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PROCESS FOR PREVENTING CORROSION OF FERROUS METALS

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20 Claims. (Cl. 252—8.55)

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The present invention relates to the inhibition of corrosion of corrodible ferrous metal surfaces by corrosive fluids. More particularly, the invention relates to a process for inhibiting the corrosivity of fluids produced from subsurface earth formations exposed to corrodible ferrous metal conduits and attendant equipment through which the fluids are flowed and processed.

In the production of oil and gas, soluble sulfides are often produced from subsurface formations and in the presence of water will attack or corrode ferrous metal conduits and attendant equipment with which the crude oil or gas comes into contact. In the production of such oil and gas there is usually produced brine along with the sour crude or sour gas. These brines may contain corrosive sulfides which may include alkali metal sulfides, alkaline earth metal sulfides, acid sulfides, such as hydrogen sulfides, and/or organic sulfides. The well fluids, such as crude oil and gas, and the brines associated therewith may also contain carbon dioxide, a weak inorganic acid, organic acids and the like. The brines containing hydrogen sulfide or carbon dioxide and organic acids are especially corrosive to iron and steel equipment. Since the corrosive materials occur in or are introduced into the fluids originating in the subsurface formations, corrosion may occur throughout the ferrous metal conduits and attendant equipment through which the fluids from the subsurface formations are flowed and produced. In some cases, the corrosion may be more or less localized to a limited portion of the conduits from which fluids from the subsurface formations are produced. In any case, the corrosion of the conduits and attendant ferrous metal equipment may be so severe as to require replacement of either or of both. As is well recognized, such replacements can be and often are extremely expensive. The expense is not limited merely to the cost of replacing the corroded equipment but may also involve killing the well in order to make repairs and to replace the corroded equipment. Not only is the cost of killing a well high but there is a loss in revenues due to having a well off production for repairs as a result of the corrosion. Corrosion may, on occasion, be so severe as to result in failure of the equipment in which event the well may run wild. Enormous losses may be incurred when such happens.

The present invention may be described briefly as involving the prevention of corrosion of ferrous metals exposed to a corrosive solution in which there is incorporated in the corrosive solu-

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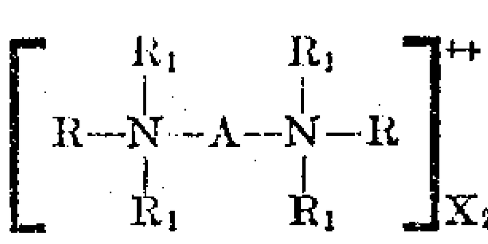
tion an effective amount of a double, long-chain quaternary ammonium salt represented by the formula:



In the formula R is a radical having an alkyl chain containing at least 8 carbon atoms or a radical having at least 8 carbon atoms and a benzyl group; R_1 is an alkyl radical having no more than 2 carbon atoms or a radical containing a benzyl group; A is a normal hydrocarbon chain having from 4 to 16 methylene groups, an aryl radical, or an alkyl substituted aryl radical, while X is a halogen such as chlorine, bromine, or iodine.

The invention also has to do with the prevention of corrosion in oil and gas well equipment by incorporating in the well an effective amount of a double, long-chain quaternary ammonium salt as represented by the foregoing structural formula.

When the double, long-chain quaternary ammonium salt, as has been described, is injected into the well, it suitably may be injected into the annulus and displaced upwardly into the tubing or oil string. If desired, the double, long-chain quaternary ammonium salt employed in the present invention may be used to coat the tubing string before it is arranged in the well and thereby obtain quickly the desired protection.

One method of injecting the double, long-chain quaternary ammonium salt employed in the present invention is to dissolve it in a suitable solvent, such as water, or an aromatic hydrocarbon solvent, such as represented by benzene, toluene, xylene and the higher members of the same homologous series.

It may be desired to inject the corrosion inhibitor, in accordance with my invention, either continuously or intermittently. Continuous application is the preferred method.

In the practice of the present invention for the protection of metal equipment of oil and gas wells such as those producing well fluids containing an acidic constituent, such as hydrogen sulfide, carbon dioxide, organic acids and other corrosive materials as has been mentioned, the double, long-chain quaternary ammonium salt may be introduced into the annulus of the well between the casing and the producing string, where it becomes intimately admixed with the well fluid and may be pumped or flowed from the well with the corrosive fluids. Thus, the inner wall of the casing and the outer and inner walls of the tubing string and the inner surfaces of the auxiliary equipment, such as wellhead equipment, flow lines and the like, are contacted with the double, long chain quaternary ammonium salt and protected from corrosion from the corrosive materials in the well fluid.

It may be desirable to introduce the double, long-chain quaternary ammonium salt, the identity of which has been given, into the annulus by means of a mechanical pump so that a small amount of the material in a suitable solvent, as has been specified, is introduced continuously or intermittently, as is desired.

The amount of the double, long-chain quaternary ammonium salt to be employed depends on the corrosivity of the corrosive solution. The amount of the double, long-chain quaternary ammonium salt necessary to protect adequately the ferrous metal surfaces to which it is applied will be only a small concentration in the corrosive fluid. For example, an amount from about .0001% to about .005% by weight will give effective protection in substantially all corrosive fluids produced from subsurface formations.

The double, long-chain quaternary ammonium salts employed in the practice of the present invention are exemplified by those double, long-chain quaternary ammonium salts as represented by the foregoing structural formula. Specific examples of such compounds are decamethylene bis(dimethyl cetyl ammonium bromide), tetramethylene bis(dimethyl cetyl ammonium bromide), butene bis(nonyl benzyl dimethyl ammonium chloride), butyne bis(2 octyl benzyl dimethyl ammonium chloride) and butane bis(nonyl) benzyl dimethyl ammonium chloride. Other compounds of a similar nature which may be employed in the practice of the present invention are described in U. S. Patents 2,525,777, 2,525,778 and 2,525,779, issued October 17, 1950, to de Benneville and Gormly. The double, long-chain quaternary ammonium salts described by de Benneville et al. are also excellent inhibitors for corrosion for use in my invention.

In order to illustrate the beneficial results obtained in the practice of the present invention the following examples are given:

In order to test the effectiveness of tetramethylene bis(dimethyl cetyl ammonium bromide) a fifty-fifty mixture of West Texas crude oil and West Texas brine was saturated with hydrogen sulfide and divided into three portions. To one portion 0.003% by weight of tetramethylene bis(dimethyl cetyl ammonium bromide) was added and to another portion 0.001% by weight of the tetramethylene bis(dimethyl cetyl ammonium bromide) was added. The third portion of the mixture of West Texas crude oil and West Texas brine saturated with hydrogen sulfide without addition of tetramethylene bis(dimethyl cetyl ammonium bromide) was used as a control. Mild carbon steel coupons were immersed 31 times a minute for a period of 14 days in each of the 3 portions of the mixture saturated with hydrogen sulfide. After the period indicated, it was found that the coupons in the corrosive solution which contained no tetramethylene bis(dimethyl cetyl ammonium bromide) had been corroded at a rate of 0.025 inch per year. The corrosion rate of the solution of crude oil and brine saturated with hydrogen sulfide was reduced 92% by 0.003% by weight of the tetramethylene bis(dimethyl cetyl ammonium bromide) and was reduced 22% by 0.001% by weight of the tetramethylene bis(dimethyl cetyl ammonium bromide).

Decamethylene bis(dimethyl cetyl ammonium bromide) was tested in a similar mixture of West Texas crude oil and West Texas brine saturated with hydrogen sulfide in three concentrations as follows: 0.003% by weight, 0.001% by weight, and 0.0005% by weight. After the carbon steel coupons had been immersed 31 times per minute for a period of 14 days in the corrosive solution, it was found that when compared with the control coupons, 0.003% by weight of decamethylene bis(dimethyl cetyl ammonium bromide) had effected 99% reduction in corrosivity, 0.001% by weight of the decamethylene bis(dimethyl cetyl ammonium bromide) had effected a reduction in corrosivity of 75%, and 0.0005% by weight of decamethylene bis(dimethyl cetyl ammonium bromide) had effected a reduction in corrosion rate of 27%.

Since it has been known to use quaternary ammonium compounds other than the double, long-chain quaternary ammonium salts as corrosion inhibitors, a comparison was made between the conventional quaternary ammonium salts and the double, long-chain quaternary ammonium salts employed in accordance with the present invention. Thus, varying amounts of dimethyl benzyl lauryl ammonium chloride, cetyl trimethyl ammonium bromide, and stearyl dimethyl benzyl ammonium chloride were compared with butene bis(nonyl benzyl dimethyl ammonium chloride), butyne bis(2 octyl benzyl dimethyl ammonium chloride), and butane bis(nonyl benzyl dimethyl ammonium chloride). In these comparative tests varying amounts of the several inhibitors of the prior art and the corrosion inhibitors employed in the present invention were added to a mixture of fifty-fifty West Texas crude oil and West Texas brine which had been saturated with hydrogen sulfide and mild carbon steel coupons were immersed 31 times a minute in the corrosive solution of crude oil and brine containing hydrogen sulfide for a period of 14 days and at the end of the period the coupons were removed and compared to determine the corrosion rate by reduction in per cent. In short, metal coupons were immersed in the corrosive solution in the absence of any inhibitor and the percentage reduction effected by the several inhibitors was determined by comparison with the blanks. The data obtained in the following table illustrate the effectiveness of the several inhibitors:

Table

	Concentration, Percent by Wt.	Corrosion Reduction, Percent
Dimethyl benzyl lauryl ammonium chloride	0.002	77
Do	0.001	35
Cetyl trimethyl ammonium bromide	0.002	49
Do	0.001	12
Stearyl dimethyl benzyl ammonium chloride	0.0025	90
Do	0.00125	30
Butene bis(nonyl benzyl dimethyl ammonium chloride)	0.001	99
Do	0.0005	67
Butyne bis(2 octyl benzyl dimethyl ammonium chloride)	0.001	91
Do	0.0005	90
Butane bis(nonyl benzyl dimethyl ammonium chloride)	0.001	84
Do	0.0005	53

It will be seen from the data in the above table that the double, long-chain quaternary ammonium salts employed in the practice of the present invention are much more effective inhibitors than are the conventional quaternary ammonium salts.

Ortho-xylylene bis(cetyl dimethyl ammonium bromide) was added in an amount of 0.002 weight per cent to a fifty-fifty mixture of West Texas crude oil and West Texas brine which had been saturated with hydrogen sulfide. The hydrogen sulfide-saturated mixture then had mild carbon steel coupons immersed in it thirty-one times a minute for a period of fourteen days. After the period indicated, it was found that the coupons in the corrosive solution which contained orthoxylylene bis(cetyl dimethyl ammonium bromide) had been corroded at an average rate of 0.00075 inch per year. Metal coupons were also immersed in the corrosive solution to which ortho-xylylene bis(cetyl dimethyl ammonium bromide) had not been added. After a similar treatment of immersions over the same period of time it was found that the metal coupons in the corrosive solution to which no inhibitor had been added had been corroded to an extent of 0.0261 inch per year. Thus, the ortho-xylylene bis(cetyl dimethyl ammonium bromide) reduced the corrosion rate of the corrosive solution by 97%.

It will be seen from the foregoing data that I have discovered that beneficial effects are obtainable by the double, long-chain quaternary salts, as described above. I have discovered that these compounds are effective in protecting ferrous metal surfaces in contact with corrosive fluids by incorporating or applying to the ferrous metal surfaces an effective amount of the double, long-chain quaternary ammonium salts identified before.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A process for preventing the corrosion of ferrous metals exposed to a corrosive solution which comprises incorporating in said corrosive solution an effective amount of a double, long-chain quaternary ammonium salt represented by the formula:

$$\left[\begin{array}{ccccc} & R_1 & & R_1 & \\ & | & & | & \\ R- & N & -A- & N & -R \\ & | & & | & \\ & R_1 & & R_1 & \end{array}\right]^{++} X_2$$

where R is a radical selected from the group consisting of the radicals having an alkyl chain containing at least 8 carbon atoms and an alkyl chain having at least 8 carbon atoms and a benzyl group; R_1 is selected from the group consisting of the alkyl radicals having no more than 2 carbon atoms and the benzyl group radicals; A is selected from the group consisting of normal hydrocarbon chains having from 4 to 16 methylene groups, aryl radicals, and alkyl substituted aryl radicals; and X is a halogen selected from the group consisting of chlorine, bromine, and iodine.

2. A process for preventing the corrosion of ferrous metals exposed to a corrosive solution including a hydrocarbon and water which comprises incorporating in said corrosive solution an effective amount of a double, long-chain quaternary ammonium salt represented by the formula:

$$\left[\begin{array}{ccccc} & R_1 & & R_1 & \\ & | & & | & \\ R- & N & -A- & N & -R \\ & | & & | & \\ & R_1 & & R_1 & \end{array}\right]^{++} X_2$$

where R is a radical selected from the group consisting of the radicals having an alkyl chain containing at least 8 carbon atoms and an alkyl chain having at least 8 carbon atoms and a benzyl group; R_1 is selected from the group consisting of the alkyl radicals having no more than 2 carbon atoms and the benzyl group radicals; A is selected from the group consisting of normal hydrocarbon chains having from 4 to 16 methylene groups, aryl radicals, and alkyl substituted aryl radicals; and X is a halogen selected from the group consisting of chlorine, bromine, and iodine.

3. A method for preventing the corrosion of ferrous metals exposed to a corrosive solution which comprises incorporating in said corrosive solution an effective amount of decamethylene bis(dimethyl cetyl ammonium bromide).

4. A process for preventing the corrosion of ferrous metals exposed to a corrosive solution which comprises incorporating in said corrosive solution an effective amount of tetramethylene bis(dimethyl cetyl ammonium bromide).

5. A process for preventing the corrosion of ferrous metals exposed to a corrosive solution which comprises incorporating in said corrosive solution an effective amount of butene bis(nonyl benzyl dimethyl ammonium chloride).

6. A process for preventing the corrosion of ferrous metals exposed to a corrosive solution which comprises incorporating in said corrosive solution an effective amount of butyne bis(2 octyl benzyl dimethyl ammonium chloride).

7. A process for preventing the corrosion of ferrous metals which comprises incorporating in said corrosive solution an effective amount of butane bis(nonyl benzyl dimethyl ammonium chloride).

8. A process for preventing corrosion in oil and gas well equipment which comprises the step of injecting into the well an effective amount of a double, long-chain quaternary ammonium salt represented by the formula:

$$\left[\begin{array}{ccccc} & R_1 & & R_1 & \\ & | & & | & \\ R- & N & -A- & N & -R \\ & | & & | & \\ & R_1 & & R_1 & \end{array}\right]^{++} X_2$$

where R is a radical selected from the group consisting of the radicals having an alkyl chain containing at least 8 carbon atoms and an alkyl chain having at least 8 carbon atoms and a benzyl group; R_1 is selected from the group consisting of the alkyl radicals having no more than 2 carbon atoms and the benzyl group radicals; A is selected from the group consisting of normal hydrocarbon chains having from 4 to 16 methylene groups, aryl radicals and alkyl substituted aryl radicals; and X is a halogen selected from the group consisting of chlorine, bromine, and iodine.

9. A process for preventing the corrosion of oil and gas well equipment which comprises incorporating into a well fluid an effective amount of a double, long-chain quaternary ammonium salt represented by the formula:

$$\left[\begin{array}{ccccc} & R_2 & & R_1 & \\ & | & & | & \\ R- & N & -A- & N & -R \\ & | & & | & \\ & R_1 & & R_1 & \end{array}\right]^{++} X_2$$

where R is a radical selected from the group consisting of the radicals having an alkyl chain containing at least 8 carbon atoms and an alkyl chain having at least 8 carbon atoms and a benzyl group; R_1 is selected from the group consisting of the alkyl radicals having no more than

2 carbon atoms and the benzyl group radicals; A is selected from the group consisting of normal hydrocarbon chains having from 4 to 16 methylene groups, aryl radicals, and alkyl substituted aryl radicals; and X is a halogen selected from the group consisting of chlorine, bromine, and iodine.

10. A method for preventing corrosion of oil and gas well equipment which comprises injecting into the well an effective amount of decamethylene bis(dimethyl cetyl ammonium bromide).

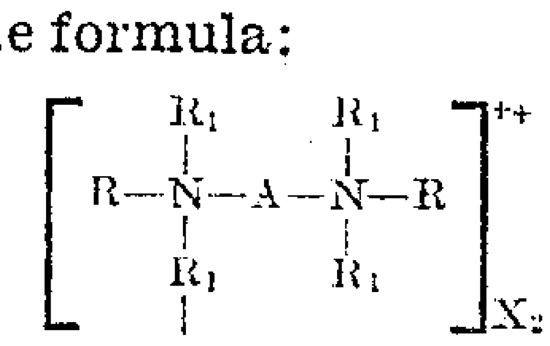
11. A method for preventing corrosion of oil and gas well equipment which comprises injecting into the well an effective amount of tetramethylene bis(dimethyl cetyl ammonium bromide).

12. A method for preventing corrosion of oil and gas well equipment which comprises injecting into the well an effective amount of butene bis(nonyl benzyl dimethyl ammonium chloride).

13. A method for preventing corrosion of oil and gas well equipment which comprises injecting into the well an effective amount of butyne bis(2 octyl benzyl dimethyl ammonium chloride).

14. A method for preventing corrosion of oil and gas well equipment which comprises injecting into the well an effective amount of butane bis(nonyl benzyl dimethyl ammonium chloride).

15. A process for preventing the corrosion of ferrous metals exposed to a corrosive solution which comprises applying to said metals a double, long-chain quaternary ammonium salt represented by the formula:



where R is a radical selected from the group consisting of the radicals having an alkyl chain containing at least 8 carbon atoms and an alkyl chain having at least 8 carbon atoms and a benzyl group; R_1 is selected from the group consisting of the alkyl radicals having no more than 2 carbon atoms and the benzyl group radicals; A is selected from the group consisting of normal hydrocarbon chains having from 4 to 16 methylene groups, aryl radicals and alkyl substituted aryl radicals; and X is a halogen selected from the group consisting of chlorine, bromine, and iodine.

16. A process in accordance with claim 1 in which the effective amount of the double, long-chain quaternary ammonium salt is in the range from about 0.0001% to about 0.005% by weight of the corrosive solution.

17. A process in accordance with claim 2 in which the effective amount of the double, long-chain quaternary ammonium salt is in the range from about 0.0001% to about 0.005% by weight of the corrosive solution.

18. A process in accordance with claim 8 in which the effective amount of the double, long-chain quaternary ammonium salt is in the range from about 0.0001% to about 0.005% by weight of a corrosive fluid in said well.

19. A process in accordance with claim 9 in which the effective amount of the double, long-chain quaternary ammonium salt is in the range from about 0.0001% to about 0.005% by weight of the well fluid.

20. A process in accordance with claim 15 in which an amount in the range from about 0.0001% to about 0.005% by weight of the double, long-chain quaternary ammonium salt based on the corrosive solution is applied to said metals.

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