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3,642,641

**CORROSION INHIBITION**

Robert J. Tedeschi, Whitehouse Station, and Paul W. Natali, Middletown, N.J., assignors to Air Products and Chemicals, Inc., Allentown, Pa.

No Drawing. Filed Dec. 31, 1968, Ser. No. 789,020

Int. Cl. C11d 7/32

U.S. Cl. 252—148

9 Claims

**ABSTRACT OF THE DISCLOSURE**

Aqueous acid solutions are inhibited against corrosion of metals, especially ferrous metals, by incorporation of a corrosion inhibiting system composed of a mixture of a major amount of 3-methyl-1-butyne-3-ol, and a minor amount of n-hexynol, preferably in the presence of ethylene diamine or urea.

This invention relates to the inhibition of metal corrosion in acidic solutions and is more particularly concerned with inhibited aqueous acid solutions suitable for the treatment of metals.

Metal cleaning baths and pickling baths generally comprise aqueous solutions of inorganic acids such as sulfuric acid, hydrochloric acid, and phosphoric acid, and are useful in the cleaning and treatment of iron, zinc, ferrous alloys, and the like.

In the use of aqueous acidic baths to treat metals, additives or inhibitors in the baths are desirable to prevent or inhibit corrosion or erosion of the metal surfaces. Similarly, in the field of oil well acidizing, it is necessary to use inhibitors in order to prevent corrosion of the oil well equipment by the aqueous acid solutions employed. Various other industrial operations also involve contact between an aqueous acidic solution and a metal, and an inhibitor must be used in order to minimize corrosion and/or consumption of the metal by such contact.

If no corrosion inhibitor is present when the aqueous acidic solution comes into contact with the metal, excessive metal loss, production of undesirable metal surface properties, excessive consumption or loss of acid, and like adverse results will be experienced. Many different types of inhibitors have been proposed, but there has been a continuing search for corrosion inhibitors which can be used effectively in small concentrations, and which are economical to produce, since the use of inhibitors is a necessary expense and it is economically prudent to keep this expense at a minimum while, at the same time, realizing the desired inhibition of metallic corrosion or consumption.

Acetylenic alcohols have been proposed as corrosion inhibitors, and several kinds have been extensively used. All acetylenic alcohols, however, are not of equal effectiveness and, indeed, some of them have very little corrosion-inhibiting effectiveness. Others, on the other hand, have been found to be very effective for this purpose. For example, Monroe et al. U.S. Pat. No. 3,049,496, shows propargyl alcohol (3-propyne-1 ol) to be a relatively effective corrosion inhibitor in 10% HCl when used in 0.4% concentration at a temperature of 150° F. On the other hand, an acetylenic alcohol such as methyl pentynol is much less effective under these conditions. However, it is not merely because methyl pentynol is a larger molecule, or because it has a branched chain that it is less effective, because ethyl octynol is an outstandingly good corrosion inhibitor, as disclosed in Herman et al. U.S. Pat. No. 3,249,548. There is, therefore, no way of predicting how effective any particular acetylenic alcohol will be or whether any particular acetylenic alcohol will be effective at all from a practical standpoint. However, em-

pirical experience has shown that some acetylenic alcohols are very poor in their corrosion inhibiting activity, whereas others are highly effective, such as the ethyl octynol mentioned above.

Unfortunately, from a practical standpoint, many of the acetylenic alcohols which can be produced most economically have very poor corrosion inhibiting activity. In order to improve the activity of some acetylenic alcohols, it has been proposed to form mixtures of certain acetylenic alcohols as disclosed, for example, in Beale et al. U.S. Pat. No. 3,231,507. However, these mixtures involve the use of acetylenic alcohols all of which, by themselves, are relatively good inhibitors. There still remains the problems of increasing the corrosion inhibiting activity of certain acetylenic alcohols which, in themselves, are poor inhibitors yet are attractive from an economic standpoint because they can be produced relatively inexpensively.

It is, accordingly, an object of this invention to provide a corrosion-inhibitor system which is effective to prevent corrosion of metal, particularly ferrous metal, by aqueous acidic solutions, but which employs, as a major component, an acetylenic alcohol of poor corrosion-inhibiting characteristics.

The discovery has been made that certain acetylenic alcohols, even when used in very small amounts, have a significant "potentiating" or "catalyzing" action upon other acetylenic alcohols of poor corrosion-inhibiting properties, so that the small amount of the "potentiating" or "catalyzing" acetylenic alcohol produces, with the acetylenic alcohol of poor corrosion-inhibiting properties, a highly effective corrosion-inhibiting system.

In accordance with this invention, it has thus been discovered that a very small amount of hexynol, which amount in itself is not effective to produce any significant corrosion inhibition will, when combined with a relatively large amount of 3-methyl-1-butyne-3-ol, which itself has little corrosion-inhibiting action, produces an inhibitor system of attractive corrosion-inhibition characteristics. In providing the corrosion-inhibiting systems of this invention, the ratio of the hexynol, i.e. the "potentiating" agent, to the 3-methyl-1-butyne-3-ol, may be as low as 1:100, preferably 1:50, and does not need to go higher than 1:10 preferably 1:20, and thus can be distinguished from mixtures of the type disclosed in the above-mentioned Beale et al. patent, the ratios being mole ratios.

The introduction of the above-described corrosion-inhibiting system in aqueous inorganic solutions has been found to have the desirable result of inhibiting or substantially preventing the corrosive action or attack of the acid upon metal surfaces with which it comes into contact. The use of this corrosion-inhibiting system in acid cleaning and pickling vats does not hinder or interfere with the desired action of the acid on the oxide, rust, grease, scale, or other undesirable surface material or coating, which is to be removed.

The inhibitor of this invention is useful, in general, in the inhibition of corrosion of metal surfaces in contact with aqueous mineral acid solutions, for example, in the acidizing of oil wells, electrolytic cleaning baths, and electrolytic refining of metals, as well as in metal cleaning and pickling baths.

The use of the hexynol-methyl butynol inhibitor system as a corrosion inhibitor for metals in aqueous mineral acid solutions is advantageous in that the hexynol methyl butynol inhibitor system can be employed as a corrosion inhibitor over a wide and useful concentration range. A further advantage of this inhibitor is that it may be used even at elevated temperatures to provide good corrosion inhibition, even when in low concentration.

The most effective amount of the hexynol-methyl butynol inhibitor system to be used in accordance with this invention can vary, depending upon local operating

conditions. Thus, the temperature and other characteristics of the acid corrosive system may have a bearing upon the amount of inhibitor to be used.

In general, it has been found that a concentration of the hexynol-methyl butynol inhibitor system between 0.01% and 2%, preferably 0.01% to 1.2%, by weight of the aqueous acidic solution is an effective corrosion inhibiting concentration, with a concentration between 0.05% to 0.75% being particularly preferred, especially for corrosive systems at elevated temperatures, e.g. in the neighborhood of 175–200° F. The acidic solution can be dilute or concentrated and can be of any of the concentrations used in treating metals, e.g. ferrous metals, for example 5 to 80%. In most operations of the character indicated, acid concentrations of 10–15% by weight are employed.

The method used to determine the inhibiting properties of the system of the invention employs metal test specimens or coupons. To prepare the coupons, they are wiped with acetone to remove any residual oils or grease, and pickled for one minute in 10% hydrochloric acid to eliminate any scale and surface film. After pickling, the coupons are dipped in sodium bicarbonate solution, rinsed well in tap water, rinsed in distilled water, and finally dried with acetone. The clean and dry specimens are then weighed to the nearest 0.1 mg. In carrying out the evaluation, hydrochloric acid of 10% by weight concentration is used. The inhibitor system is added to 4 oz. test bottles, 100 ml. of the acid then added to each bottle; and the mixture shaken vigorously. The bottles are suspended in a constant-temperature bath consisting of a bell jar filled with ethylene glycol and equipped with a stirrer. The temperature is regulated to maintain the samples at 175±2° F. The bottles are placed in the bath ½ hour before the test coupons are added to insure temperature equilibrium. The weighed coupons, in duplicate, are then supported on glass hooks in the test bottles and the bottles are covered with watch glasses during the testing period of 2 hours. At the end of the testing period, the bottles are removed from the bath, the coupons withdrawn, rinsed with water, sodium bicarbonate solution, distilled water, and dried in acetone, then weighed to measure weight loss. Corrosion-inhibiting properties are conveniently expressed as percent inhibition, using the following formula:

Percent Inhibition

$$= \frac{\text{Wt. loss of blank} - \text{wt. loss of test coupon}}{\text{wt. loss of blank}} \times 100$$

When the acid concentration and temperatures are such that the blank would be completely consumed by the acid solution in the absence of an inhibitor, the foregoing formula can be converted to

Percent Inhibition

$$= \frac{\text{Original wt. test coupon} - \text{wt. loss of test coupon}}{\text{original wt. test coupon}} \times 100$$

#### EXAMPLE 1

Using the testing procedure described above, and employing test coupons of mild steel 1 in. x 2 in. x 1/16 in. in size, mixtures comprising various proportions in moles of n-hexynol (H) and 3-methyl-1-butyne-3-ol (MB) were added to 10% hydrochloric acid, each mixture being added in the amount of 0.1% by weight of the acid, and evaluated for corrosion-inhibiting activity. At the same time a blank test, using the same acid and the same temperature but without any inhibitor, was made as well as well as a test using 3-methyl-1-butyne-3-ol alone in the amount of 0.1% by weight. The following results were obtained:

Inhibitor	Total amount, percent	Percent inhibition
MB	0.1	76
H plus MB (1:10)	0.1	93
H plus MB (1:12)	0.1	94
H plus MB (1:20)	0.1	94
H plus MB (1:30)	0.1	93
H plus MB (1:40)	0.1	94
H plus MB (1:100)	0.1	94
Blank		0

These tests show the positive action of the combination of n-hexynol and 3-methyl-1-butyne-3-ol in accordance with this invention in inhibiting meal corrosion in an acid solution. Surprisingly the percent inhibition remains substantially constant in the range of H-MB concentrations with which this invention is concerned, showing the unique potentiating action of n-hexynol upon 3-methyl-1-butyne-3-ol.

The combination of n-hexynol and 3-methyl-1-butyne-3-ol in the proportions indicated is as shown by the foregoing tests highly effective as a corrosion inhibitor. However, as the acid concentration is increased, e.g. to 15%, and the temperature is raised, e.g. to 200° F., the inhibitory action of the H-MB combination loses some of its effectiveness. It has been discovered, however, that by combining ethylene diamine or urea with the H-MB combination described above, the inhibiting action of the combination can be greatly increased and highly effective inhibition can be achieved even at high concentrations and temperatures. Suitable weight ratios between the combined hexynol and methyl butynol, and the urea or ethylene diamine, are 1:5 to 5:1, with weight ratios of 1:1 being particularly effective. This aspect of the invention is illustrated by the data set forth below which were obtained by carrying out the test procedure described above but with 15% HCl at 200° F. for 16 hours. In these tests one part of an H-MB mixture of 1 to 10 ratio was combined with one part by weight of ethylene diamine and one part by weight of urea, with a total amount of combined inhibitor of 0.5% by weight of the acid being employed in each sample. When ethylene diamine and urea are employed, they are advantageously combined with the acetylenic alcohol pair by dissolving them in a small amount of water and then adding the resulting aqueous solution to the acetylenic alcohols, e.g. 25% aqueous solutions, the water being excluded from the quantity calculations.

#### EXAMPLE 2

Inhibitor:	Percent inhibition
H+MB (1:10)+ethylene diamine	99+
H+MG (1:10)+urea	99+

The coupons used in the foregoing experiments were cut from a 1/16 in. sheet of a mild steel having the following typical analysis: 0.15% max. carbon, 0.30–0.60% manganese, 0.04% phosphorous, 0.05% sulfur, the balance iron.

It will be understood that various changes and modifications may be made in the operations described in the foregoing without departing from the scope of the invention as defined in the appended claims. It is intended, therefore, that all matter contained in the above description of the invention shall be interpreted as illustrative only and not as limitative.

We claim:

1. A metal corrosion-inhibitor mixture for use with aqueous mineral acids which consists essentially of 1-hexyn-3-ol and 3-methyl-1-butyne-3-ol in the relative molar ratios of 1:10 to 1:100.

2. An inhibitor mixture as defined in claim 1 wherein the hexynol and the butynol are present in the molar ratios of 1:20 to 1:50.

3. An inhibitor mixture as defined in claim 1 further containing ethylene diamine or urea.

4. The ethylene diamine or urea is present in a weight ratio

5

between the combined hexynol and methyl butynol of 1:5 to 5:1.

5. A corrosion-inhibited mineral acid comprising an aqueous solution of the mineral acid and a small, effective amount of a corrosion-inhibiting mixture consisting essentially of 1-hexyn-3-ol and 3-methyl-1-butyne-3-ol in the molar ratios of 1:10 to 1:100.

6. A corrosion-inhibited acid as defined in claim 5 wherein said corrosion-inhibiting mixture is present in the amount of 0.01% to 2.0% by weight.

7. An inhibited mineral acid as defined in claim 6 wherein the hexynol and the butynol are present in the molar ratios of 1:20 to 1:50.

8. An inhibited mineral acid as defined in claim 5 further containing ethylene diamine or urea.

9. An inhibited mineral acid as defined in claim 8 wherein the ethylene diamine or urea is present in a weight ratio between the combined hexynol and methyl butynol of 1:5 to 5:1.

6

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LEON D. ROSDOL, Primary Examiner

A. I. RADY, Assistant Examiner

U.S. Cl. X.R.

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