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CORROSION-INHIBITED MINERAL ACIDS

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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 combination of 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol.

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. The need is also for corrosion inhibitors which are effective at high temperatures, e.g. 200° F. and above, such as are encountered in various operations involving acidic solutions, particularly oil-well acidizing where higher and higher temperatures are encountered as the well extends further into the earth.

While various corrosion-inhibiting agents have been proposed, all of such agents are not of equal effectiveness and of the many hundreds of agents which have been contemplated, only a few are sufficiently active to be commercially attractive. This is particularly true in the case of high-temperature operations. Some inhibitors which have been proposed are reasonably effective at low and moderate temperatures, but fail completely when high temperatures are encountered.

There has, therefore, been a continuing search for more effective inhibitors, or for ways of making a given inhibitor more effective. This search has involved the discovery of combinations of inhibitors which act together to provide an inhibitor system. However, many of these systems involve relatively expensive components so that, while they may be relatively effective in their corrosion-inhibiting activity, there are disadvantages from an

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economic standpoint, particularly if they have to be used in substantial quantities in order to bring about the desired corrosion-inhibiting activity. Similarly, many of these systems are ineffective at elevated temperatures. In particular, there is a need for a corrosion-inhibiting system comprising a plurality of components wherein relatively inexpensive compounds of poor corrosion-inhibiting action can be catalyzed or "potentiated" by the other component or components of the system so that the combination has a high corrosion-inhibiting activity even at elevated temperatures.

It is accordingly an object of this invention to provide a novel corrosion-inhibiting system involving a combination of agents which is highly effective from the standpoint of corrosion-inhibiting activity and which is, at the same time, commercially attractive.

It is a further object of this invention to provide a novel corrosion-inhibiting system comprising a combination of agents wherein one agent has a strong potentiating or catalyzing action upon the other agent so that the corrosion-inhibiting effectiveness of the combination is greater than the additive action of the components of the combination.

It is another object of the invention to provide a corrosion-inhibiting system of the character indicated which is effective at high temperatures.

In accordance with this invention, it has been discovered that the above and other objects can be achieved by the provision of a corrosion-inhibiting system comprising a combination of 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol. The ratio between these two components of the corrosion-inhibiting system may vary, but the best results are obtained with weight ratios ranging between 1:10 and 10:1, preferably between 1:5 and 5:1 and most suitably between 1:2 and 2:1.

The acetylenic alcohol-acetylenic glycol inhibitor system of this invention is useful, in general, in the inhibition of corrosion of metal surfaces in contact with aqueous mineral acid solutions, such as hydrochloric acid, sulfuric acid, and phosphoric acid, for example in the acidizing of oil wells, in electrolytic cleaning baths, and electrolytic refining of metals, as well as in metal cleaning and pickling baths. The use of the above-described ethyl octynol-diethyl tetradecynol inhibitor system of this invention for corrosion inhibition of metals in aqueous mineral acid solutions is advantageous in that this corrosion inhibitor system can be employed in such acid solutions over a wide and useful concentration range. A further advantage of this inhibitor system is that it may be used at elevated temperatures to provide satisfactory corrosion inhibition, even when in relatively low concentration.

The most effective amount of the corrosion-inhibiting system to be used in accordance with this invention can vary, depending upon local operation conditions. Thus, the temperature and other characteristics of the acid corrosive system may have a bearing upon the amount of inhibitor to be used. The higher the temperature and/or the higher the acid concentration, the greater is the amount of corrosion inhibitor required to give optimum results. In general, however, it has been found that a concentration of the corrosion-inhibiting system of the invention between 0.01 and 2%, preferably between 0.01% to 1.2%, by weight of the aqueous acidic solution is an effective corrosion-inhibiting concentration, although higher concentrations can be used when conditions make them desirable, with a concentration between 0.05% to 0.75% by weight being of most general use, at elevated temperatures, e.g. in the neighborhood of 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, or for operations involving contact of acidic solutions with such metals, e.g. oil-well acidizing,

and the like, for example 5 to 80%. In most operations of the character indicated, acid concentrations of 10-15% by weight are employed, and nonoxidizing inorganic acids are used. However it is not intended to limit the invention to any specific use of acidic solutions or with respect to any specific metal or acid.

The method used to determine the inhibiting properties of the system of the invention employs 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 15% by weight concentration is used in order to duplicate oil-well acidizing conditions. 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 $200 \pm 2^\circ \text{F}$. The bottles are placed in the bath $\frac{1}{2}$ 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 16 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 temperature are such that the blank would be completely consumed by the acid in the absence of an inhibitor, the foregoing formula can be expressed as:

Percent inhibition

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

EXAMPLE

Using the testing procedure described above, and employing test coupons of mild steel 1 in. x 2 in. x $\frac{1}{16}$ in. in size, a mixture comprising 3 parts by weight of 4-ethyl-1-octyn-3-ol and 1 part by weight of 1,10-diethyl-7-tetradecyn-6,9-diol was added to 15% hydrochloric acid, the mixture being added in the amount of 0.5% by weight of the acid, and the mixture evaluated for corrosion-inhibiting activity. At the same time a blank test, using the same acid but without any inhibitor, was made. Using the data obtained from these tests and applying the data in the formula set forth above for calculating percent inhibition, the following results were obtained:

Inhibitor:	Percent inhibition 16 hrs.
4 - ethyl - 1 - octyn - 3 - ol plus 1,10 - diethyl-7 - tetradecyn - 6,9 - diol	99+
None	—

These tests show the positive action of the combination of 4 - ethyl - 1 - octyn - 3 - ol and 1,10 - diethyl-7-tetradecyn - 6,9 - diol in accordance with this invention in inhibiting metal corrosion in an acid solution of high

concentration at an elevated temperature only slightly below the boiling point of water, over a prolonged period of time, the components of the system being relatively inexpensive chemicals in the corrosion-inhibiting field.

While the inhibitor system of this invention can be prepared from individual quantities of 4-ethyl-1-octyn-3-ol and 1,10 - diethyl - 7 - tetradecyn - 6,9 - diol, a particularly advantageous source of these two chemicals is the reaction mixture obtained by the ethynylation of butyraldehyde with acetylene, using the well-known reaction wherein 2-ethylhexaldehyde and acetylene are reacted in the presence of a catalyst in an inert solvent medium, most commonly an ether, the reaction being carried out at various temperatures but which generally lie in the range of 0 to 50°C . This reaction, which was originally proposed by Favorskii, and has been improved upon by several other workers, is well-described in the literature, and reference is made, for example, to the book "Acetylenic Compounds" by Thomas F. Rutledge (Reinhold Book Corp., 1968), especially pages 146 to 149, and to the footnotes referred to therein. In a typical operation the aldehyde and the acetylene are reacted in an acetal or an ether as the reaction medium at substantially atmospheric pressure at a temperature of 20 to 30°C ., using solid KOH as catalyst in amounts which are substantially stoichiometric (usually slightly in excess) with respect to the aldehyde, the acetylene being in excess of the stoichiometric quantity. The thus-produced mixture of 4 - ethyl - 1 - octyn - 3 - ol and 1,10 - diethyl - 7 - tetradecyn - 6,9 - diol will vary in composition somewhat, depending upon the specific reaction conditions, but the ratio of 4-ethyl - 1 - octyn-3-ol to 1,10-diethyl - 7 - tetradecyn - 6,9 - diol usually lies within the range of 5:1 to 1:4, and most commonly is about 1:1 to 2:1. The inert reaction medium is readily separated by distillation, but minor amounts of the solvent, e.g. up to 10% by weight or more, may be present and such presence does not interfere with the activity of the acetylenic hydroxy compounds. The mixture may also contain minor amounts of by-products produced by condensation, aldolization, or other reactions and are also unobjectionable. Such by-products may range up to 10% by weight but are usually less than about 5% by weight.

It will be understood that a reaction mixture of the character indicated is particularly attractive from a commercial standpoint since purification of the product of the ethynylation reaction is not required, yet the important benefits of the combination of 4-ethyl-1-octyn-3-ol with 1,10-diethyl-7-tetradecyn-6,9-diol in the system of this invention are realized in the critical area of corrosion inhibition, i.e. high acid concentrations and high temperatures. The results shown in the foregoing test data are obtained when such a reaction mixture is employed in providing the corrosion-inhibiting system of this invention.

The coupons used in the foregoing experiments were cut from a $\frac{1}{16}$ 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 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 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol wherein 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol are present in the relative weight ratios of 1:10 to 10:1.

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2. A corrosion-inhibited acid as defined in claim 1 wherein the corrosion-inhibiting mixture is present in the amount of 0.01% to 2% by weight.

3. An inhibited mineral acid as defined in claim 4 wherein 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol are present in the relative weight ratios of 1:4 to 5:1.

4. An inhibited mineral acid as defined in claim 2 wherein 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol are present in the relative weight ratio of 1:2 to 2:1. 10

5. An inhibited mineral acid as defined in claim 2 wherein the mineral acid is hydrochloric acid.

6. A method of inhibiting corrosion of metals in a mineral acid wherein the mineral acid contains a small, effective amount of a corrosion-inhibiting mixture consisting essentially of 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol wherein 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol are present in the relative weight ratios of 1:10 to 10:1. 15

7. A method as defined in claim 6 wherein the corrosion-inhibiting mixture is present in the mineral acid in the amount of 0.01% to 2% by weight. 20

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8. A method as defined in claim 7 wherein 4-ethyl-1-octyn-3-ol and 1,10-diethyl-7-tetradecyn-6,9-diol are present in the relative weight ratios of 1:4 to 5:1.

9. A method as defined in claim 7 wherein the mineral acid is hydrochloric acid.

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