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INHIBITING CORROSION IN OIL WELLS

Joseph F. Chittum, Whittier, and Frederic W. Schremp, Fullerton, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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This invention relates to a method of inhibiting the corrosion of metal surfaces and pertains particularly to an improved method and composition for inhibiting the corrosion of ferrous metal surfaces in contact with brines produced from an oil well incident to the production of petroleum.

The brines formed in subterranean formations are usually highly saline due mainly to dissolved sodium chloride. The brines also usually contain carbon dioxide, both in solution and as a gas. Other substances, such as hydrogen sulfide, may be in the well water in various localities. The brine is therefore a corrosive medium which attacks the metal surfaces with which it comes in contact and often creates an environment wherein metal surfaces are more susceptible to electrochemical and electrolytic corrosion. This susceptibility is especially noticeable in ferrous metal equipment which is exposed to flowing brine or in which the well products are treated or stored during the separation of the crude oil from the brine.

It will be appreciated that many factors contribute to the corrosive environment found in oil wells. Such factors include not only the composition of the brine, some components of which have been mentioned above, but also temperature conditions, the velocity of fluid flow through or over the well apparatus, the amount of oxygen and carbon dioxide available to contribute to the corrosive conditions, cyclic stress in pumping equipment, particular components of the crude oil and other factors, some of which are still unknown. As a result, the development of corrosion inhibitors for oil field use has been done largely on an empirical basis, since it has been found that inhibitors which may be effective under conditions of other industrial usage are not always effective in oil wells.

The problem of protecting the ferrous metal equipment such as the tubing, rods and pumps in pumping wells and the casing and tubing in flowing wells has received a great deal of attention in oil field practice.

As described in our copending application, Serial No. 159,814, filed December 1, 1961, now U.S. Patent No. 3,127,932, issued April 7, 1964, corrosion of metal surfaces exposed to corrosive well fluids is very effectively inhibited by bringing together in the well brine a mixture of a ferrocyanide ion and a borate ion, both in aqueous solution and each in a concentration of at least 5 p.p.m. The combination gives a synergistic effect in inhibiting corrosion in oil well applications with relatively low concentrations of the inhibiting components of the corrosive fluids. Effective corrosion inhibition can be obtained with sufficient water-soluble ferrocyanides and water-soluble borates to give concentrations of 5 to 140 p.p.m. for each of the ferrocyanide ion and borate ion. The preferred ranges for most effective corrosion inhibition at the minimum total concentration of the respective ions in solution are 7 to 100 p.p.m. of the ferrocyanide ion and at least 10 p.p.m. of the borate ion.

Although the synergistic combination of the water-soluble ferrocyanide and water-soluble borate is highly effective in inhibiting corrosion due to corrosive oil well brines having moderate contents of salts such as sodium chloride together with other corrosion-inducing materials such as carbon dioxide and hydrogen sulfide often found in such brines, the ferrocyanide-borate treatment forms a

blue scale in the presence of dissolved ferrous ions in the brine. When the ferrous ion content is higher than 5 p.p.m. and especially above 10 p.p.m., the scale formation sometimes becomes so pronounced as to require that the rods in a pumping well be pulled from the well in order to remove the accumulated scale.

The present invention provides a solution for this problem. We have found that very effective inhibition of corrosion of metal surfaces in contact with brines containing more than 5 p.p.m. of ferrous ion can be obtained with the combination of ferrocyanide and borate, while avoiding the scale formation usually associated with this combination in brines having such ferrous ion contents, by also incorporating in the brine a small amount of antimony sulfide. Antimony sulfide is unique in its ability to inhibit formation of scale by ferrocyanides in oil well brine environments; many agents expected to have iron sequestering properties are not effective enough to prevent such scale formation. We have also found that the combination of antimony sulfide with the ferrocyanide and borate is very effective in inhibiting sudden stress potential in sucker rods, thereby indicating a reduction in corrosion fatigue and rod-breaking tendency. While the ferrocyanide-borate-antimony sulfide combination is especially suited for inhibiting corrosion of ferrous metal surfaces exposed to brines containing more than 5 p.p.m. of ferrous ion, the combination is very effective for inhibiting corrosion by oil well brines having lesser amounts of dissolved ferrous ion. With salt contents above 4–5% sodium chloride, the present combination including antimony sulfide provides effective corrosion control, whereas in such environments, other inhibitors such as the organics and the arsenicals drop off rapidly in their effectiveness. The present combination is effective not only in the presence of highly saline brine but also in the presence of the amounts of hydrogen sulfide which are associated with sour crudes. Hence, the combination is of general utility for inhibiting corrosion in the presence of oil well brines.

Furthermore, we have found that the ferrocyanide coacts with the antimony sulfide in increasing its solubility but also in stabilizing dispersions of antimony sulfide in brines. While antimony sulfide alone is only soluble in a neutral aqueous solution to the extent of about 2 p.p.m. and in acidic solutions to about 10 p.p.m., the presence of ferrocyanide ion in an amount of 1–10 parts per part of antimony sulfide increases the solubility of antimony sulfide in acidic solutions such as the usual oil field brines to about 12–15 p.p.m. Additionally, the ferrocyanide ion stabilizes precipitates of antimony sulfide such as are formed when caustic solutions of antimony sulfide are introduced into a well along with the ferrocyanide and borate. For example, when a 10% caustic solution of antimony sulfide, along with ferrocyanide and borate, is introduced into a brine to produce concentrations of 5 p.p.m. of antimony sulfide, 5 p.p.m. of ferrocyanide ion and 15 p.p.m. of borate ion and the brine is acidified to a pH of 5.5 with carbon dioxide, a dark orange dispersion of antimony trisulfide is formed but remains stably dispersed in the presence of the ferrocyanide and borate ions. Thus, antimony sulfide with the ferrocyanide and borate is a combination having synergistic properties with the antimony sulfide preventing scale formation by the interaction of ferrocyanide with ferrous ions in the oil well brine and with the ferrocyanide plus borate not only increasing the solubility of antimony sulfide in the brine but also stabilizing any undissolved dispersion of antimony sulfide in the brine. Further the present invention contemplates inhibiting corrosion of ferrous metal surfaces in contact with oil well fluids including crude oil, brine and carbon dioxide by incorporating with said fluids in an intimate mixture prior to the time said fluids contact said ferrous metal surfaces an aqueous caustic solution of antimony

sulfide in an amount sufficient to produce a concentration of 1 to 20 p.p.m. of antimony sulfide in said brine.

As indicated above, the addition of antimony sulfide greatly reduces the tendency of ferrocyanide-borate to form undesirable scale in oil wells. Tests illustrating this property were carried out as follows: an oil well brine containing 3% sodium chloride and 10 p.p.m. of ferrous ions (added for test purposes as ferrous chloride) at well temperatures (i.e., about 160° F.) was pumped for 1 hour through a glass apparatus simulating a well pump and containing four glass check valves on which the ferrocyanide scale is deposited. The relative amounts of scale are determined by the gain in weight of the check valves. In the comparative tests the brine was treated with sufficient sodium ferrocyanide and sodium tetraborate to produce in the brine a concentration of 20 p.p.m. of ferrocyanide ion and 50 p.p.m. of borate ion calculated as BO_3, with and without the addition of various amounts of antimony trisulfide in aqueous sodium hydroxide (10%) solution. All solutions were saturated with CO_2 to a pH of 5.5. The results of the series of tests are given in the following table.

Table I

Amount of Sb_2S_3 added to brine (p.p.m.):	Amount of scale formed (mg.)
0	25.9
1	13.6
1.6	15.5
3	8.6
4	5.6

The above data indicate the effectiveness of antimony sulfide in reducing the tendency of ferrocyanide-borate to form scale in the presence of ferrous ions in brine.

Another advantage of the antimony sulfide-ferrocyanide-borate inhibiting combination is its ability to reduce sudden stress potential. The rod stretcher test is based upon the theory that sucker rod breaks result from corrosion fatigue and that corrosion fatigue results from the successive growth of a crack under cyclic stress. The crack grows because applied cyclic stress causes repeated sudden stress above the yield point at the base of the crack where the lines of force are concentrated. A sudden stress produces a sudden shift in the iron potential in the anodic direction. The shift in the anodic direction causes loss of metallic iron from the base of the crack. Inhibitors that suppress the sudden stress potential of a rod will thereby suppress the growth of a corrosion fatigue crack and thus the incidence of rod breaks. The rod stretcher test for measuring the sudden stress potential for carbon magnesium steel in a brine containing 3% sodium chloride as influenced by added inhibitors is carried out as follows: A heavy iron beam is pivoted at a point located at nine-tenths of its total length. The long lever arm of the beam is attached to a cylinder provided with a plunger attached to the base of the apparatus and with means for increasing the pressure within the cylinder. A pony rod is fastened between the end of the short lever arm of the beam and the base of the apparatus. A Lucite cell or chamber is fastened around the pony rod to form a cup surrounding the rod. Positioned in the cell is a short section of a rod as a reference. The test liquid under investigation is placed in the cell and is in contact with the pony rod and vertically held reference rod. By applying a known pressure in the cylinder under the plunger for a short time, the short arm of the beam is moved upward, thus stretching the pony rod. The potential change between the pony rod and the reference rod that exists in the short period of stress is measured by means of an oscilloscope. Pictures are taken of the oscilloscope signals. The load that is put on the pony rod is calculated from the known surface area of the plunger, the known applied pressure and the length of the lever arms of the beam.

In the test, a load is applied momentarily, about 2 seconds usually being sufficient, to the pony rod. The load is about that which reaches the yield point of the rod, i.e., about 50,000 p.s.i. for ordinary carbon steel rods. During the application of the load, the signal on the oscilloscope reaches a peak height indicative of the sudden stress potential or transient. The inhibition of sudden stress potential due to the additives is calculated in terms of corrosion fatigue inhibition ("CFI") as follows:

$$CFI = \frac{100(S_o - S_i)\ \text{percent}}{S_o}$$

where S_o is the signal height above the base line with brine without inhibitor added, and S_i is the signal height with brine with the inhibitor added. In one case, sodium ferrocyanide and sodium tetraborate were added to produce in the brine concentrations of 20 p.p.m. of ferrocyanide and 50 p.p.m. of borate ion. In another case for comparative purposes, antimony sulfide in a 10% sodium hydroxide solution was also added to produce a concentration of 20 p.p.m. of antimony sulfide in the brine. The results of the tests above were as follows:

Table II

	Inhibition of corrosion fatigue, percent
Without Sb_2S_3	30–40
With Sb_2S_3	82–85

The above data show that the addition of antimony sulfide more than doubled the inhibition of corrosion fatigue as indicated by the sudden stress potential.

As indicated above, the corrosion inhibiting composition of the present invention comprises a mixture of a water-soluble ferrocyanide and a water-soluble borate together with a scale-inhibiting amount of antimony sulfide. In forming a suitable concentrate of inhibitor for injection into a well, caustic, such as sodium or potassium hydroxide, is incorporated into the aqueous solution. In caustic solutions, 4–5% by weight of antimony sulfide can be introduced (no hydrogen sulfide being formed) and with the proportionate amounts, as specified elsewhere herein, of ferrocyanide and borate, the amount is increased to about 6–7%. Thus, the combination of antimony sulfide in caustic solution with ferrocyanide and borate gives a more concentrated solution of active ingredients suitable for use in treating oil wells. Usually a concentration of 3–20% of caustic is sufficient to increase substantially the amount of antimony sulfide that can be stably dispersed in the aqueous medium. By far, most preferable for an inhibitor composition of general utility with maximum concentration of active ingredients is that composed of water-soluble ferrocyanide, water-soluble borate, antimony sulfide and caustic in the above proportion to the amount of antimony sulfide. The concentration of ferrocyanide ion in the brine can be somewhat less than that specified in our copending application Serial No. 159,814, and can be as low as 1–2 p.p.m. so long as there is a complementary amount of antimony sulfide to make up to a total of at least 3 p.p.m., and preferably at least 5 p.p.m. However, usually the concentration for each of the ferrocyanide ion and borate ion is at least 5 p.p.m. with 140 p.p.m. usually being the upper limit. The preferred ranges at the minimum total concentration of the respective ions in solution are 7 to 100 p.p.m. of the ferrocyanide ion and at least 10 p.p.m. of the borate ion. The concentration of dispersed antimony sulfide can range from 0.1 p.p.m., preferably from 1 p.p.m. to about 50 p.p.m. although usually no more than 10 p.p.m. of antimony sulfide is required.

Generally, 2 to 20 parts of antimony sulfide per 20 parts of ferrocyanide suffice, although with the lower amounts of ferrocyanide, larger proportions such as 2 to 5 parts of antimony sulfide per part of ferrocyanide are used.

In those instances where the well brine naturally contains a borate in solution, then in accordance with the method of this invention, sufficient quantities of a water-soluble ferrocyanide and antimony sulfide usually in caustic solution are introduced into the well fluids to produce in the brine a concentration of ferrocyanide ion of at least 3 p.p.m. and a concentration of antimony sulfide of at least 0.1 p.p.m. If the well brine is lacking in borate, or if the concentration of borate ion is below that desired, then a water-soluble borate is also introduced to bring the borate ion concentration at least to 5 p.p.m.

The following tests in a brine containing 10 p.p.m. of ferrous ion illustrate the effectiveness of various combinations of antimony sulfide and a mixture of sodium ferrocyanide and sodium tetraborate in a proportion of 14 parts of ferrocyanide ion and 56 parts of borate ion calculated as BO_3. In each test there was introduced into the brine sufficient of the antimony sulfide and the ferrocyanide-borate mixture to give a total of 12 p.p.m. of antimony sulfide plus ferrocyanide ion. The test employed an apparatus in which a test specimen made of SAE 1020 mild steel was submerged in an aqueous solution made to simulate an average corrosive oil well brine. This test solution was made from tap water to which was added 3% by weight of sodium chloride and sufficient ferrous chloride to give a ferrous ion content of 10 p.p.m. The solution was saturated with carbon dioxide and contained gaseous bubbles of this substance. During the tests, the acidity of the test solution ranged from a pH of 5.5 to 5.7 and being maintained at this pH by bubbling CO_2 into the solution. The solution was agitated by mechanical means in the region of the test specimen to cause a current of solution together with the entrapped CO_2 gas to impinge on and flow over the surface of the specimen. The solution was circulated through the test chamber at the rate of 50 cc. per minute and was maintained at a temperature of 72° C.

The base rate of corrosion of the test specimen was established by running the brine through the test cell without any corrosion inhibitor being added to it. Subsequently an aqueous solution of the material to be tested for corrosion-inhibiting qualities was pumped continuously into the test cell at a measured rate and intimately mixed with the brine to produce the desired concentration of inhibitor in the brine as measured in the effluent from the test cell. Thus, by selecting the material to be injected into the test cell and controlling its concentration in the brine solution from test to test, the effects of the antimony sulfide and the ferrocyanide-borate mixture separated from each other and the effects obtained by having these agents present simultaneously in the solution were obtained.

The effects of the agents added to the brine were measured by determining the change in the electrical resistance of the test specimen due to corrosion of its surface. A recording-type, self-balancing potentiometer was used to continuously record the changes in resistance during the test. The corrosion-inhibiting effects of the agents in solution are recorded in terms of percent inhibition. This percentage is derived from the relationship

$$\frac{100(S_a - S_b)}{S_a}$$

where:

S_a is the base rate of corrosion of the test specimen,

S_b is the rate of corrosion four hours after starting injection of the inhibiting agent into the brine.

The results of these tests are given in the following table:

Table III

Sb_2S_3 (p.p.m.)	Ferrocyanide ion (p.p.m.)	Percent Inhibition
0	12	0
3	9	72
6	6	80
8	4	89
9	3	83
12	0	85

The data illustrate that the presence of ferrous ion has a substantial deleterious effect on the corrosion inhibiting properties of the ferrocyanide-borate mixtures and that antimony sulfide in combination with the ferrocyanide-borate mixture is effective to inhibit corrosion substantially.

In each of the tests described above, a very adherent and tough film of noncorrosive material was promptly deposited in the ferrous metal surfaces of the test specimens. The persistence of the film produced on the test specimen after stopping the injection of the additives into the brine of the test cell indicated a continuing type of protection.

As illustrated by the data in Tables I and III above, the presence of antimony sulfide in the inhibiting composition not only decreases the formation of scale from the ferrocyanide reacting with the dissolved ferrous ions but also increases the corrosion inhibition.

While the present combination of active components is especially effective for inhibiting scale formation from the ferrocyanide in the presence of ferrous ions in the brine, the following test shows that the effectiveness of such combination is largely independent of the iron content in the brine. These tests were carried out substantially as described above for those tests reported in Table III, but with varying contents of ferrous ion in a 3% sodium chloride brine and concentrations of 5 p.p.m. ferrocyanide ion, 15 p.p.m. borate ion and 5 p.p.m. antimony sulfide.

Table IV

Iron count (p.p.m. ferrous ion):	Percent inhibition
0	90
10	92
25	90
50	86

Further, the present inhibitor combination is effective in inhibiting corrosion in the presence of hydrogen sulfide as shown in the following test results obtained as above with a 3% sodium chloride brine containing 20 p.p.m. sulfide ion (which is comparable to sour crude brines). For purposes of the test, the sulfide ion was added as potassium sulfide. The test specimens were 1020 plain carbon steel and in one test, the brine was treated to contain 5 p.p.m. ferrocyanide ion, 15 p.p.m. borate ion and 5 p.p.m. antimony sulfide, and in another test the brine was treated with 10 p.p.m. ferrocyanide ion and 30 p.p.m. borate ion. The results are given in the following table.

Table V

Inhibitor composition:	Percent inhibition
Sb_2S_3+ferrocyanide+borate	79
Ferrocyanide+borate	40

Another desirable property of the present inhibitor combination is that it tends to inhibit emulsion formation, whereas dichromate, which sometimes is used as a corrosion inhibitor, has a strong emulsifying tendency. This distinction was found with an Inglewood crude oil which is known to emulsify in brine easily. The emulsion-inhibiting property of the present inhibitor combination is important since any inhibitor agent which promotes the formation of emulsion has limited usefulness.

In carrying out the treatment of a well in accordance with the present invention, a concentrated mixture of the antimony sulfide and ferrocyanide and borate ions in solution may be prepared and injected into the well to provide corrosion inhibition, either continuously at a measured rate or by batch treatment. In either case the amount of concentrated solution placed in the well is controlled to produce the desired level of concentration of the component ions in the well fluids. For example, a concentrated solution suitable for treating a well producing 100 barrels of brine a day may be made of the following proportions of components:

Antimony sulfide	lbs	6.1
Sodium hydroxide	lbs	3.0
Sodium ferrocyanide	lbs	8.6
Sodium tetraborate	lbs	22.3
Water	gals	200

This composition when introduced into the oil well continuously over a seven-day period will give a continuous concentration in solution of approximately 15 p.p.m. of antimony trisulfide, 15 p.p.m. of ferrocyanide ion and 55 p.p.m. of borate ion and will effectively inhibit corrosion of the ferrous metal surfaces exposed to the corrosive well fluid. This same proportion of components present in 100 barrels of brine may, of course, be used to inhibit effectively the corrosion of the walls of tanks or vessels in which well fluids are processed or stored. This same proportion of components, reduced or increased in quantity in accordance with the volume of brine to be inhibited, may, of course, be used to inhibit effectively the corrosion of the walls of tanks or vessels in which well fluids are processed or stored.

It will be appreciated that it is not necessary for the purposes of this invention to place the respective components in solution prior to the time they are introduced into the well fluids. It is possible, of course, to introduce these components into an oil well in solid form either singly or as a mixture and permit the solution to take place directly in the well fluids. Thus, the dry mixture of components may be introduced into the well in the form of pellets or sticks which may be weighted to sink to the bottom of the well where they will go into the solution. For example, a solid stick can be formed by melting sodium tetraborate decahydrate and stirring into the melt powdered sodium ferrocyanide and antimony sulfide until a homogeneous dispersion is obtained and then allowing the melt to solidify. The inhibiting mixture thus will be created in the lowermost portion of the apparatus which it is designed to protect, and its inhibiting action will be effective throughout all of the portions of the well and the apparatus associated therewith to which it is carried by the well fluids. This technique of introducing a dry mixture of the components into a corrosive fluid whose action it will inhibit is also applicable to flow lines, tanks and such other apparatus.

As illustrated above, this invention provides a method and compositions for protecting metal surfaces from the action of corrosive fluids by intermixing in solution in these fluids relatively low concentrations of antimony sulfide most effectively with ferrocyanide and borate ions for utility in the presence of brines of high salinity, ferrous ion content, carbon dioxide and hydrogen sulfide. Particularly, the method and composition of this invention are effective when employed with oil field brines to inhibit the corrosion of the ferrous metal apparatus with which the brines come in contact.

It is apparent that many modifications and variations of this invention may be made without departing from the inventive concept. The foregoing examples are presented by way of illustration of the several embodiments of the invention, and it is not intended that they be interpreted as limitations of the scope of the appended claims.

We claim:

1. In the method of inhibiting corrosion of ferrous metal surfaces in contact with an oil field brine containing at least 5 p.p.m. of ferrous ion which comprises incorporating in said brine a water-soluble ferrocyanide in an amount sufficient to produce in solution in said brine a concentration of 5 to 140 p.p.m. of ferrocyanide ion and a water-soluble borate in an amount sufficient to produce a concentration of 5 to 140 p.p.m. of borate ion, the improvement for inhibiting said corrosion which comprises also incorporating in said brine antimony trisulfide in an amount sufficient to reduce substantially the tendency of ferrocyanide scale to be produced, and said amount being from 0.1 to 50 p.p.m.

2. The method of inhibiting corrosion of ferrous metal surfaces in contact with an oil field brine containing 10 to 100 p.p.m. of ferrous ion, which method comprises incorporating in said brine a water-soluble ferrocyanide and a water-soluble borate in amounts sufficient to produce in solution 5 to 140 p.p.m. of each of ferrocyanide and borate ions together with a caustic solution of at least one antimony trisulfide in an amount to produce in solution antimony trisulfide in a concentration of 1 to 10 p.p.m. for each 10 p.p.m. of ferrocyanide ion.

3. The method of inhibiting corrosion of ferrous metal surfaces exposed to oil well fluids including crude oil, brine, carbon dioxide and hydrogen sulfide and characterized by a pH above 5.0 which comprises incorporating with said fluids in an intimate mixture prior to the time said fluids contact said ferrous metal surfaces an aqueous solution of ferrocyanide in an amount to produce a concentration of ferrocyanide ion in said fluids in the range of 5 p.p.m. to 140 p.p.m., an aqueous solution of a water-soluble borate in an amount to produce a concentration of borate ion in said fluids of not less than 5 p.p.m. and an aqueous caustic solution of antimony trisulfide in an amount to produce a concentration thereof in said fluids of 0.1 to 15 p.p.m.

4. A corrosion-inhibiting composition consisting essentially of a water-soluble ferrocyanide in an amount sufficient to produce in an aqueous solution a concentration of 5 p.p.m. to 140 p.p.m. of ferrocyanide ion, a water-soluble borate in an amount sufficient to produce a concentration of 5 p.p.m. to 140 p.p.m. and antimony sulfide in an amount sufficient to produce a concentration of 0.1 to 20 p.p.m. of the sulfide.

5. A corrosion-inhibiting composition consisting essentially of a water-soluble ferrocyanide in an amount sufficient to produce in an aqueous solution a concentration of 5 to 140 p.p.m. of ferrocyanide ion, a water-soluble borate in an amount sufficient to produce a concentration of 5 p.p.m. to 140 p.p.m. and a caustic solution of antimony sulfide in an amount sufficient to produce a concentration 0.1 to 20 p.p.m. of the sulfide.

6. The method of inhibiting corrosion of ferrous metal apparatus in an oil well containing fluids comprising crude oil and brine and in which said brine contains in solution at least 5 p.p.m. of borate ion, which comprises combining with said borate-containing brine in the well a water-soluble ferrocyanide in an amount sufficient to produce a concentration of ferrocyanide ion in said brine of not less than 5 p.p.m. and antimony sulfide in an amount of 0.1 to 20 p.p.m. in said brine.

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JULIUS GREENWALD, *Primary Examiner.*