United States Patent Office 3,243,379 Patented Mar. 29, 1966

3,243,379

CORROSION INHIBITOR FOR HOT ACIDS

Edwin E. Claytor, Jr., Tulsa, Okla., assignor to Pan American Petroleum Corporation, Tulsa, Okla., a corporation of Delaware

No Drawing. Filed Aug. 2, 1963, Ser. No. 299,464
8 Claims. (Cl. 252—148)

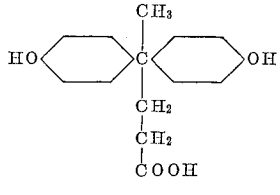
This invention relates to corrosion inhibitors. More particularly, it relates to inhibitors for hot acids.

When an oil-producing formation of an oil well is acidized to increase the oil-producing ability of the well, the metal parts such as the tubing and casing in the well are exposed to acid. If the well is deep and has a high temperature at its bottom, the metal parts and the acid will be at high temperatures. High temperatures greatly increase the rate of reaction of the acid with the tubing and casing of the well. Due to the greater depth and higher temperatures of recently drilled wells, the requirements for high temperature acid corrosion inhibitors have increased. Arsenic compounds such as sodium arsenite, particularly in combination with oil or a little wetting agent, provide considerable protection. The principal difficulty with arsenic is that the small amount of corrosion which occurs at high temperatures is localized in small areas. Therefore, a little metal loss may result in complete penetration of tubing and casing by small pits while most of the metal is corroded very little.

Organic inhibitors have been previously proposed. An example is the reaction product of propargyl alcohol with high boiling mixed polyalkylpyridines. These have been used successfully at temperatures somewhat above 200° F. At temperatures near or above 300° F., even these inhibitors lose much of their effectiveness.

An object of this invention is to provide an acid corrosion inhibitor which does not permit pitting and is effective at temperatures of about 300° F. Another object is to provide a method of inhibiting the corrosion of ferrous metals at high temperatures. A more specific object is to provide a method for acidizing high temperature oil wells. An additional specific object is to provide an inhibited acid solution for use at elevated temperatures.

In general I accomplished the objects of my invention by using as an inhibitor a material which may be called polyglycidyl Diphenolic Acid. Both Diphenolic Acid and DPA are trademarks for 4,4-bis(4-hydroxyphenyl)pentanoic acid. As used herein the terms Diphenolic Acid and DPA mean only the compound, the structural formula of which is:



When Diphenolic Acid is reacted with epichlorohydrin, the reaction is much the same as the bisphenol. The principal difference is that the epichlorohydrin reacts with the carboxylic acid group as well as with the phenolic groups. A monomer is thus formed with Diphenolic Acid having three epoxide groups rather than the two characteristic of the bisphenol reaction product. The possibilities of cross-linking are therefore greater with the polyglycidyl Diphenolic Acid.

The object of using an inhibitor is to apply to the metal surfaces an acid-resistant film. The conditions of the acidizing process impose certain requirements on the film-forming materials. The film is not to be formed in a process separate from the acidizing steps. The film-forming materials are to be added to the acid itself. The protective film must be deposited from the aqueous acid solution onto the metal walls. If the polyglycidyl Diphenolic Acid is to be further polymerized and cross-linked, the catalyst or reactant must not act too soon, near the top of a well for example, but must act only at the elevated temperatures where the corrosion inhibitor is most needed.

I have found that these requirements can be met by using as the polymerizing agent for the polyglycidyl Diphenolic Acid a relatively high molecular weight primary amine having at least about 12 carbon atoms per molecule. Lower molecular weight amines may react too rapidly at low temperatures. In addition, the lower molecular weight amines may not be adsorbed onto metal surfaces strongly enough to act as anchors for the epoxy resin which forms by reaction of the amine with the polyglycidyl Diphenolic Acid. The preferred amine has the formula $RNH(CH_2)_3NH_2$ where R is an aliphatic hydrocarbon radical having about 16 to 18 carbon atoms. This amine is known to be strongly adsorbed on ferrous metals and has been found to provide a desirable degree of controlled polymerizing reaction with the polyglycidyl Diphenolic Acid at temperatures from about 200 to 350° F. The amine should not contain more than about 30 carbon atoms since such high molecular weight amines usually are not sufficiently reactive for my purposes.

The polyglycidyl Diphenolic Acid is not particularly soluble in either water or petroleum fractions such as kerosene. It has a limited solubility in aromatic hydrocarbons, such as benzene and toluene, and a good solubility in oxygenated solvents, such as the ketones. A particularly desirable solvent is cyclohexanone. Materials of this class are also good solvents for the amines. To facilitate handling, it is usually advisable to dissolve the polyglycidyl Diphenolic Acid and the amine in a solvent. A convenient concentration in the solvent is about 25 percent by weight. The desired amount of inhibitor can then be simply introduced into the acid as it enters the pump which transports the acid down the well or to any other place of use.

A mixture containing about 15 percent by weight of polyglycidyl Diphenolic Acid, 10 percent by weight of mixed amines having the formula $RNH(CH_2)_3NH_2$, and about 75 percent by weight cyclohexanone was prepared. This preparation was allowed to stand in a bottle at a temperature of about 80° F. for over two months. There was no evidence of settling, separation, or reaction. It will be apparent, therefore, that this composition can be prepared well in advance of use without fear of premature polymerization. The concentration of the solvent in the inhibitor composition can be as low as about 50 percent by weight or as high as about 90 percent by weight.

The mixture stored in the bottle was employed as an inhibitor of high temperature acid corrosion in a series of tests where the effectiveness of the inhibitor was compared to that for several other inhibitors. The results are presented in Table I. In these tests pre-weighed jections of metal cut from J–55 oil well tubing were placed in aqueous 15 percent hydrochloric acid solutions containing the inhibitor to be tested. The temperature was then raised to the level indicated in the table. After 48 hours, at 125° F., and 4 hours at 270° F. and 329° F., the sections of steel were removed from the acid, cleaned and reweighed. The concentration of inhibitors in the tests at 125° F. was 2 percent by weight except for the alkylpyridines and propargyl alcohol inhibitor where the concentration was only 0.5 percent by weight. At 270° F. and 329° F., the inhibitor concentrations were all 1 percent by weight.

Table I

Inhibitor	Grams Wt. Loss at Temperature Indicated		
	125° F.	270° F.	329° F.
Alkylpyridines+Propargyl Alcohol	0.013	7.9	9.2
Amine Salt of Dimer Diester DPA	0.024	1.9	8.1
Polyglycidyl DPA+Amine	0.115	1.8	3.4
DPA Monoamide	0.020	1.9	5.7
Sodium Arsenite+Wetting Agent	----------	0.024	0.10

In the table DPA means Diphenolic Acid. The amine used to form a salt of the dimer diester DPA and the monoamide of DPA was the same mixture of amines having the formula $RNH(CH_2)_3NH_2$ used with the polyglycidyl DPA. The dimer diester DPA was formed by reacting 2 mols of DPA with 1 mol of a mixture of dimer acids having the average formula $C_{32}H_{62}(COOH)_2$. The dimer acid linked 2 DPA molecules together through phenolic linkages so the resulting molecule had two carboxylic acid groups.

It will be apparent from the data in Table I that there are many materials which are more effective as acid corrosion inhibitors at low temperatures than polyglycidyl DPA. It will also be apparent, however, that the organic inhibitors generally lose much of their effectiveness at temperatures around 300° F. while the polyglycidyl DPA and amine inhibitor retains considerable inhibiting action even at 329° F. The test panels remained smooth and unpitted. The very small weight loss allowed by sodium arsenite is to be noted. The steel panels in these tests were deeply pitted, however. In addition, many operators hesitate to use arsenic since it is poisonous to farm animals and man. It also has undesirable effects on many refinery catalysts. The polyglycidyl DPA and amine inhibitor is not poisonous and has no known adverse effects in refinery operations. Therefore, it will be apparent that this inhibitor can be used in acidizing high temperature wells, particularly where the use of arsenic is not permissible.

The cross-linking potential of the triglycidyl Diphenolic Acid is better than that of the glycidyl ethers of diphenols such as the bisphenols, for example.

When a polyphenol reacts with epichlorohydrin, several reactions are possible and all occur to some degree. Therefore, the reaction product is not a pure compound, but is a mixture of a variety of compounds. The ratios of end products can be affected by the ratio of polyphenol to epichlorohydrin by the pH of the reaction mixture, by the reaction temperature, and the like. Ordinarily, one epichlorohydrin molecule should be provided for each phenolic group. In the case of Diphenolic Acid, another epichlorohydrin should be provided for the carboxylic acid radical. The ratio of reactants can be changed considerably without greatly affecting the results. In the case of Diphenolic Acid, for example, the molecular ratio of epichlorohydrin to Diphenolic Acid is preferably 3 to 1. This forms triglycidyl Diphenolic Acid. The ratio may vary from about 1.5 to 1 to about 6 to 1, however, to form other polyglycidyl Diphenolic Acids as well as triglycidyl Diphenolic Acid.

Theoretically, each primary amine group reacts with two epoxide radicals in the curing operation. Therefore, sufficient amine should be provided to supply about one primary amine group for each two epoxide radicals. In the case of the preferred amine having one primary amine group and one secondary group, however, less amine should be used because the secondary amine group can react with an epoxide radical. Thus, one molecule of the amine having the formula $RNH(CH_2)_3NH_2$ can react with three epoxide radicals. Triglycidyl Diphenolic Acid has three epoxide radicals per molecule. Therefore, about one mol of the amine should be used for each mol of triglycidyl Diphenolic Acid. This means that on a weight basis about two parts by weight of the amine should be used for each three parts by weight of the triglycidyl Diphenolic Acid. Again, considerable variation is possible, the preferred ratio of triglycidyl Diphenolic Acid to this particular amine varying between about 1 to 1 and about 3 to 1.

It should be recognized that the epoxide linkages can react with each other as well as with amines. Therefore, while primary amines are greatly preferred because of their cross-linking ability and strong adsorption on metals, secondary and tertiary amines can also be used. For example, fair results have been obtained by use of 2-heptadecylimidazoline. This amine is known to be strongly adsorbed on ferrous metals, which may explain its beneficial action in combination with the trigylcidyl Diphenolic Acid. The imidazolines have one secondary amine group which can react with the epoxide polymer to attach the polymer firmly to the metal surface.

The concentration of the polyglycidyl Diphenolic Acid and amine combination in the acid solution should be about the same as for most acid corrosion inhibitors. That is, the concentration should be between about 0.1 and about 5 percent by weight of the acid solution, preferably about 1 or 2 percent. The concentration depends to some extent, of course, on the conditions of use. If a strong acid such as hydrochloric acid or sulfuric acid is used and the temperature is high, a high concentration of inhibitor should be used. If the acid is relatively weak, such as acetic acid, for example, or if the concentration of acid is low, then the inhibitor concentration can also be low.

While the invention has been described principally in connection with acidizing oil wells, it will be apparent that the inhibitor is also useful in other applications where hot acid is used as in steel pickling operations, acid cleaning of boilers, petroleum refinery equipment, and the like. Still other variations in the invention and additional applications will occur to those skilled in the art. The invention should, therefore, be limited only by the following claims and not by the examples given above.

I claim:

1. A corrosion inhibited aqueous acid solution for use in contact with surfaces at temperatures from about 200° F. to about 350° F. comprising water, hydrochloric acid, polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and a primary amine having from about 12 to about 30 carbon atoms per molecule, the weight ratio of said polyglycidyl acid to said amine being between about 1 to 1 and about 3 to 1 and said polyglycidyl acid being prepared by reacting epichlorohydrin and 4,4-bis (4-hydroxy phenyl) pentanoic acid in a molar ratio from about 1.5 to 1 to about 6 to 1, and the concentration of the combination of amine and polyglycidyl acid being from about 0.1 to about 5 percent by weight of the aqueous acid solution.

2. The composition of claim **1** in which said polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid is triglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and said amine has the formula $RNH(CH_2)_3NH_2$ where R is an aliphatic hydrocarbon radical having about 16 to 18 carbon atoms.

3. A composition for inhibiting corrosion of metals by an aqueous acid solution at an elevated temperature from about 200° F. to about 350° F. comprising polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid, a primary amine having from about 12 to about 30 carbon atoms per molecule and a solvent for said polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and said amine, said solvent being present in an amount of about 50 to about 90 percent by weight of the composition, the weight ratio of said polyglycidyl acid to said amine being between about 1 to 1 and about 3 to 1 and said polyglycidyl acid being prepared by reacting epichlorohydrin and 4,4-bis (4-hydroxy phenyl) pentanoic acid in a molar ratio from about 1.5 to 1 to about 6 to 1.

4. The composition of claim **3** in which said poly-

glycidyl 4,4-bis (4-hydroxy phenyl) petanoic acid is triglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid, said amine has the formula $RNH(CH_2)_3NH_2$ where R is an aliphatic hydrocarbon radical having about 16 to 18 carbon atoms, and said solvent is cyclohexanone.

5. A method for inhibiting the corrosion of a mild steel surface by an aqueous solution of hydrochloric acid at temperatures from about 200° F. to about 350° F., said method comprising contacting said surface with said solution having dispersed therein a polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and an aliphatic amine having from about 12 to about 30 carbon atoms per molecule, the weight ratio of said polyglycidyl acid to said amine being between about 1 to 1 and about 3 to 1 and said polyglycidyl acid being prepared by reacting epichlorohydrin and 4,4-bis (4-hydroxy phenyl) pentanoic acid in a molar ratio from about 1.5 to 1 to about 6 to 1, the concentration of the combination of amine and polyglycidyl acid being from about 0.1 to about 5 percent by weight of the aqueous acid solution.

6. The method of claim 5 in which said polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid is triglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and said amine has the formula $RNH(CH_2)_3NH_2$ where R is an aliphatic hydrocarbon radical having about 16 to 18 carbon atoms.

7. In a method in which an aqueous solution of hydrochloric acid comes into contact with a ferrous metal surface at an elevated temperature from about 200° F. to about 350° F. and causes corrosion of said surface, the improvement comprising incorporating into said solution, before the solution comes in contact with said surface, a mixture of a polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and a primary amine having from about 12 to about 30 carbon atoms per molecule, the weight ratio of said polyglycidyl acid to said amine being between about 1 to 1 and about 3 to 1 and said polyglycidyl acid being prepared by reacting epichlorohydrin and 4,4-bis (4-hydroxy phenyl) pentanoic acid in a molar ratio from about 1.5 to 1 to about 6 to 1, and the concentration of the combination of amine and polyglycidyl acid being from about 0.1 to about 5 percent by weight of the aqueous acid solution.

8. The method of claim 7 in which said polyglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid is triglycidyl 4,4-bis (4-hydroxy phenyl) pentanoic acid and said amine has the formula $RNH(CH_2)_3NH_2$ where R is an aliphatic hydrocarbon radical having about 16 to 18 carbon atoms.

References Cited by the Examiner

UNITED STATES PATENTS

2,933,520	4/1960	Bader	260—559 X
3,031,402	4/1962	Nelson	252—559 X
3,085,075	4/1963	Lockshin et al.	260—404.5

JULIUS GREENWALD, *Primary Examiner.*

H. B. GUYNN, *Assistant Examiner.*