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CORROSION PREVENTION IN OIL WELLS

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This invention relates to corrosion prevention and in particular concerns compositions and methods for preventing corrosion in oil wells.

In many of the oil-producing areas of the United States the production of crude oil is accompanied by the production of aqueous brines containing dissolved carbon dioxide and/or hydrogen sulfide. Such brines are highly corrosive with respect to ferrous metals, and are responsible for frequent failures of metallic equipment associated with the well, e. g., the well tubing, sucker rods and sucker rod boxes, pump parts, gathering lines, tanks, etc. In numerous instances the corrosion damage is so severe as to require replacement of sucker rods and pump parts as often as once a month and replacement of at least part of the tubing string as often as once a year. The cost of such replacement, together with the cost of constant inspection and the loss in oil production during the frequent periods when the well is shut down for inspection and replacement, is a major factor in the cost of the oil produced. Among those who have been most closely associated with the problem of preventing corrosion in oil and gas wells it is generally conceded that the most satisfactory solution lies in the use of chemical corrosion inhibitors which can be introduced directly into the well and admixed with the well fluids before the latter can come into substantial contact with metallic well equipment.

Among the wide variety of materials which have been suggested for use as corrosion inhibitors in this manner are the reaction products of fatty acids with alkanolamines, e. g., the reaction products of such acids as oleic, ricinoleic, linoleic, linolenic, and stearic acids with such alkanolamines as triethanolamine, di-isopropanolamine, tributanolamine, etc. These products, however, do not provide satisfactory control of corrosion in deep wells where elevated temperatures of the order of 80°–120° C. normally prevail.

It is accordingly an object of the present invention to provide improved means for preventing corrosion in wells.

Another object is to provide means for preventing corrosion induced by oil well brines in the presence of carbon dioxide and/or hydrogen sulfide at the moderately elevated temperatures and pressures which exist within relatively deep wells.

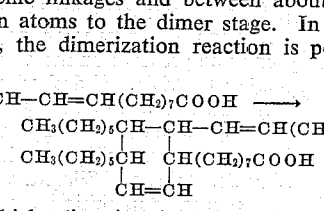
A further object is to provide improved corrosion inhibitors for use in oil wells and the like.

Other and related objects will be apparent from the following detailed description of the invention, and various advantages not specifically referred to herein will be apparent to those skilled in the art upon employment of the invention in practice.

I have now found that the above objects and attendant advantages may be realized through the provision and use of corrosion inhibiting compositions comprising as the essential active ingredient a tertiary amino ester of a dimerized fatty acid. More particularly, I have found that the lower alkanolamine esters of dimerized fatty acids

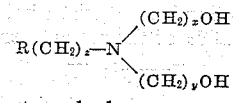
can be dissolved or dispersed in well fluids to inhibit the corrosion of ferrous metals thereby to a remarkable extent even under exceptionally adverse conditions of temperature and pressure. Such esters are effective in very small amounts, and may be introduced directly into the well bore as such. However, they are usually more conveniently employed as solutions in petroleum hydrocarbon or other suitable solvents. As is hereinafter more fully explained, they may be advantageously employed in conjunction with dispersing agents adapted to promote uniform dispersion in both the aqueous and oil phases of the well effluent.

The term "dimerized fatty acid" is employed herein and in the chemical art to designate a class of dibasic acids formed by polymerizing fatty acids containing at least two ethylenic linkages and between about 16 and about 22 carbon atoms to the dimer stage. In the case of linoleic acid, the dimerization reaction is postulated as follows:



Other acids which dimerize in this manner include linoelaidic, linolenic, licanic, arachidonic, clupanodonic, eleostearic, etc. In general, the polymerization is carried out simply by heating the monomeric acid at an elevated temperature, e. g., above about 250° C., while avoiding decarboxylation and cracking. U. S. Patent No. 2,482,761 gives further details. A typical dimerized fatty acid of this type is available commercially from Emery Industries, Inc. under the trade name "Emery 955 Dimer Acid," and because of its avilability is preferred in preparing the present class of corrosion inhibitors. Such product is obtained by dimerizing linoleic acid obtained from vegetable oils, e. g., soya oil, linseed oil, corn oil, etc., and is a viscous liquid containing about 85% of dilinoleic acid, about 12% of trilinoleic acid and about 3% of the monomer. It has a molecular weight of about 600 and an acid value of about 180–192, and is insoluble in water but soluble in alcohol, ether, benzene, acetone, and petroleum hydrocarbons.

The alkanolamines which are esterified with the above-described dimerized fatty acids are characterized by containing a tertiary nitrogen atom and at least 2 alkanol groups, and may be represented by the generic formula:



where R represents a hydrogen atom or an hydroxyl group, and x, y and z each represents an integer between 2 and 6. The class thus includes alkyl dialkanolamines such as ethyl diethanolamine, propyl diethanolamine, ethyl di-n-propanolamine, n-butyl di-isoamylamine, etc., and trialkanolamines such as triethanolamine, tri-isopropanolamine, tri-tert.butanolamine, tri-n-hexanolamine, di-ethanol-mono-propanolamine, etc. Triethanolamine is preferred.

The esterification reaction is carried out in the conventional manner, i. e. by heating a mixture of the alkanolamine and dimerized acid at a suitable reaction temperature while removing water from the system. If desired, an esterification catalyst such as benzenesulfonic acid may be employed. Usually the reaction proceeds smoothly at temperatures between about 230° F. and about 340° F. and is complete in from about 2 to 6 hours. At temperatures above about 340° F. insoluble polymers are formed, and accordingly it is preferred to operate at a temperature between about 270° F. and about 320° F.

Completion of the reaction is determined either by measuring the water evolved or by determining the acid value of the product. In order to suppress oxidation, the reaction is preferably carried out in an inert atmosphere, and since the reaction mixture and ester product are relatively viscous an inert reaction solvent may be advantageously employed. Relatively high-boiling aromatic petroleum hydrocarbons, e. g., kerosene extract, are preferred for such purpose since they conveniently serve as vehicles for the hereinafter described inhibitor compositions, although other solvents may be employed if desired.

The alkanolamine esters which form the present class of corrosion inhibitors are relatively light-colored viscous liquids having the general chemical properties of mono- or di-esters depending upon the quantity of alkanolamine employed for the esterification. Both the mono- and di-esters have corrosion inhibiting properties, and either may be employed as a corrosion inhibitor in accordance with the invention, although the mono-ester is usually preferred. Accordingly, in carrying out the esterification reaction the alkanolamine and dimerized acid reactants may be provided in mole proportions varying from about 1/1 to 0.5/1. If desired, the reaction solvent may be separated from the ester product by distillation, but it is usually more convenient to allow the solvent to remain with the ester to facilitate its handling.

The following examples will illustrate the preparation of several of the corrosion inhibiting esters of the present class but are not to be construed as limiting the invention. All proportions are given in parts by weight.

Example I

Approximately 40 parts (0.066 mole) of dimerized linoleic acid ("Emery 955 Dimer Acid"), 5 parts (0.033 mole) of triethanolamine, and 36 parts of kerosene extract (boiling range 400°–600° F.) were charged to an oil-jacketed kettle and heated at 320° F. with stirring for about 6 hours by circulating hot oil through the jacket. During the heating the surface of the reaction mixture was blanketed with nitrogen. Upon completion of the reaction, as indicated by approximately the theoretical reduction in the acid value of the mixture, the product was cooled and stored without removal of the solvent. The yield was approximately 70 parts.

Example II

The preparation of Example I was repeated, employing an equimolecular amount (0.066 mole) of the triethanolamine and heating at 275°–325° F. for 6 hours. The product obtained resembled that of Example I in appearance, but was somewhat more viscous and had a saponification value indicating it to consist of about 80% of the diester and about 20% of the mono-ester.

Example III

Example II was repeated employing a reaction temperature of about 350° F. in an attempt to shorten the time required to complete the reaction. After 2 hours' heating the reaction mixture became an insoluble polymeric gel, indicating that at such high reaction temperature the predominant reaction is one of polymerization.

In treating a well to inhibit corrosion therein in accordance with one embodiment of the invention, the inhibitor is simply introduced into the well fluid via the well tubing or casing in an amount sufficient to effect a substantial degree of corrosion inhibition. Such amount will depend primarily upon the nature of the well fluid and the temperatures and pressures prevailing within the well, but highly satisfactory results are usually obtained, even under exceptionally adverse conditions, when the weight of inhibitor in the well is maintained between about 0.001 and about 0.01 percent of the weight of the fluid in the well. As previously stated, the inhibitors of the present class are most conveniently employed in the form of a solution in a suitable solvent.

According to a preferred embodiment of the invention, the inhibitors of the present class are employed in conjunction with one or more dispersing agents which may or may not have corrosion inhibiting properties of their own. The primary purpose of such agents is to promote uniform dispersion of the inhibitor in the well fluid, and since such fluid comprises both water or brine and oil, the dispersing agents may be either water- or oil-soluble, or both. A mixture of two or more types of dispersing agents may also be employed. A wide variety of both types of dispersing agents are known and any of them may be employed in preparing corosion inhibiting compositions comprising the present class of esters as the essential active ingredient. Oil-soluble sulfonic acids, such as the petroleum sulfonic acids, and the salts thereof, and non-ionic dispersing agents such as the Spans and Tweens and the fatty acid amides are preferred. Compositions of this type ordinarily comprise between about 5 and about 20 percent by weight of the ester inhibitor, and between about 70 and about 90 percent by weight of a solvent for the ester, with the remainder being made up by one or a mixture of dispersing agents. The composition may also contain scale inhibitors such as the polyphosphates and scale-inhibiting acids.

The following examples will illustrate typical corrosion inhibiting compositions provided by the invention, but are not to be construed as limiting the same:

Example IV

	Parts by weight
Mono-triethanolamine ester of dimerized linoleic acid	10
Kerosene extract (B. R.=400–600° F.)	80
Sodium petroleum sulfonate	8
Sorbitan tri-oleate (Span 80)	2

Example V

Di-(mono-ethyl-di-n-propanolamine) ester of dimerized linolenic acid	20
Kerosene extract (B. R.=400–600° F.)	78
Sorbitan tri-oleate (Span 80)	2

Example VI

Di-tri-isobutanolamine ester of dimerized linoleic acid	2
Toluene	82
Castoramide	5
Sodium petroleum sulfonate	5

Example VII

Mono-tri-n-propanolamine ester of dimerized eleostearic acid	25
Kerosene extract (B. R.=400–600° F.)	70
Tween 20	3
Castoramide	2

Example VIII

Mono-triethanolamine ester of dimerized linoleic acid	8
Kerosene extract (B. R.=400–600° F.)	80
Sodium salt of alkylated benzene sulfonic acid	8
Castoramide	4

Example IX

Mono-triethanolamine ester of dimerized linoleic acid	5
Benzene	90
Diethylene glycol mono-stearate	5

In the above examples, the term "castoramide" designates the reaction product of castor oil fatty acids or castor oil itself with diethanolamine.

In testing various materials to determine their corrosion inhibiting properties, I have found that test procedures which are carried out at ordinary temperatures and pressures do not reflect accurately the behavior of the test composition in a well. Thus, inhibitors which appear satisfactory when tested by adding the same to an oil well brine and thereafter contacting the inhibited brine with metal strips at atmospheric temperatures and pressures often prove unsatisfactory when placed in an actual well.

Accordingly, I have employed the following rigorous testing method which has been found to simulate actual well conditions to a high degree: Two 6-inch lengths of steel sucker rod are polished with emery, washed, and accurately weighed. These test specimens are then mounted side-by-side on the head of a 4-liter rocking autoclave. Two hundred ml. of kerosene containing 2 drops of the corrosion inhibitor to be tested are then introduced into the autoclave, and the head is bolted on. The autoclave is then purged with carbon dioxide to remove free air. Three and one-half liters of 3% aqueous sodium chloride from which dissolved air has been removed by purging with carbon dioxide are then introduced into the autoclave, and the latter is pressured up to about 20 p. s. i. g. with carbon dioxide. The simulated well fluid in the autoclave thus contains about 30 p. p. m. of the corrosion inhibitor being tested. Kerosene is employed as the hydrocarbon phase of the simulated well fluid since it is not known to contain any of the naturally-occurring corrosion inhibitors which are present in some crudes. The autoclave and the contents are heated at 100–110° C. under an autogenous pressure of about 70 p. s. i. g. for 24 hours. Upon completion of the heating period the autoclave is cooled to atmospheric temperature and opened, and the test specimens are removed, washed, and weighed. The efficiency of the inhibitor is calculated as follows:

$$\text{Efficiency} = \frac{W_1 - W_2 \times 100}{W_1}$$

where W_1 is the loss in specimen weight (total of both specimens) with an uninhibited fluid and W_2 is the loss in specimen weight (total of both specimens) with the inhibited fluid.

The following table sets forth the results obtained when several of the present corrosion inhibitors and compositions were tested in accordance with the foregoing procedure:

Composition No.	1	2	3	Blank
Product of Example I, Percent	100	20		0
Kerosene Extract (B. R.=400-600° F.), Percent		70	70	0
Span 80, Percent		4	4	0
Sodium petroleum sulfonate, Percent		4	4	0
Castoramide,[1] Percent		2	2	0
Product of Example II, Percent			20	0
Change in Wt., mgs.	−34.2	−0.9	+0.3	−800
Efficiency, Percent	96	99.9	100.0	0

[1] Reaction product of castor oil fatty acids and diethanolamine.

Composition No. 2 was introduced into a deep well near Sinton, Texas, in such amount as to provide approximately 50 parts of the active ingredient per million parts of well fluid, and such concentration was maintained by the daily addition of about 2 quarts of the composition down the well tubing. Prior to addition of the composition the well effluent contained about 60 p. p. m. of iron. With the composition in the well, the iron content of the effluent dropped to about 5 p. p. m. and has remained at such value for about 4 months.

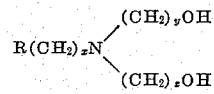
Composition No. 3 was introduced into three wells in Southern California. One of these wells originally had an iron count (p. p. m. of iron in the well effluent) of about 65, but had been treated with a commercial inhibitor whereby the iron count was reduced to about 20–35 p. p. m. After treatment with Composition No. 3 the iron count dropped to about 1.5 p. p. m. and has been maintained at this value for over two months by the daily addition of about 1 quart of the composition to the well. The other two wells had iron counts of about 25 and about 65 p. p. m., respectively. In both cases, treatment with Composition No. 3 reduced the iron count to about 2 p. p. m.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the materials and methods employed,

provided the compositions or steps stated by any of the following claims, or the equivalent of such stated compositions or steps, be obtained or employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. A corrosion inhibiting composition for use in oil wells comprising a solution of an ester of a dimerized polyunsaturated fatty acid containing from 16 to 22 carbon atoms and an alkanolamine having the general formula:



wherein x, y and z each represents an integer between 2 and 6, inclusive, and R represents a substituent selected from the class consisting of hydrogen and hydroxyl, in an organic solvent.

2. A composition according to claim 1 wherein the ester is a di-ester.

3. A composition according to claim 1 wherein the ester is a mono-ester.

4. A composition according to claim 1 containing sufficient of a dispersing agent to effect dispersion of the said ester in well fluids.

5. A corrosion inhibiting composition for use in oil wells comprising a solution of a trialkanolamine ester of a dimerized polyunsaturated fatty acid containing from 16 to 22 carbon atoms, the alkyl groups of said trialkanolamine each containing from 2 to 6 carbon atoms, in an organic solvent.

6. A composition according to claim 5 wherein the trialkanolamine is triethanolamine.

7. A composition according to claim 5 wherein the dimerized fatty acid is dilinoleic acid.

8. A composition according to claim 5 wherein the said ester is the di-triethanolamine ester of dilinoleic acid.

9. A composition according to claim 5 wherein the said ester is the mono-triethanolamine ester of dilinoleic acid.

10. A corrosion inhibiting composition for use in oil wells comprising between about 5 and about 20 percent by weight of a trialkanolamine ester of a dimerized polyunsaturated fatty acid containing from 16 to 22 carbon atoms, the alkyl groups of said trialkanolamine each containing from 2 to 6 carbon atoms, between about 70 and about 90 percent by weight of an organic solvent for said ester, and the remainder comprising a dispersing agent for dispersing said ester in well fluids.

11. A composition according to claim 10 wherein the said dispersing agent is a mixture of a petroleum sulfonate and a non-ionic dispersing agent.

12. A composition according to claim 10 wherein the said ester is the mono-triethanolamine ester of dilinoleic acid.

13. A composition according to claim 10 wherein the said ester is the di-triethanolamine ester of dilinoleic acid.

14. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 1.

15. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 5.

16. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 7.

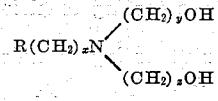
17. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 9.

18. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 10.

19. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 11.

20. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of the composition defined by claim 12.

21. The method for reducing the corrosiveness of oil and gas well fluids towards ferrous metals which comprises admixing with said fluids a corrosion inhibiting amount of an ester of a dimerized poly-unsaturated fatty acid containing from 16 to 22 carbon atoms and an alkanolamine having the general formula:



wherein x, y and z each represents an integer from 2 to 6 and R represents a substituent selected from the class consisting of hydrogen and hydroxyl.

22. A method according to claim 21 wherein the said ester is a trialkanolamine ester of a dimerized poly-unsaturated fatty acid containing from 16 to 22 carbon atoms, the alkyl groups of said trialkanolamine each containing from 2 to 6 carbon atoms.

23. A method according to claim 21 wherein the dimerized fatty acid is dilinoleic acid.

24. A method according to claim 21 wherein the said ester is the mono-triethanolamine ester of dilinoleic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,520,356	Bishop	Aug. 29, 1950
2,614,980	Lytle	Oct. 21, 1952
2,614,981	Lytle	Oct. 21, 1952
2,646,399	Hughes	July 21, 1953