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CORROSION INHIBITION

John G. Milligan, Austin, Tex., assignor to Jefferson Chemical Company, Inc., Houston, Tex., a corporation of Delaware

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16 Claims. (Cl. 252—8.55)

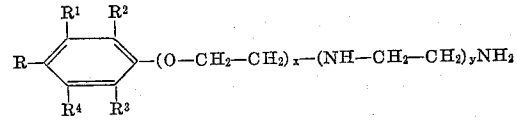
The instant invention pertains to inhibiting the corrosion of metals in contact with corrosive substances. More particularly the invention relates to inhibiting the corrosivity of petroliferous well fluids containing carbon dioxide or hydrogen sulfide brines to corrodible metal conduits and attendant equipment through which the fluids are flowed and processed. In addition, the invention relates to the control of sulfate-reducing bacteria, *Desulfovibrio desulfuricans*, in petroleum recovery systems.

In oil and gas condensate fields the production of fluids from subsurface formations is often accompanied by extremely severe corrosion of corrodible metal apparatus which is contacted by the fluid mixture produced. In some instances it is found the fluid contains substantial amounts of carbon dioxide to form carbonic acid. These fluids are classified by the petroleum art as "sweet." In other cases the fluid includes sulfide brine which may contain alkali metal sulfide, alkaline earth metal sulfide and acid sulfide such as hydrogen sulfide and/or organic sulfides. Those brines containing hydrogen sulfide are especially corrosive to iron and steel equipment for the hydrogen sulfide attacks the metal to form the iron sulfides. The hydrogen sulfide containing petroliferous fluids are generally designated as "sour." Since the aforementioned corrosive materials occur in or are introduced into the fluids originating in subsurface formations, corrosion may occur throughout the metal apparatus through which the fluids are flowed and produced. In other instances corrosion may be more or less localized to a specific area of the metallic apparatus. Corrosion whether intensive or extensive if permitted to continue unabated will damage the equipment which contacts the corrosive petroliferous fluid and may damage this equipment to such an extent as to require a replacement.

In addition to the corrosion caused by chemical substances such as hydrogen sulfide and carbon dioxide, corrosion is also caused by living organisms such as sulfate-reducing bacteria. Sulfate-reducing bacteria are frequently found in petroliferous fluid producing formations and accentuate the corrosion action of the petroliferous fluids in that the sulfate-reducing bacteria give off large quantities of corrosive hydrogen sulfide which is absorbed by the petroliferous fluid which, in turn, contacts the corrodible metals of the producing apparatus. As a further complication, these sulfate-reducing bacteria often multiply in petroliferous produicng formations to such an extent as to cause a serious plugging of the pores of the producing formations with the resultant decrease of flow of fluid from said formation.

The primary object of my invention is to provide a method of substantially inhibiting corrosion of corrodible ferrous metals by corrosive well fluids. Another object is to provide corrosion inhibited well fluid compositions. Still another object is to reduce the plugging by sulfate-reducing bacteria of oil and gas field producing formations.

In accordance with the objects of the present invention the corrosion of corrodible ferrous metals by corrosive well fluids containing brine, carbon dioxide, sulfides and/or sulfate-reducing bacteria is eliminated or substantially reduced by introducing or incorporating in the corrosive well fluids a corrosion inhibiting amount of an N-substituted polyamine of the structural formula



where R is an alkyl radical having from 6 to 12 carbon atoms and R^1, R^2, R^3 and R^4 are the same or different radicals selected from the group consisting of hydrogen and an alkyl group having from 1 to 3 carbon atoms, where x is an integer from 1 to 4 inclusively and where y is an integer from 1 to 3 inclusively. Specific examples of the N-substituted polyamines contemplated herein are p-nonylphenoxyethoxyethyl ethylenediamine, p-nonylphenoxyethoxyethyl diethylenetriamine, p-hexylphenoxyethyl ethylenediamine, p-dodecylphenoxyethoxyethoxyethyl triethylenetetraamine and p-isodecyl-m-methylphenoxyethyl diethylenetriamine.

The N-substituted polyamines may be introduced into corrosive well fluids in amounts in the range of between 10 and 500 p.p.m. (parts per million by weight), preferably between 20 and 150 p.p.m. based on the weight of the well fluid.

The polyamine inhibitors may be added to systems to be protected in undiluted form. However, for more accurate control of inhibitor concentration and to insure proper mixing with the corrosive fluids, petroleum oil solutions containing from about 10 to 70 wt. percent of the inhibitor are preferably employed. Although the use of petroleum oil as a carrier is the most economical, other carriers may be employed such as kerosene, benzene and ethyl alcohol.

The corrosive fluids while including carbon dioxide, hydrogen sulfide, acetic acid, propionic acid and other organic acids as well as the inorganic sulfide salts and sulfate-reducing bacteria may also include the mineral acids such as hydrochloric and sulfuric acids. The corrosive action of these mineral acids is also inhibited by the N-substituted polyamines contemplated herein.

In employing the polyamine corrosion inhibitor and bactericide in the method and composition of the present invention, the polyamine may be introduced into the corrosive fluid and allowed to come into contact with the ferrous metal surfaces and/or reservoir formations containing the corrosive fluids.

When the polyamines contemplated herein are employed to protect ferrous metal oil and gas well equipment from attack by corrosive well fluids, the polyamine may be suitably introduced into the annulus between the casing and the tubing string and thence introduced into said tubing string adjacent to the lower end thereof as the corrosive well fluid is produced up the tubing. Distribution of the inhibitor throughout the well fluid producing system can be aided by introducing the inhibitor into part of the produced well fluid and recommitting this inhibited part into the well system through the annulus between the tubing string and well casing. It is also contemplated in the practice of the present invention that the polyamine inhibitor may be introduced into an injection well and admixed with the corrosive well fluid in the subsurface reservoir adjacent the well formation from which the corrosive fluid is being produced.

It is also contemplated that the polyamines of the invention may be used in so called permanent well completion techniques to protect exposed surfaces of ferrous metal casings located below the open end of a tubing string permanently located in the casing above the uppermost of a series of hydrocarbon productive intervals. The polyamine inhibitor may be suitably introduced from the annulus formed by the well casing and tubing string

and directed downwardly from the lower open end of the tubing in the casing and then caused to flow upwardly in the tubing string by increasing the effective length of the tubing utilizing a tubular member to extend from the lower open end of the tubing to the point where the corrosive fluid enters the casing through the perforations.

It is contemplated in the practice of the present invention that the polyamine inhibitor may also suitably be introduced into the well head equipment as the hydrocarbons are produced, to protect flow lines and lease tanks and the like which are exposed to corrosive well fluids.

The corrosive well fluids may comprise both light and heavy hydrocarbons such as condensate including gaseous hydrocarbons and gasoline components as well as crude oils which contain bacteria and brine saturated with hydrogen sulfide and/or carbon dioxide.

The following examples further illustrate my invention:

EXAMPLE I

This example illustrates the preparation of the polyamines contemplated herein. More specifically it recites a means of preparing p-nonylphenoxyethoxyethyl ethylenediamine.

A mixture of 2290 grams of bis(2-chloroethyl)ether, 440 grams of p-nonylphenol and 92 grams of sodium hydroxide was stirred at 135° C. for 1 hour. During this time some water distilled off and a small amount of foam appeared on the solution. The mixture was then stirred with 300 grams of water at 70° C. until all of the by-product salt (NaCl) was dissolved. The aqueous and organic layers were separated by decantation and the organic layer was fractionally distilled under reduced pressure. During the distillation of the organic layer 510 grams of p-nonylphenoxyethoxyethyl chloride was collected at 199–202° C. at 5 millimeters Hg pressure absolute.

A mixture of 327 grams of p-nonylphenoxyethoxyethyl chloride (produced above), 607 grams of 79 wt. percent aqueous ethylenediamine, 80 grams of butanol solvent and 40 grams of sodium hydroxide was stirred at 103° C. for 30 minutes. The liquid reaction mixture was then decanted from the precipitated sodium chloride by-product. The decanted liquid separated into two distinct layers. The upper layer was freed of the butanol solvent by distillation leaving 340 grams of crude product. The crude product was fractionally distilled and 290 grams of p-nonylphenoxyethoxyethyl ethylenediamine were collected at 206–231° C. under 1.5 millimeters Hg pressure absolute. This product is a mobile yellow colored liquid.

In addition to the preparation of the diamine p-nonylphenoxyethoxyethyl diethylenetriamine was also prepared substantially utilizing the above described procedures except that diethylenetriamine was substituted for ethylenediamine. The p-nonylphenoxyethoxyethyl diethylenetriamine was left as the residue after the diethylenetriamine was stripped off under reduced pressure.

EXAMPLE II

This example illustrates the corrosion inhibiting properties of the polyamines contemplated herein.

The corrosion test simulated corrosion of oil well producing equipment and was conducted in 4-ounce polyethylene bottles fitted with polyethylene caps. Simulated corrosion conditions were effected by preparing a treated mixture of brine and oil for the bottles. 90 milliliters of brine solution which was prepared from sodium chloride, calcium chloride and distilled water were added to each bottle. The brine contained 10 wt. percent sodium chloride and 0.5 wt. percent calcium chloride. 10 milliliters of a 36–38° API gravity oil from a mineral base petroleum crude source were also added to each of the polyethylene bottles. This mixture was then saturated for 5 minutes with either hydrogen sulfide (to simulate sour well fluids) or carbon dioxide (to simulate sweet well fluids). The hydrogen sulfide and carbon dioxide

gases were introduced into the oil-brine mixtures through a fritted glass dispersion tube of medium porosity. After saturation with hydrogen sulfide or carbon dioxide, 1 milliliter of 6 wt. percent aqueous acetic acid and a cleaned, weighed metal test coupon were added to each test bottle and the system was closed for testing. In those instances in which the effectiveness of an inhibitor was to be determined the inhibitor was added to the oil-brine mixture prior to saturation with hydrogen sulfide or carbon dioxide gas. The inhibitor was added to give an inhibitor concentration of 100 p.p.m. in the oil-brine mixtures.

The corrosiveness of the system was determined by its effect on metal coupons prepared from mild steel bar-stock. The coupons were machined from the bar-stock to a smooth finish, the final dimensions being about ⅛" x ½" x 2". These machined coupons were all stored under oil prior to use and were thoroughly washed with 5 separate portions of petroleum ether followed by drying and weighing at the time of use.

The corrosion tests were conducted in a corrosion test oven designed to maintain a constant temperature and to rotate the test bottles containing the metal coupon and a simulated oil-brine solution at a constant speed of 2 revolutions per minute during the test. The temperature of the oven was set at 120±2° F. These conditions were maintained for a 69–72 hour exposure period. At the end of the exposure period the coupons were removed from the bottles, thoroughly washed, dried and reweighed.

The value of the tested corrosion inhibitors was determined by comparing the weight loss of the coupons from the inhibited test solutions to the weight losses of coupons exposed to similar but uninhibited sweet and sour oil-brine solutions. The data and results are reported in subsequent Table I. It is to be noted that the percent corrosion inhibition found in Table I was calculated by the formula

$$\text{Percent corrosion inhibition} = 100 - \frac{\text{mg. wt. loss in inhibited solution}}{\text{mg. wt. loss in uninhibited solution}} \times 100$$

Table I

AVERAGE CORROSION IN SIMULATED SWEET AND SOUR OIL-BRINE MIXTURES

Inhibitor [1]	Type of Brine	Number of Test Coupons	Average Coupon Wt. Loss, Mg.	Average Percent Inhibition
None	Sweet	24	124	
A	Sweet	6	48	61
B	Sweet	6	49	60
None	Sour	24	171	
A	Sour	6	45	74
B	Sour	6	70	59

[1] A=p-nonylphenoxyethoxyethyl diethylenetriamine; B=p-nonylphenoxyethoxyethyl ethylenediamine.

EXAMPLE III

This example illustrates the effectiveness of the polyamines contemplated herein in controlling sulfate-reducing organisms (*Desulfovibrio desulfuricans*) which contribute to the corrosion of oil and gas well producing equipment as well as to the plugging of the pores in producing formations.

The test method utilizes a natural brine contaminated with *Desulfovibrio desulfuricans* as the inoculum. The inoculum is added to a series of incubator tubes in a quantity of 20 mls. per tube. To each tube the desired quantity of bactericide is then added. The tubes are subsequently incubated for a period of about 3 weeks at 37° C. At the end of that period a count of the bacteria in each tube is then made. The test data is reported below in Table II.

Table II

BACTERIAL CONTENT IN BRINE SOLUTIONS

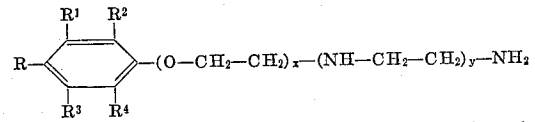
Inhibitor [1]	Concentration, p.p.m. Inhibitor/ml. brine	No. of Bacteria/ml. Brine
Blank	0	30
A	10	15
A	15	2
A	20	0
B	10	2
B	15	0
Blank	0	700
A	20	7
B	10	7
B	15	0

[1] A=p-nonylphenoxyethoxyethyl diethylenetriamine; B=p-nonylphenoxyethoxyethyl ethylenediamine.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

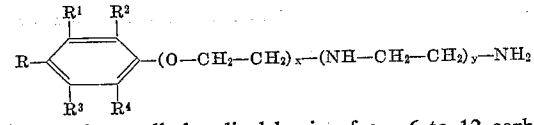
I claim:

1. A method for protecting preventing corrosion of ferrous metal surface by a corrosive petroliferous fluid containing a corrosive component selected from the group consisting of carbon dioxide and sulfide brines which comprises the steps of adding a corrosion inhibiting amount of a corrosion inhibitor to at least a portion of said fluid to provide a mixture and contacting said ferrous surface with said mixture, said inhibitor have the formula



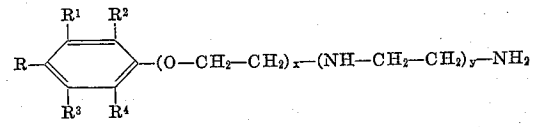
where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3, and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

2. A method for reducing the corrosiveness of a corrosive petroliferous fluid containing a corrosive component selected from the group consisting of carbon dioxide and sulfide brines to a ferrous metal surface in a borehole fluidly communicating a petroliferous subsurface formation with the surface of the earth, said borehole containing a corrosive petroliferous fluid in contact with said ferrous metal surface, said method comprising the steps of adding an inhibiting amount of corrosion inhibitor to at least a portion of said petroliferous fluid to provide a mixture and contacting said ferrous metal surface in said borehole with said mixture, said corrosion inhibitor having the formula



where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3, and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

3. In a method for producing a petroliferous fluid from a subsurface petroliferous formation through ferrous metal tubing contained in an at least partially cased borehole communicating said formation with the surface of the earth, said petroliferous fluid containing a corrosive component selected from the group consisting of carbon dioxide and sulfide brines, the improvement for reducing the corrosiveness of said fluid to said tubing which comprises the steps of introducing a portion of said fluid and a corrosion inhibiting amount of a polyamine inhibitor into the annulus between said casing and said tubing to provide a mixture, from thence introducing said mixture into said tubing adjacent the lower end thereof and producing said mixture up said tubing in contact with the surface thereof, said polyamine inhibitor having the formula

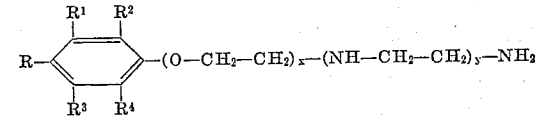


where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3, and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

4. A method as in claim 3 wherein the corrosion inhibitor is p-nonylphenoxyethoxyethyl diethylenetriamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said inhibitor.

5. A method as in claim 3 wherein said corrosion inhibitor is p-nonylphenoxyethoxyethyl ethylenediamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said corrosion inhibitor.

6. In a method wherein a subsurface petroliferous formation is penetrated by at least two boreholes communicating said formation with the surface of the earth, at least the first of said boreholes being an injection borehole and at least the second of said boreholes being a producing borehole, said producing borehole containing a ferrous metal conduit, and wherein a petroliferous fluid is produced through said producing borehole, said petroliferous fluid containing a corrosive component selected from the group consisting of carbon dioxide and sulfide brines, the improved method for reducing the corrosiveness of said petroliferous fluid to said conduit in said producing well which comprises the steps of injecting a polyamine corrosion inhibitor into said petroliferous formation through said first injection well to provide a mixture of said corrosion inhibitor with said petroliferous fluid and producing said mixture through said producing borehole in contact with said conduit, said corrosion inhibitor being introduced into said petroliferous formation in a quantity sufficient to provide a corrosion inhibiting amount of said inhibitor in said mixture, said polyamine corrosion inhibitor having the formula

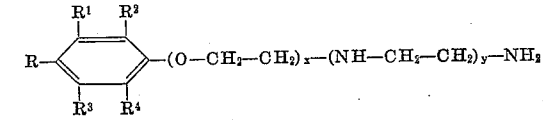


where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3, and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

7. A method as in claim 6 wherein said corrosion inhibitor is p-nonylphenoxyethoxyethyl diethylenetriamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said corrosion inhibitor.

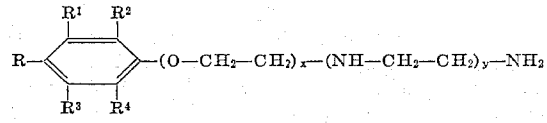
8. A method as in claim 6 wherein said corrosion inhibitor is p-nonylphenoxyethoxyethyl ethylenediamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said corrosion inhibitor.

9. A method for preventing corrosion of a ferrous metal surface by a corrosive petroliferous fluid containing a sulfate-reducing bacteria which comprises the steps of adding a corrosion inhibiting amount of a corrosion inhibitor to at least a portion of said fluid to provide a mixture and contacting said ferrous surface with said mixture, said inhibitor having the formula:



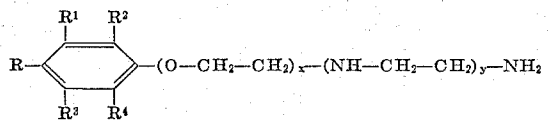
where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3 and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

10. A method for reducing the corrosiveness of a corrosive petroliferous fluid containing sulfate-reducing bacteria to a ferrous metal surface in a borehole fluidly communicating a petroliferous subsurface formation with the surface of the earth, said borehole containing a corrosive petroliferous fluid in contact with said ferrous metal surface, said method comprising the steps of adding an inhibiting amount of corrosion inhibitor to at least a portion of said petroliferous fluid to provide a mixture and contacting said ferrous metal surface in said borehole with said mixture, said corrosion inhibitor having the formula:



where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3 and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively, and y is an integer from 1 to 3 inclusively.

11. In a method for producing a petroliferous fluid from a subsurface petroliferous formation through a ferrous metal tubing contained in an at least partially cased borehole communicating said formation with the surface of the earth, said petroliferous fluid containing a sulfate-reducing bacteria, the improvement for reducing the corrosiveness of said fluid to said tubing which comprises the steps of introducing a portion of said fluid and a corrosion inhibiting amount of a polyamine inhibitor into the annulus between said casing and said tubing to provide a mixture, from thence introducing said mixture into said tubing adjacent the lower end thereof and producing said mixture up said tubing in contact with the surface thereof, said polyamine inhibitor having the formula:

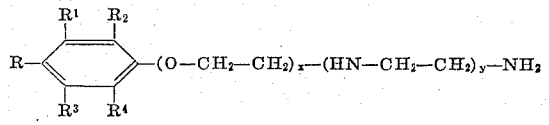


where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3 and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

12. A method as in claim 11 wherein the corrosion inhibitor in p-nonylphenoxyethoxyethyl diethylenetriamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said inhibitor.

13. A method as in claim 11 wherein said corrosion inhibitor is p-nonylphenoxyethoxyethyl ethylenediamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said corrosion inhibitor.

14. In a method wherein a subsurface petroliferous formation is penetrated by at least two boreholes communicating said formation with the surface of the earth, at least the first of said boreholes being an injection borehole and at least the second of said boreholes being a producing borehole, said producing borehole containing a ferrous metal conduit, and wherein a petroliferous fluid is produced through said producing borehole, said petroliferous fluid containing sulfate-reducing bacteria, the improved method for reducing the corrosiveness of said petroliferous fluid to said conduit in said producing well which comprises the steps of injecting a polyamine corrosion inhibitor into said petroliferous formation through said first injection well to provide a mixture of said corrosion inhibitor with said producing borehole in contact with said conduit, said corrosion inhibitor being introduced into said petroliferous formation in a quantity sufficient to provide a corrosion inhibiting amount of said inhibitor in said mixture, said polyamine corrosion inhibitor having the formula:



where R is an alkyl radical having from 6 to 12 carbon atoms, where R^1, R^2, R^3 and R^4 are radicals selected from the group consisting of hydrogen and C_1 to C_3 alkyl radicals, where x is an integer from 1 to 4 inclusively and y is an integer from 1 to 3 inclusively.

15. A method as in claim 14 wherein said corrosion inhibitor in p-nonylphenoxyethoxyethyl diethylenetriamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said corrosion inhibitor.

16. A method as in claim 14 wherein said corrosion inhibitor is p-nonylphenoxyethoxyethyl ethylenediamine and wherein said mixture contains from about 10 to about 500 p.p.m. by weight of said corrosion inhibitor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,229,024	Bruson	Jan. 21, 1941
2,252,828	Alquist et al.	Apr. 19, 1941
2,523,177	Yowell et al.	Sept. 19, 1950
2,564,753	Cox	Aug. 21, 1951
2,692,231	Stayner et al.	Oct. 19, 1954
2,745,809	Cardwell et al.	May 15, 1956
2,882,227	Lindberg	Apr. 14, 1959
2,952,635	Spivack et al.	Sept. 13, 1960