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CORROSION INHIBITOR CONTAINING THE ETHYNYLATION REACTION PRODUCT OF BUTYRALDEHYDE WITH ACETYLENE

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ABSTRACT OF THE DISCLOSURE

A corrosion inhibitor, having particular utility in connection with aqueous solutions of mineral acids, comprises the reaction product obtained by the ethynylation of butyraldehyde with acetylene. This reaction product is a complex material which contains, inter alia, 1-hexyn-3-ol and 5-decyn-4,7-diol.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application 789,014 filed Dec. 31, 1968 now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

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.

(2) Description of the prior art

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

In the use of aqueous acidic baths to treat metal, additives or inhibitors are desirable in the baths 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 surface, and an inhibitor must be used in order to minimize corrosion and/or consumption of the metal by such contact.

If no such 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 the like adverse results, will be experienced.

Many different types of inhibitors have been proposed but, nonetheless, there has been a continuing search for corrosion inhibitors which can be used effectively in small concentrations and which are economical to produce. While the use of inhibitors is a necessary expense, it is still 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. 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.

Pure acetylenic alcohols have been proposed as inhibitors (e.g. 1-hexyl-3-ol as in U.S. Pat. 3,428,566) and binary mixtures of alkynols have also been suggested (e.g. in U.S. Pat. 3,231,507). Alkynols have also been proposed as components of corrosion inhibitor mixtures which also include oxyalkylated naphthenic acid (e.g. U.S. Pat. 3,382,179). Mono and polyhydric acetylenic alcohols are also suggested as an inhibiting agent in a chemical brightening solution for stainless steel (i.e. U.S. Pat. 3,125,475). These pure acetylenic materials, however, are relatively expensive. Furthermore, those pursuing the search for commercially viable corrosion inhibitors are always seeking new inhibitors which have superior corrosion-inhibiting characteristics.

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 the systems involve relatively expensive components so that, while they may be relatively effective in their corrosion-inhibiting activity, there are disadvantages from an economic standpoint. This is particularly so if they have to be used in substantial quantities in order to bring about the desired corrosion-inhibiting activity. Similarly, many of the systems are ineffective at elevated temperatures.

In particular, there is a need for a corrosion-inhibiting material comprising a plurality of components which is, in and of itself, effective and economically viable. The material would be even more attractive were it to have the characteristic of serving as a base for the addition of relatively inexpensive compounds which, per se, have little or poor corrosion-inhibiting action but which would be catalyzed or "potentiated" by the basic corrosion inhibitor composition. Thus the total combination would have a high corrosion-inhibiting activity, even at elevated temperatures, even when it contained a high percentage of materials which, per se, are poor corrosion inhibitors.

SUMMARY OF THE INVENTION

The corrosion inhibitor of the invention is the reaction product of the ethynylation of butyraldehyde with acetylene. The type of reaction involved is known to those skilled in the art as a Favorskii reaction. It is described, generally, in the literature as—for example—in "Acetylenic Compounds" by Thomas F. Rutledge C. (Reinhold Book Corp., 968) pages 146 to 149.

In preparing the material, butyraldehyde 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 which generally

lie in the range of 0° C. to 50° C. Suitable solvents include, for example, dioxane, tetrahydro furan, isopropyl ether and dimethyl formamide.

In a typical operation, the butyraldehyde and the acetylene are reacted in an acetal or an ether as the reaction medium at substantially atmospheric pressure at a temperature of 0 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 contains 1-hexyn-3-ol and 5-decyn-4,7-diol in hexyn in varying amounts depending upon specific reaction conditions. The ratio of 1-hexyn-3-ol to 5-decyn-4,7-diol varies depending on reaction temperatures but usually lies within the range of about 2.25:1 to about 1.25:1. The inert reaction medium may be readily separated from the product, as by distillation.

It should be emphasized that the reaction product is not just a simple binary mixture of the two identifiable products mentioned above. It also contains other unidentifiable materials which contribute to its efficacy as a corrosion inhibitor. These materials are produced by condensation, aldolization and other reactions and can constitute up to about 15%, most often from 8 to 10% of total product. Their presence can best be understood by reference to the following equations:

(a) $CH_3CH_2CH_2-CHO + HC\equiv CH \longrightarrow CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}-C\equiv CH$ (I)

(b) (I) + $CH_3CH_2CH_2-CHO \longrightarrow CH_3CH_2CH_2-\underset{\underset{OH}{|}}{CH}-C\equiv C-\underset{\underset{OH}{|}}{CH}-CH_2CH_2CH_3$ (II)

(c) $2CH_3CH_2CH_2-CHO \longrightarrow CH_3CH_2CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CHO$ (III)

(d) (III) + $HC\equiv CH \longrightarrow CH_3CH_2CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C\equiv CH$ (IV)

(e) (IV) + $CH_3CH_2-CHO \longrightarrow CH_3CH_2CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C\equiv C-\underset{\underset{OH}{|}}{CH}-CH_2CH_2CH_3$ (V)

(f) $nCH_3CH_2CH_2-CHO \longrightarrow CH_3CH_2CH_2\left[-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\right]_n-CHO$ (VI)

(g) (VI) + HC≡CH ⟶ Ethynl polyols (VII)

(h) (VII) + $CH_3CH_2-CHO \longrightarrow$ sec-Acetylenic polyols (VIII)

Reaction (a) yields 1-hexyn-3-ol (I). Reaction (b) yields 5-decyn-4,7-diol (II). However, reactions (c) and (f) yield aldol compounds (III) and (VI). Reaction (d) can produce compounds like (IV) which are isomers of (II). Higher molecular weight ethynyl polyols (VII) and acetylenic polyols (V and VIII) can also be produced. It is thus seen that the nature of the reaction product is incapable of precise identification despite the fact that it comprises (I) and (II).

The reaction product is particularly attractive from a commercial standpoint since purification of the product of the ethynylation reaction is not required. Important benefits of the particular acetylenic alcohols and other reaction products are realized when dealing with the critically corrosive environment of high acid concentrations and high temperatures.

The reaction product is particularly suitable for potentiating urea, acrylonitrile, methacrylonitrile and other selected nitrogen-containing compounds such as, for example, ammonia or aliphatic amines which contain up to 3 carbon atoms per molecule.

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

The most effective amount of the corrosion-inhibiting composition of the 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. 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 inhibitor of the invention of between 0.01 and 2%, preferably between 0.01% and 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% and 0.75% by weight being of the most general use, at elevated temperatures (e.g. those in the neighborhood of 200° F.). The acidic solution can be dilute or concentrated and can be of any of the concentrations customarily 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 non-oxidizing inorganic acids are used.

Neither the foregoing abstract of the disclosure nor summary of the invention is intended to limit or otherwise restrict the scope of this invention. Their function is solely in connection with information retrieval. The true scope of the invention is to be determined from a reasonable interpretation of the appended claims.

From the foregoing summary it will be apparent that it is an object of the invention to provide a novel corrosion inhibitor 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-inhibitor comprising a combination of reaction products which combination has a strong potentiating or catalyzing action upon materials which, per se, are not particularly effective corrosion-inhibitors so that the corrosion-inhibiting effectiveness of the combination is greater than the additive action of the components were their activity to be related to their weight percentage of total inhibitor composition.

It is still another object of the invention to provide a corrosion-inhibitor of the character described which is effective at high temperatures, economical to use and effective over wide ranges of concentration and under a wide variety of operating conditions.

These and other objects of the invention will be apparent to those skilled in the art from a consideration of the detailed non-limiting exemplification which follows:

DESCRIPTION OF THE PREFERRED EMBODIMENT

A typical reaction product, suitable for use as a corrosion inhibitor of the invention, is made is follows. 1.5 moles of KOH are pre-ground in a stainless steel Waring Blender at high speed for 5 minutes, using 200 cc. of a solvent (e.g. dioxane). The finely-divided base-slurry is quickly transferred to a 1-liter reactor, prepurged with nitrogen and protected from atmospheric moisture. The blender is quickly rinsed with two 50 cc. portions of the dry solvent to make a total solvent volume of 300 cc. All weighings of KOH are carried out in the dry box (relative humidity 0%), as well as charging of the blender. The adverse effect of water is avoided by using dry solvent.

After the slurry is placed in the reactor, the temperature is adjusted to 15–20° C. Acetylene is gradually metered into the well-stirred slurry, using entrance and exit wet test meters. The wet acetylene emerging from the entrance meter is dried through a 2-foot alumina column, a calcium carbide tower and, finally, an alumina tower before being bubbled below the surface of the stirred KOH-isopropyl ether slurry. The absorption of acetylene is slightly exothermic and occasional cooling is needed to maintain a temperature no greater than 15° C. Once saturation takes place, as evidenced by gas evolution on the exit meter, the feed of acetylene is reduced to maintain saturation.

With the reaction temperature controlled in the range of 10–15° C., one-half mole of n-butyraldehyde is added to form the corresponding ethynyl carbinol-KOH complex. Thereafter the remainder of the stoichiometric requirement (i.e. a total of 1 mole) of the aldehyde is added. Temperature is maintained below about 15° C. until the reaction is complete. Upon completion of the reaction, the solvent is distilled off to leave a reaction product suitable for direct use as the corrosion inhibitor of the instant invention.

Reactions conducted in this manner produce products containing from 50–65% 1-hexyn-3-ol and a amount of 5-decyn-4,7-diol which may range independently from 30–40%. The unidentified materials range in weight percent from about 7 to about 15.

Tests were made to demonstrate the effectiveness of the material using a reaction product of the type heretofore described which contained 58.5% of the hexynol, 33.7% of the decyn diol and 7.8% of unidentifiable material. Its performance was compared with a synthetic aqueous binary mixture containing the same weight percents of pure hexynol and pure decyn diol as its sole active ingredients.

The method used to determine the inhibiting properties of the materials employed test specimens or coupons of type 1010 steel. The coupons were cleaned with perchloroethylene to remove any residual oils or grease and pickled for exactly five minutes in 15% hydrochloric acid to eliminate any scale and surface film. After pickling, the coupons were dipped into sodium bicarbonate solution, rinsed well in tap water, rinsed in distilled water and finally dried with acetone.

The cleaned and dried specimens were then weighed on a microbalance to four decimal places until a constant weight was obtained. Each coupon was tested in a Corning glass-lined pressure vessel having an inside volume of approximately 500 cc. To the vessel, 150 ml. of 15% hydrochloric acid were added along with predetermined weight percent of the inhibitor being tested. A control was also run in each instance using no inhibitor whatsoever. Tests were made at several temperatures and test results are tabulated below.

TABLE 1

(Tests at 250° F.)

Inhibitor	Percent by wt.	Coupon weight loss (mg.) after 1 hr.
None		57.1
Binary mixture	1	2.0
Do	0.6	2.2
Reaction product	1	1.5
Do	0.6	1.7

TABLE 2

(Tests at 275° F.)

Inhibitor	Percent by wt.	Coupon weight loss (mg.) after 1 hr.
None		173.2
Binary mixture	1	2.5
Do	0.6	2.4
Reaction product	1	1.6
Do	0.6	2.2

TABLE 3

(Tests at 300° F.)

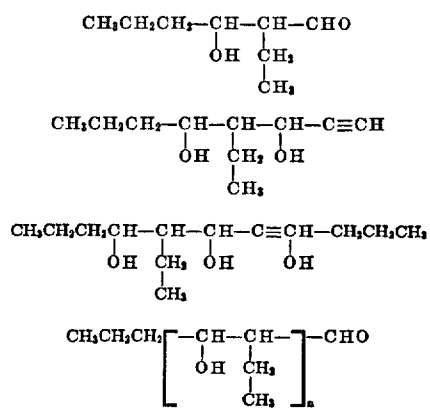
Inhibitor	Percent by wt.	Coupon weight loss (mg.) after 1 hr.
None		306.3
Binary mixture	1	2.8
Do	0.6	2.9
Reaction product	1	1.9
Do	0.6	2.9

These tests and others indicate that the reaction product is more effective as a corrosion inhibitor than would be a comparable binary mixture of the hexynol and the decyn diol.

The reaction mixture is economical to produce. While pure 5-decyn-4,7-diol sells for $1.20/# and 1-hexyn-3-ol at $.93/# a reaction product of the type in question can be marketed for $.65/#. Accordingly, said product is the type of commercially attractive, highly effective material consistent with the objects set forth above.

We claim:

1. A corrosion inhibitor for aqueous solutions of mineral acids consisting essentially of the reaction product obtained by the ethynylation of n-butyraldehyde with acetylene in excess of the stoichiometric quantity in the presence of solid KOH in an inert solvent medium at temperatures in the range of about 0 to 50° C. and by the removal of said solvent, said reaction product containing at least about 85 up to about 93% by weight 1-hexyn-3-ol and 5-decyn-4,7-diol and about 7 to about 15% by weight of a material selected from the group consisting of



ethynyl polyols, sec-acetylenic polyols and mixtures thereof, wherein the ratio of said hexynol to said decyn-diol is in the range of from about 2.25:1 to about 1.25:1.

2. The inhibitor of claim 1 wherein said ethynylation is performed at temperatures in the range of 0° to 30° C.

3. The inhibitor of claim 2 wherein said ethynylation occurs at temperatures below about 15° C. and where, consequently, the ratio of hexyonl to decyn-diol is increased.

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134—3, 41; 252—8.55 E, 148, 151, 392