

1

3,378,488

CORROSION INHIBITOR AND METHOD OF INHIBITING CORROSION IN OIL WELLS

Kenneth H. Nimerick, Tulsa, Okla., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Filed Apr. 29, 1965, Ser. No. 451,993

15 Claims. (Cl. 252-8.55)

ABSTRACT OF THE DISCLOSURE

Corrosive ingredients present in such fluids as natural gas, petroleum and petroleum derivatives are inhibited from attack on metals in contact therewith by admixing with said fluid or in a noncorrosive ingredient-containing fluid and applying such treated fluid to the metal surfaces prior to contact with the fluid containing the corrosive ingredients, the following mixture: (1) a monocarboxylic fatty acid having between about 10 and about 24 carbon atoms per molecule; (2) a polymeric acid having between about 24 and about 48 carbon atoms per molecule; (3) aminoethylethanolamine; and (4) a partial ester of glycerol or an alkylene glycol of 2 to 5 carbon atoms and a polymeric acid of the nature of that required for ingredient (2) which also contains therein the unreacted acid and glycerol or glycol.

The invention pertains to a corrosion inhibitor and method of inhibition of corrosive attack of fluids on metal and particularly to inhibition of the attack of corrosive ingredients present as contaminants in crude oil and in natural gas on metal in contact therewith during the production thereof.

Corrosion of metals in contact with many fluids is a continuing problem. Petroleum and natural gases, for instance, contain combined sulfur, nitrogen and the like, in acidic compounds which pit, etch, and, in time, cause such weakening and deterioration of metal pipes, coils of heat exchangers, fractionating columns, cracking units, pump parts, treating and storage tanks, and the like that sections or complete units must ultimately be replaced unless the corrosion is effectively inhibited. A particularly difficult aspect of the problem is the prevention of downhole corrosion, i.e. corrosion of pipes, pump parts such as sucker rods, screens and the like, which are positioned in a wellbore during production.

The severity of the corrosive problem has prompted extensive study thereof and evaluation of particularly promising techniques and materials to alleviate it. Such study has resulted in some success.

However, the problem has been only partially solved since the use of any of the known inhibitors, which are generally acceptable in industry, have not inhibited the corrosion to the extent desired, as evidenced by some pitting and etching of metal coupons during the more exacting corrosion tests, by representative samples obtained from oil producing fields. A need for more effective corrosion inhibitors and method of use still remains.

The invention is a corrosion inhibitor and method of use which results in substantially no pitting, etching, nor other evidence of corrosion, as tested by the more exacting tests, e.g. a NaCl-CaCl₂ brine, saturated with H₂S gas and containing glacial acetic acid.

The method of the invention may be practiced by either of the following procedures: (a) admixing an effective amount of the corrosion inhibitor of the invention with a fluid (which may or may not contain corrosive material) and contacting the metal surfaces to be protected to provide a protective film on the surface or (b) admixing an

2

effective amount of the corrosion inhibitor periodically with the corrosive fluid which normally comes in contact with a metal through production, use, or storage. Procedure (a) is usually referred to as film protection and procedure (b) as batch protection. The use of each procedure in producing oil or gas containing corrosive contaminants may be illustrated as follows: (a) a hydrocarbon liquid (which may be the oil being produced) is admixed with the corrosion inhibitor and forced back into the formation to be gradually flowed out with the produced oil or gas; (b) corrosion inhibitor in a fluid is continuously or periodically injected or bled into the annulus between the casing and tubing of a well, migrates downwardly, and intermixed with the oil being produced up the tubing. As a modification of the batch method the well may be closed after injecting corrosion inhibitor and circulated for a time.

The corrosion inhibitor of the invention comprises a mixture of (1) a monocarboxylic fatty acid having between about 10 and 24 carbon atoms per molecule; (2) a polymeric acid having between about 24 and 48 carbon atoms per molecule; (3) aminoethylethanolamine; and (4) a partial ester of glycerol or an alkylene glycol of 2 to 5 carbon atoms and a polymeric acid of the nature of that required for ingredient (2) which also contains therein the unreacted acid and glycerol or glycol.

(1) Illustrative of the monocarboxylic fatty acids to employ are capric, lauric, myristic, palmitic, stearic, arachidic, behemic, lignoceric, dodecylenic, palmitoleic, oleic, ricinoleic, petroselenic, vaccenic, linoleic, linolenic, eleosteric, licanic, parinaric, gadoleic, arachidonic, cetoleic, erucic, and selacholeic. It may also include rosin acids.

The monocarboxylic fatty acid may be a mixture of such acids. It is preferably unsaturated or a mixture consisting of at least about 10% of unsaturated monocarboxylic acids. It may be entirely aliphatic acids but advantageously may consist in a minor proportion of rosin acids including both pimaric and abietic acids. Without defeating the objectives of the invention, the monocarboxylic acid employed may contain the minor or trace amounts of polycarboxylic acids including dimer and to a less extent trimer acids which are sometimes present in crude acids available on the market. Tall oil fatty acids are the preferred monocarboxylic acid to employ. The mode of preparation and properties of tall oil fatty acids are well known and described in the literature, e.g. Kirk-Othmer Encyclopedia of Chemical Technology, vol. 13, pages 572 to 577. Tall oil fatty acids are obtained as a byproduct from the kraft or sulfate pulping operation and comprise predominantly a mixture of oleic and linoleic acids with a small percent of aliphatic saturated acids and rosin acids. Illustrative of readily available tall oil fatty acids for use in the practice of the invention are Acintol FA-1, Acinol FA-2, and Crofatol No. 5 obtainable on the market. Details of the manner of preparation and properties of Acinol are available in published literature from the Arizona Chemical Company, Rockefeller Plaza, New York and of Crofatol from Crosby Chemicals, Inc., Picayune, Miss.

(2) The polymeric acid is largely a dimer but usually includes some trimer and may also include trace amounts of monoacids. The more typical acid for use in the practice of the invention is that consisting predominantly of dimerized carboxylic acids wherein each repeating unit contains between 12 and 24 carbon atoms. It is substantially a saturated acid, but may contain minor amounts of unsaturants. A typical acid for use in the practice of the invention is Empol 1014 to 1024, e.g. 1022, a polymerized fatty acid which consists essentially of a C₃₆ dimer acid resulting from the dimerization of naturally occurring C₁₈ unsaturated fatty acids of which the major constituent of

tall oil acid is illustrative. Empol 1014 to 1024 are described in the literature and available upon request from Emery Industries, Inc., Caren Tower, Cincinnati 2, Ohio.

(3) The aminoethylethanolamine is available from numerous sources. It need not be chemically pure, but commercial or technical grades thereof are acceptable.

(4) The partial ester is substantially the monoester of a polymerized carboxylic acid and glycerol or an alkylene glycol of from 2 to 5 carbon atoms. The polymerized carboxylic acid may be the same or different from that employed as ingredient (2) above. A typical acid to employ is Emery 3363-D acid. This acid is described briefly in published literature, e.g. Data Sheet No. 6A, dated Oct. 19, 1962, from Emery Industries. It is described therein as having the following properties:

Acid value	235
Saponification value	390
Percent unsaponifiable	not over 0.50
Percent ash	not over 0.70
Iodine value	11
Viscosity at 25° C. (Brookfield 29,000 cps.)	

The ratio of the glycol or glycerol and polymerized acid is preferably about a 1:1 molar; however, a ratio of between about 0.6 and 1.4 molar weights of each reactant is satisfactory.

The partial ester is prepared as follows: Glycerol or the selected glycol, e.g. ethylene glycol, are admixed in a suitable vessel and the resulting mixture to an advanced temperature of between about 250° F. and 500° F., usually between about 350° F. and 425° F., until the glycerol or glycol is between about 35% and 65%, usually between about 45% and 55%, esterified. The desired extent of esterification can be observed by weighing the amount of water produced in the reaction. Water as a byproduct of esterification is usually permitted to proceed until an amount of at least about 0.45 mole of water per equivalent of glycerol or glycol employed in the reaction mixture is formed; esterification is then considered to have progressed to a sufficient extent. Water in excess of that which is desired to remain in admixture with the partial ester formed may be removed, as explained more fully hereinafter. The unreacted acid and glycerol, present in the complex mixture, is not separated therefrom. However, the mixture, for ease of presentation, is usually referred to herein as the partial ester.

The partial ester so formed is then admixed in a suitable reaction vessel with the proper amounts of the selected monocarboxylic fatty acid and the selected polymerized acid. The resulting mixture is then admixed with the aminoethylethanolamine. The amounts of the reactants employed, by weight of the reaction mixture, are: between about 20 and about 60 percent, preferably between about 30 and about 50 percent, of the monocarboxylic acid; between about 8 and about 40 percent, preferably between 18 and 36 percent, of the polymerized acid; between about 7 and about 36 percent, preferably between 10 and 30 percent, of the previously prepared partial ester; and between about 16% and 30%, preferably between 20 and 25 percent, of aminoethylethanolamine to make 100 percent by weight of reaction mixture.

The temperature, while admixing the acids with the partial ester, is not critical so long as it is below the esterification temperature, i.e., below about 285° F. The temperature usually employed in this step is between about 100° F. and 165° F. Room temperature is quite satisfactory but results in a loss of time due to the additional waiting time thereafter necessary to raise the temperature for subsequent esterification.

Aminoethylethanolamine is then admixed with the mixture of acids and partial ester in an amount of between about 16 and about 30 percent, as above stated, based on the total weight of the reaction mixture.

It is sometimes helpful to include a small percent, e.g. 0.1 to 1.0 percent by weight, of an anti-emulsifying agent,

e.g. one of those described in U.S. Patents 2,944,978 to 2,944,985, inclusive and 2,854,427 to 2,854,429, inclusive, to De Groote or De Groote et al.

The resulting mixture, although exothermic and rising in temperature without aid of outside heat to perhaps between 125° and 225° F., is further heated to between about 300° F. and about 550° F., but usually between about 350° F. and about 510° F. until the unesterified hydroxy groups of the glycerol or glycol are substantially all reacted with the amine.

The water formed in the reaction, as desired, is then removed until an amount of water equivalent to from 2% to 10% of the total weight of the initial reaction mixture is removed. In an amount of water much in excess of about 10% by weight of the total weight of the initial charge is removed, the product shows a tendency to become undesirably viscous and even to solidify. The product so formed appears to be essentially a secondary amide containing some ester bonding. It is oil-dispersible. It shows unusual resistance to emulsification, is highly stable under extremes of temperature, and forms a film on metal surfaces with which it is brought in contact, to which it persistently adheres.

The following examples are illustrative of the preparation of the inhibitor of the corrosion of metal in accordance with the practice of the invention.

Example 1

Substantially equivalent molecular weights of the polymerized acid identified as Emery 3363D (hereinafter described) and of glycerol were admixed in a suitable vessel and heated to about 400° F. until an amount of water equal to about 0.50 mole per equivalent of glycerol in the initial reaction mixture was produced. The reaction was then discontinued. The product formed was shown to be a mixture of a partial ester and unreacted acid and glycerol.

The product so formed (referred to herein for brevity as the partial ester) was then admixed at room temperature with a dimer fatty acid identified as Empol 1022 (hereinafter described), and a tall oil fatty acid in amounts sufficient to provide the following equivalent proportions: 0.29 equivalent weight of the partial ester; 0.50 equivalent weight of the tall oil fatty acid; and 0.23 equivalent weight of the dimer acid Empol 1022. To this mixture was admixed 0.68 mole weight of aminoethylethanolamine. The resulting mixture was heated to 525° F. As water formed during the reaction, it was drawn off until 1.7 moles of water had formed and been removed. The reaction was then discontinued. The composition so made is illustrative of the corrosion inhibitor of the invention.

Example 2

Another example was performed which employed ethylene glycol instead of glycerol as follows:

One equivalent weight of ethylene glycol (31 grams/equivalent) and 1 equivalent weight of Emery 3363D acid (234 grams/equivalent) were admixed and heated at about 500° F. until 9 milliliters water were formed. This indicated 50% esterification.

0.29 equivalent weight of the partial ester so formed (75 grams), 0.50 equivalent weight of tall oil fatty acid (144 grams), and 0.232 equivalent weight of polymerized acid, known as Empol 1022 (67 grams) were admixed at about 100° F. Thereafter 0.682 equivalent weight of aminoethylethanolamine (71 grams) was admixed therewith and the resulting reaction mixture heated to about 500° F. 31 milliliters of byproduct water formed together with the reaction product during the reaction. The reaction product is representative of the corrosion inhibitor of the invention.

The inhibitor made employing either the partial ester of glycerol or of the selected glycol may be used as made, or for convenience it may be admixed with a suitable carrier, e.g. a mixture of a polar solvent (e.g. iso-

butanol) and a liquid hydrocarbon. Illustrative of the corrosion inhibitor in a suitable carrying medium of this nature is one consisting of 30% of the corrosion inhibitor, 10% to 20% isobutanol, and balance kerosene. Any other polar organic solvent may be employed in place of the isobutanol.

If there is a tendency to emulsify, a small percent of an anti-emulsifying agent may be admixed therewith.

Although kerosene or mixtures of kerosene and a polar solvent of the nature of a lower alcohol, is commonly used to disperse the corrosion inhibitor, such organic solvents as hydrocarbons generally halogenated hydrocarbons, ketones, ethers, esters, aldehydes, and aldehydes, and alcohols in general may be used.

Examples were run employing a corrosion inhibiting composition consisting of 30% by weight of the corrosion inhibitor of the invention in 20% isobutanol, 49.5% kerosene, and 0.5% anti-emulsifying agent. The anti-emulsifying agent was the reaction product of (1) an ethylene oxide and 2,3-butylene glycol acid and (2) an amine. The composition containing 30% of the active corrosion inhibitor made employing glycerol is designated hereinafter Inhibitor X and the composition containing 30% of active corrosion inhibitor made employing a glycol is designated hereinafter Inhibitor J.

For use in the tests a corrosive test brine was prepared which consisted of an aqueous solution of 10% NaCl, 0.5% CaCl₂ and 0.08% of glacial acetic acid and the solution so made then saturated with H₂S gas. A sufficient amount of the Inhibitor X prepared as described in Example 1 or Inhibitor J prepared as in Example 2 above was admixed with kerosene (previously also saturated with H₂S) as a carrying agent to yield the parts per million of the 30% Inhibitor X or J composition in the test solutions which are set out in the tables, when the kerosene containing the inhibitor is admixed with the corrosive test brine in volume proportions of between 10% and 20% kerosene plus inhibitor and between 80% and 90% corrosive brine. The brine-kerosene mixture is referred to as the test composition. The tests conducted were of two types: one to simulate the film-forming protective technique and the other to simulate the batch protective technique.

The film-forming test was carried out by first weighing and then placing steel shims 5 mils thick, 6 inches long, and 3/8 inch wide in the corrosive brine-kerosene mixture, either without inhibitor, or containing the inhibitor according to the invention and rotated therein for one hour at 122° F. (except as otherwise noted) in accordance with standard corrosion testing procedure. The tests wherein no inhibitor was employed were for comparative purposes and are sometimes designated herein blanks. The tests employing the corrosion inhibitor according to the invention thus provided a protective film on the shims. The shims so treated were thereafter removed from the brine-kerosene bath containing the corrosion inhibitor (except the blanks) and placed individually in bottles containing 90% brine and 10% kerosene mixture but which in all instances of the film-forming technique, did not contain any corrosion inhibitor. The test shims were retained therein for an additional hour at 122° F. The purpose of this second stage is to remove any excessive deposits of inhibitor from the metal surface so that the inhibition of corrosion, which is measured, is provided by the film only without aid from any inhibitor present in the test solution. The shims were then placed on a wheel rotating in an additional portion of the brine and kerosene mixture which (as in Stage 2) did not contain any added corrosion inhibitor. The purpose of the third stage is to determine the extent of protection afforded the shims by the adhering film against corrosive fluids and to make sure that all inhibition to corrosion is due to the adhering film. The shims were retained therein for 64 additional hours at a temperature of 122° F. They were thereafter removed, cleaned, washed, dried,

and reweighed and the percent protection afforded them by the protective film calculated as the percent protection by the following formula:

$$100 - \frac{\text{Wt. loss in test}}{\text{Wt. loss of blank}} \times 100 = \text{percent protection}$$

The weight loss is given to the nearest whole percent.

The batch test was conducted by merely admixing the desired amount of the 30% inhibitor composition with the brine-kerosene mixture in a vessel maintained at 122° F. and then placing previously weighed shims, of the type described above, on a continuously rotating corrosion wheel immersed therein for 64 hours, as in the film-forming test. The shims were then removed, cleaned, dried, and weighed and the percent protection calculated by the above formula.

Tests were conducted according to the above procedure in the following examples numbered 3 to 9 and the results set out in Tables I to VII. The procedure employed is identified in the table headings as either film-forming or batch. It should be borne in mind that the inhibitor employed in the examples was only 30% active so that only 30% of the p.p.m. stated is the inhibitor of the invention.

The results of the tests on the shims according to the above procedures, in the presence of the parts by weight of the corrosion inhibitor per million of the 90%-10% or 80%-20% brine-kerosene mixtures, are set out in the following tables. In all the tests, as aforesaid, p.p.m. means parts of the Inhibitor X or Inhibitor J, which, in either case, is a 30% solution of the corrosion inhibitor in 20% isobutanol-49.5% kerosene-0.5% anti-emulsifier, per million parts of the brine-kerosene mixture. Both the brine and kerosene in all tests were saturated with H₂S gas.

Table I shows the extent of corrosion of 5-mil thick steel shims in corrosive 90% brine-10% kerosene (saturated with H₂S) which had previously been treated by submergence in corrosive brine-kerosene mixture containing the amount of Inhibitor J (30% active) in parts per million to provide a protective film thereon. The weight loss is set forth in grams and the percent protection is calculated according to the formula above.

Example 3

This example employed Inhibitor J to demonstrate its inhibition to corrosion by the film-forming procedure.

TABLE I.—FILM-FORMING PROCEDURE

Amount of Inhibitor J	Weight Loss in Grams	Percent Protection
None.....	0.357	0
5000 p.p.m.....	0.0081	98
10,000 p.p.m.....	0.0077	98
20,000 p.p.m.....	0.0061	98
50,000 p.p.m.....	0.0060	98

Example 4

This example employed Inhibitor J to demonstrate its inhibition to corrosion by the batch procedure.

Table II shows the extent of corrosion of similar shims in a 90% brine-10% kerosene mixture (saturated with H₂S) containing the amount of Inhibitor J shown in the table.

TABLE II.—BATCH PROCEDURE

Amount of Inhibitor J	Weight Loss in Grams	Percent Protection
None.....	0.369	0
25 p.p.m.....	0.0452	88
50 p.p.m.....	0.0082	98
100 p.p.m.....	0.0060	99

Example 5

This example was similar to Example 4 except it employed Inhibitor X. Table III shows the protection against corrosion of a 90% brine-10% kerosene mixture (saturated with H₂S) when a film comprising Inhibitor X of the invention had been provided.

TABLE III.—FILM-FORMING PROCEDURE

Amount of Inhibitor J	Weight Loss in Grams	Percent Protection
None.....	0.2542	0
Do.....	0.2361	0
Do.....	0.2407	0
Do.....	0.2430	0
1,000 p.p.m.....	0.0042	98
2,000 p.p.m.....	0.0031	99
5,000 p.p.m.....	0.0042	98
10,000 p.p.m.....	0.0028	99
50,000 p.p.m.....	0.0039	99
100,000 p.p.m.....	0.0034	99

Example 6

This example employed Inhibitor X in a test composition comprising 80% corrosive brine and 20% kerosene (saturated with H₂S). Table IV shows the protection against corrosion of shims of the type above employed when a film comprising Inhibitor X is provided on the shims.

TABLE IV.—FILM-FORMING PROCEDURE

Amount of Inhibitor J	Weight Loss in Grams	Percent Protection
None.....	0.2793	0
Do.....	0.2684	0
1,000 p.p.m.....	0.0028	99
2,000 p.p.m.....	0.0039	98
5,000 p.p.m.....	0.0017	99
10,000 p.p.m.....	0.0040	98
50,000 p.p.m.....	0.0039	98
100,000 p.p.m.....	0.0035	99

Example 7

This example employed Inhibitor X to provide a protective film on the type of shims employed above against corrosion of a 50% brine-50% kerosene mixture (saturated with H₂S). The parts by weight of Inhibitor X per million parts of the brine-kerosene mixture are set out together with the weight loss and the percent protection as in the preceding tables.

TABLE V.—FILM-FORMING PROCEDURE

Amount of Inhibitor X	Weight Loss in Grams	Percent Protection
None.....	0.2902	0
1,000 p.p.m.....	0.0050	98
2,000 p.p.m.....	0.0029	99
5,000 p.p.m.....	0.0037	99
10,000 p.p.m.....	0.0056	98
50,000 p.p.m.....	0.0051	98
100,000 p.p.m.....	0.0062	98

Example 8

This example shows the effect of the temperature of the corrosive mixture. Table VI sets out the results obtained by providing a protective film on shims of the type employed above, at 175° F., against corrosion of a 90% brine-10% kerosene mixture (saturated with H₂S). For ease of comparison of the percent protection obtained in Example 6 and shown in Table III at 122° F. have been set out again in Table VI below, together with the results obtained at 175° F.

TABLE VI.—FILM-FORMING PROCEDURE

Amount of Inhibitor X	Percent Protec- tion at 122°	Wt. Loss in Grams	Percent Protec- tion at 175°
None.....	0	0.2055	0
1,000 p.p.m.....	98	0.0095	95
2,000 p.p.m.....	99	0.0085	96
5,000 p.p.m.....	98	0.0063	97
10,000 p.p.m.....	98	0.0047	98
50,000 p.p.m.....	99	0.0054	97
100,000 p.p.m.....	98	0.0039	98

Example 9

This example was run to show the protection afforded by employing Inhibitor X by the batch method. It was added directly to a 90% brine-10% kerosene mixture (saturated with H₂S) and the shims slowly rotated therein at 122° F. for 64 hours. Table VII shows the results.

TABLE VII.—BATCH TEST PROCEDURE

Concentration	Wt. Loss in Grams	Percent Protection
None.....	0.313	0
10 p.p.m.....	0.0428	86
25 p.p.m.....	0.0060	98
50 p.p.m.....	0.0031	99
100 p.p.m.....	0.0037	99

Reference to the results of Examples 3 and 5 to 8 show the high extent of protection afforded against the corrosion of a highly corrosive brine-kerosene mixture at advanced temperatures by merely providing a protective film of the inhibitor of the invention. Reference to Examples 4 and 9 shows that a very small amount of the inhibitor of the invention added directly to the corrosive brine-kerosene mixture (as opposed to providing a protective film thereon) gave excellent protection.

The relative advantages of the film-forming procedure and the batch procedure are that the former gives more lasting protection without having the inhibitor present in the corrosive liquid whereas the batch procedure, although requiring a relatively small amount of inhibitor, must be added at rather frequent intervals where the corrosive fluid in contact with the metal is changing as in a producing gas or oil well or in a transfer line.

The inhibitor of the invention lends itself well to all known techniques of corrosion inhibition employing an inhibitor in a liquid carrier including corrosion squeeze treatment, batch treatment, or extended batch treatment, each of which is explained more fully immediately following.

Squeeze treatment may be illustrated as follows: The active inhibitor is diluted to 5 to 10% by weight in a liquid diluent, i.e. kerosene or diesel oil and the so diluted solution is injected down a wellbore penetrating a subterranean formation and forced back into the formation. The pressure is then released and the well put into production. The so emplaced corrosion inhibitor gradually finds its way, over a prolonged period, into the oil or gas being produced. This method has been found especially effective in high pressure gas wells. Such treatments employing the composition of the invention have been effective for six months or more.

Batch treatment may be illustrated as follows: The active inhibitor, either diluted, e.g. 5 or 10% by weight, or more concentrated, e.g. 20-40% by weight, in a liquid hydrocarbon is put into the annulus of a cased wellbore provided with a tubing. The well is then put back into production and the inhibitor present in the annulus gradually mixes with the oil being produced, via the tubing. One variation of the batch method is to put the inhibitor in the tubing and close the well for a short time. A modification of tube injection is to drop capsules or solid sticks of inhibitor down the tubing where it disperses into the oil. The frequency of the treatments depends upon circumstances but a week or two weeks are common interims between batch treatments of this type.

An extended batch treatment may be illustrated by proceeding as in the batch treatment, but, after putting the inhibitor in the annulus, the well is closed off and the inhibitor solution is circulated by means of a pump, down the annulus and up the tubing for an extended period of time.

Although, treatments to provide protection against corrosion of well equipment are preferably carried out by dispersing the inhibitor in a suitable organic solvent, it may be injected down a producing well and mixed with the oil of the producing strata. When there is appreciable water being produced with the oil, wherein emulsions tend to form, the use of anti-emulsifying agents is recommended.

Example 10

The following example illustrates the practice of the invention.

Forty-eight gas wells in a producing field in Refugio County, Tex., were causing extensive trouble due to cor-

rosion of the metal parts of equipment in use in the wells. Analysis of condensate of the condensate recovered from gas from the wells showed an average of 200 parts of iron per million parts by weight of gas being produced.

Each of these wells was treated according to the invention as follows: The well was substantially empty of liquid when treated, except for the possibility of a small amount of water that may have seeped into it. Inhibitor X, i.e. 30% active inhibitor in 20% isobutanol-80% kerosene, was dissolved in crude oil being produced elsewhere on the lease in the formation in proportions of 5 gallons of Inhibitor X per 45 gallons of crude oil. The resulting composition was injected down the well and back into the formation at sufficient pressure to force at least some of the inhibitor well back into the formation. After treatment, the gas produced was again analyzed. The condensate of gas from no well was found to contain more than 5 parts of iron per million parts by weight of gas produced. It may have been considerably less but the field testing apparatus was not designed to measure less than 5 p.p.m. An increase in iron content of the produced gas was measurable after a few weeks. The wells were provided with continued protection by retreating them thereafter at one-month intervals.

The field treatment shows conclusively the value of the composition and method of the invention to inhibit corrosion of metal parts.

Having described my invention what I claim and desire to protect by Letters Patent is:

1. A composition having inhibiting effect on the corrosive attack of fluids on metals consisting essentially of the reaction product prepared by reacting, at a temperature of between about 300° F. and 550° F., a mixture comprising, by weight, to make a total of 100%: (a) between about 20% and about 60% of a monocarboxylic acid selected from the class consisting of fatty acids and rosin acids and having from about 10 to about 24 carbon atoms per molecule; (b) between about 8% and about 40% of a polymerized acid consisting essentially of dimerized unsaturated monocarboxylic fatty acids having from about 10 to about 24 carbon atoms per repeating unit; (c) between about 7% and about 36% of a reaction mixture comprising a partial ester formed by reacting, at above esterification temperature, a mixture consisting of between a 0.6 and 1.4 molar ratio of each of (1) a polyhydroxy compound selected from the class consisting of alkylene glycols having from 2 to 5 carbon atoms per molecule, and glycerol and (2) a polymerized monocarboxylic acid consisting essentially of dimerized unsaturated fatty acids having from about 10 to about 24 carbon atoms per repeating unit until esterification has proceeded to between about 45% and 65% of completion, and unreacted polyhydroxy compound and acid; and (d) between about 16% and about 30% of aminoethylethanolamine.

2. The composition of claim 1 wherein the molar ratio of the polyhydroxy compound and the polymerized monocarboxylic acid reaction mixture of ingredient (c) is about 1:1 molar; wherein said carboxylic acid of ingredient (a) is tall oil fatty acid; and wherein the dimerized acids of ingredient (b) consist essentially of a C₃₆ acid made by dimerizing a monocarboxylic unsaturated fatty acid having an average of 18 carbon atoms per molecule.

3. The composition of claim 1 wherein the partial ester of ingredient (c) is the reaction product of glycerol and a polymerized monocarboxylic acid having the following properties:

acid value of about 235,
saponification value of about 390,
percent unsaponified of not over 0.50,
percent ash of not over 0.70,
iodine number of about 11, and
viscosity at 25° C. (Brookfield) of about 29,000 cps.

4. The composition of claim 1 wherein the weight proportions of the ingredients are, by weight, between 30%

and 50% of tall oil fatty acid; between 18% and 36% of a dimerized unsaturated C₁₈ monocarboxylic acid; between about 10% and 30% of the reaction mixture comprising the partial ester; and between 20% and about 25% of aminoethylethanolamine.

5. The composition of claim 4 wherein the ingredients are employed in the following proportions:

about 0.50 equivalent weight of the tall oil fatty acid;
about 0.23 equivalent weight of the dimerized monocarboxylic fatty acid;
about 0.29 equivalent weight of the reaction mixture comprising the partial ester;
about 0.68 mole weight of aminoethylethanolamine.

6. The method of inhibiting corrosion of iron and steel due to contact therewith of a hydrocarbon fluid containing corrosive ingredients said method consisting essentially of admixing with said fluid at least about 1 part, by weight of the composition of claim 1, per million parts of the fluid.

7. The method of inhibiting corrosion of iron and steel due to contact therewith of a hydrocarbon fluid containing corrosive ingredients, said method consisting essentially of admixing at least 1 part, by weight of the composition of claim 2, per million parts of said fluid.

8. The method of inhibiting corrosion of iron and steel due to contact therewith of a hydrocarbon fluid containing corrosive ingredients, said method consisting essentially of admixing at least 1 part, by weight of the composition of claim 3, per million parts of said fluid.

9. The method of inhibiting the corrosion of iron and steel due to contact therewith of a hydrocarbon fluid containing corrosive ingredients, said method consisting essentially of admixing the composition of claim 1, having inhibiting effect on corrosive attack, with an organic carrier liquid selected from the class consisting of hydrocarbons and polar solvents to make a fluid composition and contacting said metal with said composition to provide a protective film thereon.

10. The method according to claim 9 wherein said fluid composition contains at least about 100 parts of said composition per million parts of said fluid.

11. The method of inhibiting corrosion of downhole metal parts of equipment in a wellbore used in the production of a fluid mineral from a subterranean formation which consists of injecting down the borehole and into contact with said fluid the composition of claim 1.

12. The method according to claim 11 wherein said composition is dissolved in an organic carrier liquid and thereafter injected down the borehole at sufficient pressure to force it back into the formation and to retain a portion thereof therein from whence it slowly leaches out and into the fluid mineral during production thereof.

13. The method according to claim 12 wherein said organic carrier liquid is a mixture of an organic polar solvent and a liquid hydrocarbon.

14. The method according to claim 13 wherein said organic polar solvent is isobutanol and said hydrocarbon liquid is kerosene, each being present in an amount of between 10 and 90 percent by weight to make a total of 100%.

15. The method according to claim 13 wherein said organic carrier liquid contains a small but effective amount of an anti-emulsifying agent.

References Cited

UNITED STATES PATENTS

2,763,612	9/1956	Raifsnider et al.	252—8.55
2,888,401	5/1959	Hughes et al.	252—8.55
2,941,943	6/1960	Kirkpatrick et al.	252—392 X
2,976,245	3/1961	Copes	252—396 X

LEON D. ROSDOL, *Primary Examiner*.

H. B. GUYNN, *Assistant Examiner*.