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ACID CORROSION INHIBITORS

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ABSTRACT OF THE DISCLOSURE

The invention is a method of pickling and cleaning a metal above hydrogen in the electromotive series in which the metal is contacted with an aqueous acid containing a small but effective amount up to 0.5 percent by weight of (1) an amino thiol or amino thioether, such compounds being further characterized by the amino nitrogen and sulfur atoms being separated from each other by divalent two carbon atom hydrocarbon groups or (2) an N,N′ ethylene thiourea.

This invention relates to a method of inhibiting corrosion of metals by acids and more particularly pertains to a method of pickling and cleaning acid corrodible metals by treating the metal with an aqueous acid containing certain thioamino compounds and thereafter removing the thioamino compound from the metal surface.

Aqueous acids are often used in treating a variety of metals, particularly for pickling and cleaning. In order to reduce the corrosive effects of the acid on metals which are above hydrogen in the electromotive series of elements, inhibitors are commonly used. Among the inhibitors which can be used are certain long chain alkyl amines which have limited solubility in aqueous acid media. These long chain alkyl amines when used on reactive metals such as iron, steel, acid reactive iron alloys, copper and aluminum, coat the metal substrate and react with dissolved polyvalent metal ions to form an objectionable scum. With iron, the reaction produced is a brown, sticky, slimy material. If not removed from the iron surface, it tends to act as a corrosion center. If the surface of the iron or iron alloy is pitted to some degree, it is especially difficult to remove the amine-iron salt reaction product from the surface. Certain sulfur-containing compounds, such as thiols and thio acids, can be used as inhibitors in alkaline systems, but they suffer from the drawback of very low solubility in aqueous acidic media and they react with polyvalent metal ions to form insoluble salts which deposit on the surface of the metal.

The most effective way of removing scale, rust and grime from ferrous metals is to treat the surface with an aqueous acid by spraying, dipping, brushing or wiping. Representative acids that are useful for this purpose include strong mineral acids such as hydrochloric acid, sulfuric acid, nitric acid and phosphoric acid, and organic acids such as acetic, hydroxy acetic, formic, citric, maleic, sulfamic and oxalic acids. The preferred acids are the non-oxidizing acids which include the halo-acids and organic acids mentioned above.

I have found that if small but effective amounts, up to about 0.5 percent by weight of certain amino thiols

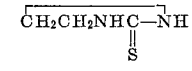
or amino thioethers in which the amino nitrogen and sulfur atoms are separated from each other by divalent two carbon atom hydrocarbon groups or an N,N′ ethylene thiourea, the corrosive effects of the aqueous acids are inhibited, the inhibitors and their reaction products are soluble in aqueous acid media, so that they leave the surface of ferrous metals clean and bright with no deposit that needs a secondary removal step. Usually, from 0.02 to about 0.2% by weight of the inhibitors suffice for protecting iron against corrosion by aqueous acids in cleaning treatments.

Representative compounds which can be used in accordance with this invention include, but are not limited to, 2-mercaptoethyl amine, thioethylamine

$$[(H_2NCH_2CH_2)_2S]$$

$$H_2NCH_2CH_2S—CH_2CH_2NHCH_2CH_2NH_2$$

the product formed by reacting 1,2-dihaloethane with thioethylamine and N,N′ ethylene thiourea of the structure



thiomorpholine, 2,6-dimethylthiomorpholine, phenothiazine and methyl phenothiazines in which the methyl group is on the ring.

The dihaloethane used for reacting with thioethylamine has the structure X—CH_2CH_2—X in which X represents chlorine, bromine or iodine. The halogens can be the same or different. Stated differently, X can be any halogen having an atom weight of at least 35.5. Thus, the generic formula includes $(CH_2)_2Cl_2$, $(CH_2)_2Br_2$, $(CH_2)_2I_2$, $(CH_2)_2ClBr$, $(CH_2)_2ClI$ and $(CH_2)_2BrI$.

The thioethylamine can be reacted with any of these dihaloethanes at an elevated temperature up to 200° C. or slightly higher. With dichloroethane in the absence of a diluent the reaction becomes very vigorous when a temperature of about 85° C. is reached. For best control of the reaction, a diluent is preferred. The diluent can be ethylene dichloride or any inert material which boils at about 80° C. or higher. Typical diluents are the higher alkanes or aromatic hydrocarbons. The reaction itself is a condensation between the dihaloethylene and the thioethylamine by splitting off a hydrogen halide and proceeds according to the following formula:

$$X(CH_2)_2X + H_2N—(CH_2)_2S(CH_2)_2NH_2 \longrightarrow X(CH_2)_2NH(CH_2)_2S(CH_2)_2NH_2 + HX$$

$$\downarrow X(CH_2)_2X$$

$$X(CH_2)_2NH(CH_2)_2S(CH_2)_2NH(CH_2)_2X + HX$$

$$\downarrow H_2N(CH_2)_2S(CH_2)_2NH_2$$

$$H_2N(CH_2)_2S(CH_2)_2NH(CH_2)_2NH(CH_2)_2S(CH)_2NH(CH_2)_2X + HX$$

The condensation can continue to provide a compound having from 1 to 3 radicals of the structure

$$—HN(CH_2)_2S(CH_2)_2N(H)_{0-2}$$

and 1 to 4 radicals of the structure

$$(X)_{0-1}CH_2CH_2—$$

attached to at least one nitrogen atom of the thioamine. When a molar excess of 1,2-dihaloethane is used, the compound has terminal —CH_2CH_2X groups, and if a molar excess of the thioethylamine is used, the compound has terminal

$$—\underset{H}{N}—(CH_2)_2S(CH_2)_2—NH_2$$

groups. With equimolar amounts of reactants, one end is usually terminated with a haloethane group and the other

end of the molecule is terminated with a thioethylamine group. From one to four mols of XCH_2CH_2X can be reacted with one to 3 mols of thioethylamine to obtain acid soluble products.

The N,N' ethylidene thiourea can be made by reacting ethylenediamine with CS_2 in alkaline media.

The method for preparing

$$H_2N—CH_2CH_2SCH_2CH_2NHCH_2CH_2NH_2$$

is described in detail in detail in my copending application Ser. No. 463,919, filed June 14, 1965 now Patent No. 3,362,996.

The inhibitors are effective over a fairly wide range of temperatures. Against a strong acid such as HCl, the inhibitors, at a concentration of 0.1 to 0.2% by weight, protect ferrous metal up to a temperature of about 160–170° F., and with the organic acids, they are effective at temperatures of 300° F. or slightly higher. At the elevated temperatures, it is preferable to use increased amounts of inhibitor, so that above 170° F. it is most desirable to use about 0.5% or more to ensure protection of the metal against HCl attack.

The examples which follow are intended to illustrate the invention, not to limit it. The parts or percentages are by weight unless otherwise indicated.

EXAMPLE 1

In each instance, the test solution was prepared by adding .1% by weight of the inhibitor to the aqueous acids listed in the table. Weighed mild steel strips 1 inch x 3 inches x 1/16 inch were immersed in 200 ml. of the solutions at various temperatures for various periods of time. After immersion, the strips were rinsed with distilled water, dried and weighed. From the loss in weight, the corrosion rate in lbs. per sq. ft. per day were calculated.

The data obtained in these tests are tabulated below in Table I.

TABLE I

Inhibitor	5% HCl soln., 23° C., 6 hrs.	5% acetic acid, 25° C., 24 hrs.	5% citric acid, 180° F., 4 hrs.
None (control)	.0280	.0330	.0230
Reaction product of dihaloethane and thioethylamine	.0016	.0084	.0032
$HSCH_2CH_2NH_2 \cdot HCl$	.0023	.0295	.0101
$H_2N(CH_2)_2S(CH_2)_2NH_2$	.0013	.0121	.0004
$CH_2CH_2NHC(=S)NH$	.0016	.0073	.0010
$H_2N(CH_2)_2S(CH_2)_2NH(CH_2)_2NH_2$	.0011	.0140	.0003

The steel samples after immersion were clean and bright and had no deposit on their surfaces from any of the reactants.

EXAMPLE 2

In this test, a strip of 1 inch x 3 inches x 1/16 inch 1010 steel was immersed in 200 ml. of 5% HCl containing .01% by weight of the reaction product obtained by heating 155 g. of 1,2-dichloroethane with 60 g. of thioethylamine to 85° C. and allowing the reaction to continue by refluxing the boiling 1,2-dichloroethane, without additional heat. After cooling at room temperature, the unreacted 1,2-dichloroethane, about 98 g., was removed by distillation. The immersion temperature was 23° C. and the duration 6 hours. This small amount of inhibitor gave 65% protection to the steel.

I claim:

1. A method of pickling and cleaning a metal above hydrogen in the electromotive series comprising contacting said metals with an aqueous acid containing at least a small but effective amount up to about 0.5% by weight of a corrosion inhibitor selected from the class consisting of
   (a) compounds with the structure $RS—CH_2CH_2NH_2$ wherein R is selected from the class consisting of —H, $H_2N—CH_2CH_2$ and $H_2NCH_2CH_2NHCH_2CH_2$ groups,
   (b) N,N' ethylenethiourea,
   (c) the reaction product obtained by heating to a temperature of 85°–200° C. from 1 to 4 mols of a 1,2-dihaloethane with from 1 to 3 mols of thioethylamine,
   (d) thiomorpholine and methyl substituted derivatives thereof having from 1 to 2 methyl groups on the ring, and
   (e) phenothiazine and ring substituted derivatives thereof in which the substituent consists of 1 to 2 methyl groups.

2. The method of claim 1 in which the corrosion inhibitor is N,N' ethylenethiourea.

3. The method of claim 1 in which the corrosion inhibitor is thioethylamine.

4. The method of claim 1 in which the corrosion inhibitor is mercaptoethylamine.

5. The method of claim 1 in which the inhibitor is the product obtained by reacting from 1 to 4 mols of 1,2-dihaloethane with 1 to 3 mols of thioethylamine at a temperature of from about 85 to about 200° C.

6. The method of claim 1 in which the corrosion inhibitor is $H_2NCH_2CH_2SCH_2CH_2NHCH_2CH_2NH_2$.

7. The method of claim 5 in which the dihaloethane is dichloroethane.

8. The method of claim 5 in which the dihaloethane is dibromoethane.

9. The method of claim 1 in which the acid is a non-oxidizing acid.

10. The method of claim 1 in which the acid is HCl.

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