14 | Tall oil plus diglycidyl ether plus diethylenetriamine |  | .005 | .0075 |
| 15 | Tall pil plus diglycidyl ether plus triethylenetetramine |  | .005 | .0064 |
| 16 | Tall oil plus diglycidyl ether plus tetraethylenepentamine |  | .005 | .0009 |
| 17 | Tall oil plus diglycidyl ether plus pentaethylenehexamine |  | .005 | .0095 |
| 18 | Control | | 0 | .0251–.0472 |

* Tall oil contains a mixture of oleic, stearic and palmitic acid which provides a mixture of inhibiting compounds in which the R group corresponds to that of oleic, stearic and palmitic acid. Compounds prepared from shorter chain fatty acids such as lauric acid ($R=C_{12}H_{25}$) can also be prepared and used effectively as corrosion inhibitors.

## EXAMPLPE II

Although the inhibitors listed in Table I were effective when used alone, strong synergistic action was observed when thioethylamine was also used. No ill effects were observed and substantial reduction in the corrosion rate was obtained at temperatures as high as 336° F. The results of corrosion tests conducted as in Example I with the addition of thioethylamine to the cleaning solution are tabulated in Table II. The inhibitor numbers in Table II correspond to the run numbers in Table I.

TABLE II

| Inhibitor | | Percent thioethyl-amine | Corrosion rate (lbs./ft.²/day) at— | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Percent | | 336° F. | 304° F. | 286° F. | 280° F. | 270° F. | 250° F. |
| Number: | | | | | | | | |
| ---------- | .05 | .02 | .0096 | .0108 | .0072 | .0045 | ---------- | .0003 |
| 10 | .02 | .02 | .0095 | .0079 | ---------- | .0032 | .0033 | .0004 |
| 9 | .05 | .02 | .0100 | .0086 | ---------- | .0052 | ---------- | ---------- |
| 9 | .02 | .02 | .0097 | .0077 | ---------- | .0047 | .0028 | .0004 |
| 15 | .05 | .05 | ---------- | .0130 | ---------- | ---------- | ---------- | ---------- |
| 13 | .05 | .05 | ---------- | ---------- | ---------- | .0067 | ---------- | ---------- |
| 8 | .02 | .05 | .0212 | ---------- | ---------- | .0093 | ---------- | .0060 |
| Control | | .05 | .0443 | .044 | .0251 | .0214 | .0082 | .0054 |

## EXAMPLE III

The synergistic action was also observed with other sulfur containing compounds. Table III summarizes the results of these observations which were obtained in the manner of Example I. In each case .002 weight percent of the inhibitor used in run #12 of Table I was employed.

TABLE III

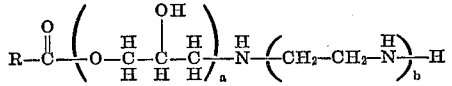
| Inhibitor | | | Corrosion rate[1] |
|---|---|---|---|
| | Percent | S-containing compound | |
| Number: | | | |
| 12 | .02 | Thioethylamine | .0048 |
| 12 | .05 | Sodium mercaptobenzothiazol | .0005 |
| 12 | .02 | Bis-ethylamine bisulfide | .0071 |
| 12 | .02 | Thiazolidine | .0092 |

[1] Pound per square foot per day at 280° F.

In a manner similar to that set out in the foregoing examples corrosion is inhibited in solutions of other ammonium substituted polycarboxylic complexing agents such as ammoninated citric acid, diammonium disodium EDTA, ammoniated nitrilotriacetic acid and ammoniated ethylenetriaminepentoacetic acid.

We claim:

1. In the method of cleaning a ferrous metal surface having a hardness deposit thereon by contacting it with an aqueous alkaline cleaning solution containing about 0.1 to 40 weight percent of an ammoniated polycarboxylic acid complexing agent, the improvement which comprises including in said solution in an amount of from 0.0005 to 0.1 weight percent a corrosion inhibiting compound of the formula:



wherein R is an alkyl or alkenyl group containing from 12 to 18 carbon atoms, *a* is 1 or 2 and *b* is 1 to 5.

2. The method of claim 1 wherein the corrosion inhibiting agent is employed in an amount sufficient to provide from 0.001 to 0.005 weight percent of the cleaning solution.

3. The process of claim 1 wherein the solution temperature is within the range of from about 90° to 400° F.

4. The process of claim 1 wherein the solution temperature is within the range of from 250° to 300° F.

5. The process of claim 1 wherein the complexing agent is ammoniated ethylenediaminetetraacetic acid.

6. The process of claim 1 wherein thioethylamine, sodium mercaptobenzthiazole, bis-ethylamine bisulfide or thioazolidine is combined with the inhibited cleaning solution.

7. The process of claim 6 wherein the sulfur containing compound is added in an amount sufficient to provide from 0.01 to 0.1 weight percent of the solution.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| 3,248,269 | 4/1966 | Bell | 134—2 X |
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U.S. Cl. X.R.

134—3, 41