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Scott et al.

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[54] **PROCESS FOR INHIBITING CORROSION**

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[52] **U.S. Cl.** ..... **21/2.7 R,** 252/148, 252/390, 252/392

[51] **Int. Cl.** **C23f 11/04,** C23g 1/06

[58] **Field of Search** 21/2.7; 252/148, 252/392, 390

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[57] **ABSTRACT**

A method for preventing corrosion of metals by an acidic environment by utilizing a corrosion inhibitor which is the reaction product of an amine having a plurality of primary or secondary amino groups and an aldehyde or ketone.

11 Claims, No Drawings

PROCESS FOR INHIBITING CORROSION

BACKGROUND OF THE INVENTION

In various types of industry numerous corrosion problems arise where a liquid acidic medium comes in contact with a metal such as steel or a copper alloy, for example, brass. These corrosion problems over a period of time result in replacement of expensive equipment and vessels and, thus, research is constantly under way for methods of preventing such corrosion problems. Carbon steel, for example, suffers the problem of fairly rapid dissolution of the metal when in contact with acids so that vessel walls, pumps, etc., are destroyed by the acid. Stainless steel on the other hand, while also subject to dissolution or erosion but at a lower rate than carbon steel, suffers greatly from cracking when subjected to a liquid medium containing certain chemical species such as inorganic chloride ions. This cracking is commonly referred to as stress corrosion cracking and eventually results in a much weakened metal even though the actual thickness of the metal may not have been reduced by any substantial amount.

The contact between a metal and a corrosive medium such as an acidic medium, may exist under normal operating conditions or may occur only periodically when an acid is utilized for cleaning. In the latter instance corrosion problems are generally quite severe due to the fact that solutions of acids which may be at high temperatures may necessarily be utilized in order to properly clean the equipment. However, it is obvious that regardless of the manner in which a corrosion problem is presented, whether it be in day to day operations or in periodic cleaning, corrosion problems are quite costly and are to be prevented if possible.

SUMMARY OF THE INVENTION

It is, thus, an object of the present invention to provide a method whereby corrosion problems due to contact of a metal with a corrosive medium may be reduced. It is another object of the present invention to provide novel materials which may be utilized in the prevention of corrosion problems in metals, especially steels and copper alloys, by liquid acidic mediums. It is a further object of the present invention to provide a method to prevent stress corrosion cracking in metals, particularly stainless steels. Additional objects will become apparent from the following description of the invention.

These and other objects are accomplished by the present invention which is one of its aspects is a method for preventing corrosion of metals in contact with a corrosive liquid medium comprising maintaining in said corrosive liquid medium a corrosion-preventing amount of a corrosion inhibitor which is the reaction product formed by reacting in the liquid phase under neutral conditions at least one carbonyl compound with at least one amine containing a plurality of amino groups, said amino groups each having at least one amine hydrogen and said amine being an acylcic amine wherein said amino groups are separated by a chain containing at least two carbon atoms or being a cyclic amine. In another aspect the present invention is a material suitable for use as a corrosion inhibitor consisting essentially of the product produced in a two stage reaction, both stages of which are conducted in the liquid phase and under neutral conditions, the first stage of which consists of mixing together at temperatures within the range of about 10° C. to 70° C. an aqueous formaldehyde solution and pentamethylene-diamine or hexamethylenediamine so as to form a solid condensation product, and the second stage of which consists of reacting at temperatures within the range of 75° C. to 200° C. said solid condensation product with cyclohexanone until dissolution of said solid condensation product occurs, followed by separation of the reaction product of said second stage from the reaction mixture to obtain said material suitable for use as a corrosion inhibitor.

DETAILED DESCRIPTION OF THE INVENTION

As may be seen from the above, the present invention is related to the prevention of corrosion problems in metals by liquid corrosive mediums. Although it is applicable to metals in general, the present invention finds its greatest use in the prevention of corrosion problems in copper alloys and steels, including carbon steel as well as the more sophisticated alloy steels such as stainless steels, nickel steels, etc. As applied to the stainless steels in particular, the present invention serves not only to reduce the corrosion problem of eroding away of metal but also reduces stress corrosion cracking. The copper alloys of which corrosion maybe prevented or reduced generally are those containing at least 50 per cent by weight of copper and include bronze and brass of various types as well as other alloys of copper with such materials as lead, nickel, aluminum, silver, zinc and tin.

The corrosive liquid mediums which cause or contribute to corrosion problems and to which the present invention is applicable are too numerous to mention in detail but most are acidic in nature and can range from aqueous solutions of an acid, such as hydrochloric acid itself, or can be solutions of acid salts such as magnesium chloride. Many problems due to the strong mineral acids and strong organic acids or metal salts thereof and the present invention finds some of its greatest use and is especially suitable in preventing corrosion by such. By "strong" in reference to an acid is meant its tendancy to ionize and is not meant in reference to its concentration. Furthermore, the present invention is most likely to be utilized in cleaning operations when a liquid acidic medium is employed. Aqueous hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, formic acid, hydroxy acetic acid, citric acid and oxalic acid are the acids to which the present invention is especially suitable although it is certainly not limited thereto.

The corrosion inhibitors of the present invention are formed by reacting certain amines with certain carbonyl compounds. The amines which may be utilized are those which have a plurality of amino groups, each of which has at least one amine hydrogen, and may be either cyclic or acyclic. By the term "amine hydrogen" is meant a hydrogen atom attached to the nitrogen atom of an amino group and therefore the amines useful in the present invention must contain at least two amino groups selected from the group consisting of primary amino groups and secondary amino groups. The requisite two amino groups may be two primary amino groups, two secondary amino groups or a secondary and a primary amino group. The preferred corrosion inhibitors, however, are formed from amines which contain a plurality of primary amino groups. Those

amines most suitable are generally free of functional groups other than amino groups and are free of ethylenic and acetylenic unsaturation although those having sulfur-containing and phosphorus-containing groups are also quite effective.

If the amine is acyclic, then two of the requisite amino groups should be separated by a chain containing at least two and preferably at least five carbon atoms. There may also be hetero atoms in the chain, such as nitrogen or oxygen, but preferably the amine is free of hetero atoms. The generally preferred acyclic amines contain at least two primary groups separated by a chain containing at least five carbon atoms. Especially preferred acyclic amines are those aliphatic diamines of the formula:

$$H_2N\text{–}R_1\text{–}NH_2 \qquad \text{I}$$

wherein R_1 is an alkylene radical, that is, a divalent hydrocarbon group free of unsaturation and of the generic formula $—C_nH_{2n}—$, of five to 15 carbon atoms wherein the two primary amino groups are separated by a chain of at least five, preferably five to ten, carbon atoms. Particularly suitable are those of the above Formula I wherein R_1 is a straight chain alkylene radical of five to seven carbon atoms. Suitable acyclic amines for use in the present invention include hexamethylenediamine, pentamethylene-diamine, heptamethylenediamine, triethylenetetramine, diethylenetriamine, 2,6-diaminooctane, and 1,6-diamino-3-ethyl hexane.

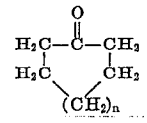
The cyclic amines useful in forming the corrosion inhibitors may be non-aromatic or aromatic. The positions of the amino groups may vary but the best inhibitors are formed from those cyclic amines wherein two primary amino groups are adjacent each other, that is, in an ortho position, when on the same ring nucleus. It is preferable that no hetero atoms be present and, therefore, the prefered cyclic amines will be carbocyclic. Also, they are preferably of six to 15 carbon atoms and contain only two primary amino groups as the sole functional groups therein. Examples of suitable cyclic amines include orthophenylenediamine, 1,2-diaminonaphthalene, 2,3-diaminonaphthalene, 1,8-diaminonaphthalene, 1,2-diaminocyclohexane, and 1,3-diaminocyclohexane.

The carbonyl compounds that maybe utilized in the present invention are those free of carboxyl groups, that is, they are ketones and aldehydes. Generally speaking, the carbonyl compounds will contain one to ten, preferably one to seven, carbon atoms and will be free of hetero atoms and also free of ethylenic and acetylenic unsaturation. Also, best results have been obtained with those compounds containing no functional groups other than carbonyl groups. The especially preferred aldehydes and ketones contain only one carbonyl group and are of the formula:



II

wherein R_2 and R_3 may be alike or different and are hydrogen, alkyl, aryl, alkaryl, araalkyl or cycloaklyl; and those alkyl substituted and unsubstituted cycloalkanones of the formula:



III

wherein n is 0, 1 or 2. Examples of suitable carbonyl compounds are formaldehyde, acetaldehyde, isobutyraldehyde, capraldehyde, lauraldehyde, benzaldehyde, the ortho, meta, para and alpha tolualdehydes, cyclohexanone, 4-methylcyclohexanone, benzophenone, 1-benzyl, 2-propanone, methyl p-tolyl ketone, phenyl propyl ketone, acetone, methyl ethyl ketone, hexyl methyl ketone and 1,4-cyclohexanedione. When formaldehyde is to be utilized, an aqueous solution is preferred but the source of such can, of course, be its other forms such as its anhydrous form trioxymethylene.

The reaction between the amines and the carbonyl compounds to form the corrosion inhibitors is generally a one stage reaction conducted in the liquid phase under neutral conditions by merely mixing the amines and the carbonyl compounds together alone or in the presence of an inert solvent. In some cases, namely when an acyclic amine and formaldehyde are reacted together, it will sometimes be desirable to further react the initial condensation produce in a second stage liquid phase reaction with additional carbonyl compound in order to make the product obtained in the first stage reaction more soluble. The initial reaction between the amine and the carbonyl compound, whether the reaction is to be conducted in one or two stages, can usually be conducted under neutral conditions at ambient temperatures, room temperature being suitable. By the term "neutral conditions" is meant that the reaction is conducted without the necessity of additional acid or basic catalysts and does not mean that the pH OF the reaction mixture is neutral. In fact, it would usually be slightly basic due to the presence of the amine. The temperature in the initial reaction may vary widely, for example, from 0° C. to 200° C., but is preferably within the range of about 10° C. to 70° C. Mixtures of amines and carbonyl compounds may be utilized in the initial reaction stage and where a second reaction stage is necessary mixtures may also be utilized.

The initial reaction between the amine and the carbonyl compound generally occurs immediately upon mixing of the two with the production of water in the reaction. In order to isolate those reaction products which are not solids, the water formed during the reaction as well as any solvent or excess reactant may be conveniently removed by distillation. In order to ease in recovery of the product it is generally desirable to use an excess of the carbonyl compound in order that the amine compound is completely reacted, the carbonyl compound usually being easier to remove by distillation than the amines. The corrosion inhibitor can, however, be formed of various molar ratios of carbonyl compound to amine, for example, 0.1:1 to 100:1, but generally the molar ratio of carbonyl compound to amine should be 0.5:1 to 10:1, and as stated above is preferably above 1:1 such that there is an excess of carbonyl compound.

As pointed out above, when formaldehyde and an acyclic amine are reacted together, the initial reaction product will generally be a solid condensation product which is relatively insoluble in most liquids. Even

though this product is effective as a corrosion inhibitor it is rendered more soluble and more effective as a corrosion inhibitor by further reacting it with additional carbonyl compound. The second stage reaction, like the first, is conducted in a liquid phase and under neutral conditions except that the reaction temperatures are generally higher and the reaction times may in some cases be longer depending on the carbonyl compound utilized in the second stage. Although it has been known according to U. S. Pat. No. 2,390,153 issued Dec. 5, 1945 to Kern, to render amine-formaldehyde reaction products soluble by further reacting them at elevated temperatures with more formaldehyde, it has not been known that other carbonyl compounds such as cyclohexanone could be utilized in the second stage reaction. are especially preferred for use in the second stage reaction as they provide rapid dissolution of the solid condensation product whereas formaldehyde and some of the other carbonyl compounds react quite slowly. Accordingly, the discovery of these new products, as well as their use, constitutes an aspect of the present invention. It is pointed out that the cycloalknones are especially preferred for use in the second stage reaction as they provide rapid dissolution of the solid condensation product whereas formaldehyde and some of the other carbonyl compounds react quite slowly.

The second stage reaction may be conducted at ordinary temperatures, however, it is much more efficient to conduct the reaction at a temperature within the range from about 75° C. to 200° C. An effective, and the preferred, method of conducting the second stage reaction has been found to merely boil the initial solid condensation product in the carbonyl compound or a solution thereof until the initial solid condensation product dissolves. Thus, the initial stage solid condensation product could be boiled in an aqueous solution of formaldehyde or in an excess of liquid cyclohexanone until dissolution occured which might occur very rapidly or take several hours depending on the conditions and the carbonyl compound used. The solvent and excess reactant may then be removed by distillation so as to isolate the reaction product inhibitor. As in the first stage reaction, it is preferred that the mole ratio of the carbonyl compound to the first stage condensation product be at least 1:1 and within the range of about 1:1 to 10:1.

The exact nature of the corrosion inhibitors of the present invention are not known as there are various reactions which theoretically could take place under the reaction conditions. Most likely it is believed that the final product is a mixture of many polymeric and monomeric compounds.

In utilizing the corrosion inhibitors of the present invention they may be merely added to and mixed with the corrosive liquid medium of concern. Very small amounts are needed and even amounts as small as one part per million (p.p.m.) by weight of the corrosive liquid will reduce corrosion. Generally speaking, about 1 to 10,000 p.p.m. based on the weight of the corrosive liquid will be utlized, the preferable range being from about 10 to 6,000 p.p.m. As used in the specification and throughout the examples and claims, "p.p.m." means parts per million by weight.

The following examples illustrate the preparation of inhibitors in accordance with the present invention. All parts and percentages are by weight unless otherwise indicated.

INHIBITOR A

About 22.5 grams of a 70% solution of hexamethylenediamine in water was poured into about 121 grams of a 35% aqueous formaldehyde solution at 25° C. Immediately about 17 grams of solid white material was formed which was isolated by filtration and dried. This material was designated as Inhibitor A.

INHIBITOR B

Seventeen grams of Inhibitor A was prepared as described above. It was then added to about 250 milliliters of cyclohexanone and boiled at atmospheric pressure (156° C.) resulting in the formation of a red solution. After evaporation of the excess cyclohexanone about 30 milliliters of a viscous red-brown material remained which was designated as Inhibitor B.

INHIBITOR C

About 20 grams of a 70% solution of hexamethylenediamine in water was poured into about 100 milliliters of cyclohexanone at room temperature with stirring. The water formed and the excess cyclohexanone was then removed by distillation. The residual material was used as a corrosion inhibitor as hereinafter set forth and was designated as Inhibitor C.

INHIBITOR D

At room temperature about 15.8 grams of solid 1,8-diaminonaphthalene was added with stirring to about 24 grams of an aqueous formaldehyde solution. The excess water and water formed during the reaction was removed by distillation resulting in a liquid residue suitable for a corrosion inhibitor and designated as Inhibitor D.

INHIBITOR E

The procedure used to prepare Inhibitor D was repeated except that about 11.6 grams of acetone was substituted for the aqueous formaldehyde. After removal of water and excess acetone the residue was recovered and designated as Inhibitor E.

INHIBITOR F

The procedure used to prepare Inhibitor D was repeated except that about 19.7 grams of cyclohexanone was substituted for the aqueous formaldehyde. The residue was recovered and designated as Inhibitor F.

The following examples illustrate the use of the corrosion inhibitors prepared above and designated as Inhibitors A through F.

EXAMPLE I

Metal coupons were cut, cleaned, weighed and placed in pint bottles. Carbon steel coupons were ¼ × ⅜ × 1½ inches and stainless steel coupons were ⅛ × ¾ × 1½ inches. Four hundred milliliters of 10% aqueous acid was poured into each container and 1,000 p.p.m. inhibitor was added. The solutions were placed in an oven and held at 200° F. for 4 hours. At the end of this time the specimens were removed, cleaned and weighed. Corrosion rates were calculated from weight loss. The results of the several runs are shown in the table below.

TABLE I

Run Number	Inhibitor	Acid	Corrosion Rate, IPY* Carbon Steel	316SS
1	None	10% HCl	8.9	3.2
2	B	10% HCl	0.61	0.072
3	C	10% HCl	0.61	0.13
4	D	10% HCl	0.75	0.15
5	E	10% HCl	1.50	0.26
6	F	10% HCl	0.80	0.13
7	None	10% H_2SO_4	16.0	0.16
8	B	10% H_2SO_4	2.60	0.13
9	None	10% Acetic	1.30	—
10	B	10% Acetic	0.84	—

* Inches per year

EXAMPLE II

In order to illustrate the improvement obtained by subjecting an acyclic diamine-formaldehyde inhibitor to further reaction with a carbonyl compound, three runs were made as follows. A carbon steel coupon 1.4 × 0.35 × 0.22 inches was placed in each of three bottles of 2-ounce capacity. The bottles were then filled with 3.8% aqueous hydrocholoric acid, the acid added to the first bottle containing no inhibitor, the acid added to the second bottle containing about 1,000 p.p.m. of Inhibitor A and the acid added to the third of the bottles containing about 1000 p.p.m. of Inhibitor B. The bottles were then placed in an oven and heated at 150° F. for 4.5 hours after which the coupons were removed, cleaned and weighed. Corrosion rates were calculated from weight loss. The corrosion rate of the coupon in the uninhibited acid was 4.7 inches per year, that of the coupon in the acid inhibited with Inhibitor A was 0.96 inches per year, and that of the coupon in the acid inhibited with Inhibitor B was 0.053 inches per year. Thus, it may be seen that the effectiveness of Inhibitor A was increased by subjecting it to a second stage reaction so as to convert it to an inhibitor of the nature of Inhibitor B.

The following example illustrates the reduction in stress corrosion cracking realized when using the corrosion inhibitors of the present invention.

EXAMPLE III

A type 316 stainless steel coupon was sheared from plate stock. The coupon was sawed in half, and each of the halves was placed in a separate one liter flask. Five hundred milliliters of 42% magnesium chloride was added to each flask. The magnesium chloride in one flask was inhibited with Inhibitor B. Althougb 5,000 p.p.m. of Inhibitor B was added, its limited solubility in 42% magnesium chloride allowed only a much smaller amount to actually go into solution. The flasks were fitted with reflux condensers, placed in mantles, and heated to the boiling point.

After 24 hours exposure, the specimens were removed and examined with a microscope. The specimen from the unihibited magneisum chloride was severely cracked on the sheared edges. There were no cracks in the sample from the inhibited magnesium chloride. The coupons were returned to the flasks and exposed an additional 48 hours. The coupon from inhibited magnesium chloride had no stress corrosion cracks after a total of 72 hours in boiling 42% magnesium chloride.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for preventing corrosion of metals in contact with an aqueous acidic liquid medium comprising maintaining in said acidic liquid medium a corrosion-preventing amount of a corrosion inhibitor consisting essentially of the reaction product formed by reacting in the liquid phase under neutral conditions;

a. at least one carbonyl compound of one to 10 carbon atoms having a single carbonyl group as the only functional group, containing no hetero atoms and free of ehtylenic or acetylenic unsaturation, and

b. at least one cylcic amine of six to 15 carbon atoms which has only two primary amino groups, is free of ethylenic and acetylenic unsaturation, and has no functional groups other than said two primary amino groups.

2. The process of claim **1** wherein the amount of inhibitor utilized is from about 10 to 6,000 p.p.m. and wherein said acidic liquid medium is an aqueous strong mineral acid or a strong organic acid.

3. The process of claim **1** wherein said amine is an aromatic amine and said carbonyl compound is formaldehyde.

4. The process of claim **1** wherein said amine is an aromatic amine and said carbonyl compound is cyclohexanone.

5. The process of claim **1** wherein said reaction product is formed by reacting the amine and the carbonyl compound at temperatures within the range of about 0° C. to 200° C. and wherein the mole ratio of carbonyl compound to amine compound used in the reaction is at least 0.5:1.

6. The process of claim **5** wherein said aqueous acidic liquid medium comprises a member of the group consisting of hydrochloric acid, sulphuric acid, phosphoric acid, acetic acid, formic acid hydroxy acetic acid, citric acid produced oxalic acid. pentamethylenediamine hexamethylenediamine so stage

7. A method for preventing corrosion of metals in contact with an aqueous acidic liquid medium, which method comprises maintaining in said acidic medium a corrosion-preventing amount of a corrosion inhibitor consisting essentially of the product poduced in a two stage reaction, both stages of which are conducted in the liquid phase and under neutral conditions, the first stage of which consists of mixing together at temperatures within the range of about 10°C to 70° C an aqueous formaldehyde solution and pentamethylenediameine or hexamethylenedq,gqne y/ as to form a solid condensation product, and the second stage of which consists of reacting at temperatures within the range of 75° C to 200° C said solid condensation product with cyclohexanone until dissolution of said solid condensation product occurs, followed by separation of the reaction product of said second sage from the reaction mixture to obtain said material suitable for use as a corrosion inhibitor.

8. A method for preventing corrosion of metals in contact with an aqueous acidic liquid medium comprising maintaining in said acidic liquid medium a corrosion-preventing amount of a corrosion inhibitor consisting essentially of the reaction product formed by reacting in the liquid phase under neutral conditions:

a. at least one carbonyl compound of one to 10 carbon atoms having a single carbonyl group as the only functional group, containing no hetero atoms and free of ethylenic or acetylenic unsaturation, and

b. At least one amine selected from the group consisting of

b1 acylic alkylene diamines of five to 15 carbon atoms having only two primary amino groups which are separated by a chain of five to 10 carbon atoms and

b2 cyclic amines of six to 15 carbon atoms which have only two primary amino groups, are free of ethylenic and acetylenic unsaturation, and have no functional groups other than said two primary amino groups, wherein said corrosion inhibitor is formed by reacting said amine and formaldehyde in an initial reaction at a temperature within the range of from about 10° C to 70° C so as to form a solid condensation product followed by further reacting in a second stage liquid phase reaction said solid condensation product with additional of said carbonyl compound, said second stage reaction being conducted at a temperature of at least 75° C. and being conducted for a period of time sufficient to cause dissolution of said solid condensation product.

9. The process of claim **1** wherein said amine is an acyclic alkylene diamine.

10. The process of claim **15** wherein the carbonyl compound utilized in said second stage reaction is cyclohexanone.

11. The process of claim **15** wherein the amount of inhibitor utilized is from about 10 to 6,000 p.p.m. an wherein said acidic liquid medium is an aqueous strong mineral acid or a strong organic acid.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,770,377 Dated November 6, 1973

Inventor(s) Robert H. Scott, H. B. Lockhart

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 2, line 38, after "problems" insert -- occur --.

In column 5, lines 16 to 20 and beginning after "reaction.", delete -- are especially preferred for use in the second stage reaction as they provide rapid dissolution of the solid condensation product whereas formaldehyde and some of the other carbonyl compounds react quite slowly. --.

In claim 6, line 36, delete "produced" and insert therefor -- and --.

In claim 6, lines 36 and 37, delete the phrase beginning with "pentamethylenediamine" and ending with "stage".

In claim 7, line 48, for "pentamethylenediameine" read -- pentamethylenediamine -- and for "hexamethylenedq, gqne y/" read -- hexamethylenediamine so --.

Signed and sealed this 21st day of May 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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(5/69)

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