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COMPOSITION AND METHOD FOR INHIBITING CORROSION IN OIL WELLS

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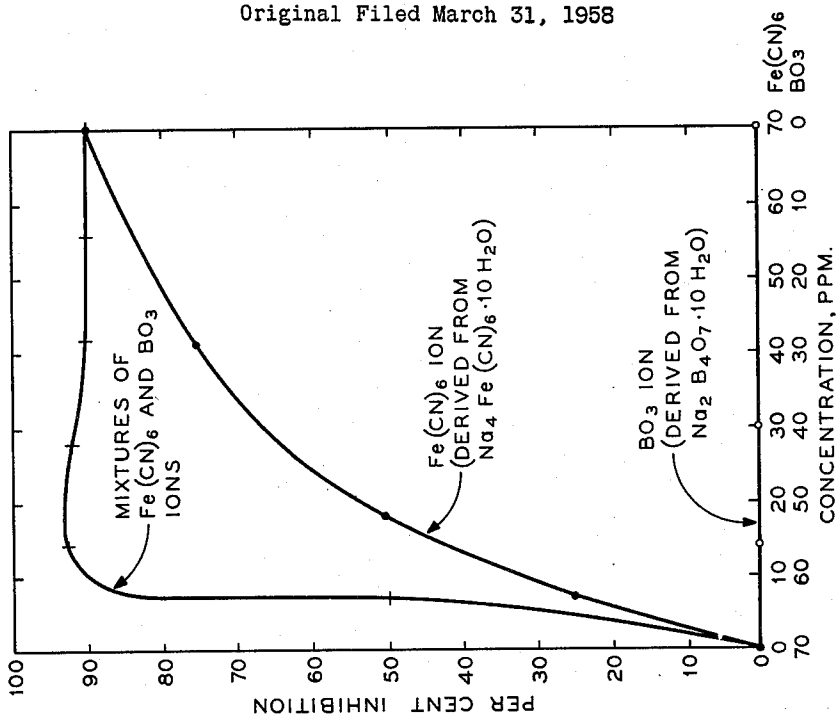


FIG. 2

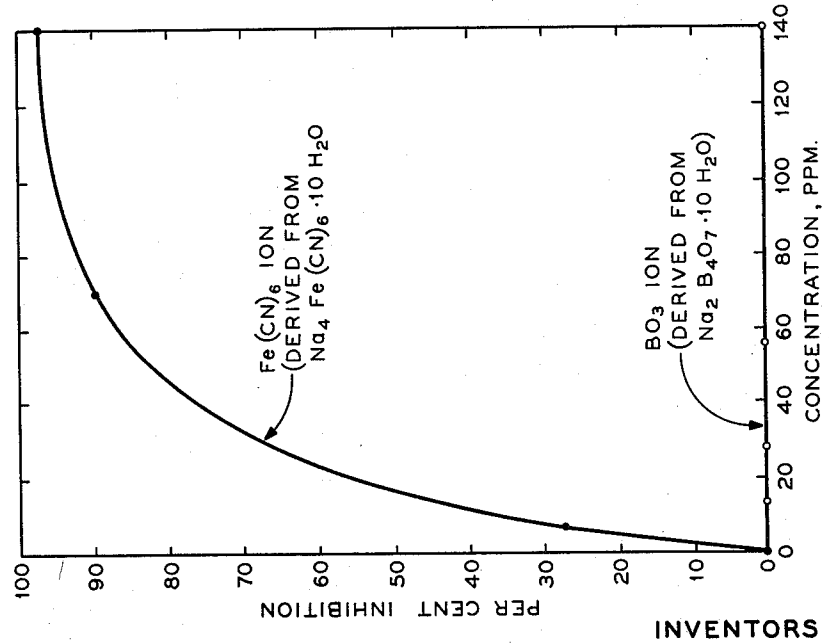


FIG. 1

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COMPOSITION AND METHOD FOR INHIBITING CORROSION IN OIL WELLS

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Continuation of applications Ser. No. 725,001, Mar. 31, 1958 and Ser. No. 725,085, Mar. 31, 1958. This application Dec. 1, 1961, Ser. No. 159,814

11 Claims. (Cl. 166—1)

This invention relates to a method for inhibiting the corrosion of metal surfaces and has particular pertinence 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.

This application is a continuation of applications Serial Nos. 725,085, filed March 31, 1958, entitled "Composition for Inhibiting Corrosion"; and 725,001, filed March 31, 1958, entitled "Method for Inhibiting Corrosion in Oil Wells," both now abandoned.

The usual brines found in subterranean formations have a relatively high saline content, principally sodium chloride, and contain also carbon dioxide, both in solution and as a gas. Other substances, such as hydrogen sulfide, may be contained in the well water in various localities. The brine is therefore the corrosive medium which attacks the metal surfaces with which it comes in contact and, perhaps of more pertinence, creates an environment in which the metal surfaces are more susceptible to electrochemical and electrolytic corrosion. This 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 it. The problem of protecting tubing rods and pumps in pumping wells from the effects of corrosion and of the casing and tubing in flowing wells has received a great amount of attention in oil field practice. Corrosion of the interface region between the separated brine and crude oil in stock tanks and storage tanks and the corrosive effects of well fluids on the walls of wash tanks also present this problem.

It is well known that corrosive well fluids can perforate a tubing string or destroy a string of sucker rod or impair the efficiency of a submerged pump in a relatively short time. Obviously, where the well fluids cause corrosion of ferrous metal, the life of the metal equipment is appreciably reduced. The end result, of course, requires that the well be taken out of production and that the damaged equipment be replaced before oil can again be produced from it.

It will be appreciated that many variable factors contribute to the corrosive environment found in the ordinary oil well. 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 available to contribute to the corrosive conditions, particular components of the crude oil and other factors, some of which are still unknown. As a result, the development of corrosion inhibitors in 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.

Various inhibitors have been developed from time to time to protect oil field equipment from corrosion and have done so with greater or less success. An example of one of the more successful inhibitor compositions comprising a solution of arsenous oxide in aqueous alkali

may be found in United States Patent 2,635,698 issued April 21, 1953, to Rohrback and McCloud. However, to exemplify the effects of some of the well fluid components on the action of a corrosion inhibitor, it has been found that this inhibitor is most effective in weak acid solutions which are free from oxygen and hydrogen sulfide, components which appear in appreciable amounts in oil well fluids found in many places. Thus, although the arsenical inhibitor is very useful in oil wells and has received considerable commercial acceptance, the particular components of oil well fluids in a particular environment to which the apparatus in the well is exposed may limit the effectiveness of this inhibitor in certain applications. Furthermore, some materials which might be expected to be useful as corrosion inhibitors in oil wells combine or react with components of the well fluids to produce undesirable side effects, such as promoting hydrogen penetration of the ferrous metal or causing the formation of blisters on it. This explanation is given to illustrate the imponderables which affect the action of a corrosion inhibitor in oil field use.

One of the objects of this invention is to provide a novel corrosion inhibitor composition for inhibiting the corrosion of metal surfaces exposed to corrosive fluids.

A further object of this invention is to provide a novel composition for inhibiting the corrosion of ferrous metal equipment installed in a producing oil well.

Another object of this invention is to provide a composition for inhibiting the corrosion of metal surfaces in contact with saline water or acetic saline solutions which contain free oxygen and/or hydrogen sulfide.

One of the objects of this invention is to provide a novel method for inhibiting the corrosion of ferrous metal equipment installed in a producing oil well.

Another object of this invention is to provide a method for inhibiting the corrosion of metallic surfaces in contact with oil well brines which contain a water-soluble borate.

Other objects will become apparent as the description of the invention proceeds.

The composition of this invention comprises a mixture of a water-soluble ferrocyanide and a water-soluble borate. The components of the composition are selected to give in an aqueous solution a concentration of ferrocyanide ion of at least 5 p.p.m. together with a concentration of borate ion of at least 5 p.p.m. The corrosion inhibiting properties of the composite solution are greatly superior to those of an aqueous solution of either of the two ions used alone. It has been found that if the ratios of the components are maintained within the limits which will be set forth hereinafter, a very effective corrosion inhibitor of general utility in oil field applications may be obtained with relatively low concentrations of the inhibiting compound in the corrosive fluids.

This invention also comprises a method for inhibiting the corrosion of metal surfaces exposed to corrosive well fluids by forming in the well brine a mixture of a ferrocyanide ion and a borate ion, both in aqueous solution. In those instances where the well brine naturally contains a borate in solution, then in accordance with the method of this invention a sufficient quantity of a water-soluble ferrocyanide is introduced into the well fluids to produce in the brine a concentration of ferrocyanide ion of at least 5 p.p.m. If the well brine is lacking in borate, or if the concentration of the borate ion in solution is below that desired, then both a water-soluble ferrocyanide and a water-soluble borate are introduced into the well fluids to produce the mixture of ions in the brine. The mixture of the solutions of the ferrocyanide ion and the borate ion produces a greatly increased corrosion inhibiting effect over that of aqueous solutions of these ions

when used alone in the ranges of concentration to which this invention is directed.

It has been found that the enhanced corrosion-inhibiting properties of the mixture of the water-soluble ferrocyanide ion and borate ion is effective in the presence of various cations including sodium, potassium, lithium, ammonium, magnesium, and calcium ions. Hence, any water-soluble ferrocyanide and borate which yield the ferrocyanide and borate ions in aqueous solution at the levels of concentration to be described hereinafter are effective for the purposes of this invention.

The accompanying drawings which form a part of this specification illustrate in graph form the corrosion-inhibiting effect of the separate components of this inhibitor mixture and also the corrosion-inhibiting effect achieved by mixing the components in accordance with this invention. For this purpose sodium ferrocyanide and sodium tetraborate were used to provide the ferrocyanide ion and borate ion in solution.

In the drawings:

FIG. 1 is a graph showing the corrosion-inhibiting effects on a ferrous metal surface of an aqueous solution of sodium ferrocyanide wherein the concentration is expressed in terms of ferrocyanide, $Fe(CN)_6$, ions and of an aqueous solution of sodium tetraborate wherein the concentration is expressed in terms of borate, BO_3, ions.

FIG. 2 illustrates in graph form the corrosion-inhibiting effects of aqueous solutions of different concentrations of the components taken separately and the synergistic effect obtained by a mixture of these components in certain ratios of concentrations.

The tests from which were obtained the data used to plot the graphs of FIGS. 1 and 2 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 sodium chloride, and 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. 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 water-soluble ferrocyanide and borate ions separated from each other and the effects obtained by having these ions 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 plotted as the ordinates of the graphs of the drawings in terms of percent inhibition. This percentage is derived from the relationship

$$\frac{100\ (Sa-Sb)}{Sa}$$

where:

Sa is the base rate of corrosion of the test specimen

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

It will be noted from the graph of FIG. 1 that sodium tetraborate has no apparent corrosion inhibiting ability in the concentration range of 0 to 70 p.p.m. BO_3 The effectiveness of the ferrocyanide ion increases on a smooth curve which becomes asymptotic at the level of 97.5% corrosion inhibition at a concentration of approximately 140 p.p.m. $Fe(CN)_6$ ion.

The graph of FIG. 2 again illustrates the corrosion-inhibiting effectiveness of the ferrocyanide ion plotted from left to right on the chart in the ranges of increasing concentration in the brine. The graph of the effectiveness of the borate ion is plotted in ranges of decreasing concentration in the brine from left to right so that the maximum concentration plotted of 70 p.p.m. is on the left side of the chart, and the concentration decreases toward the right to zero. The third curve on the chart illustrates the corrosion-inhibiting effect obtained when the ferrocyanide ion and the borate ion are present simultaneously in solution in the brine in the ratios indicated on the lower margin.

FIG. 2 clearly illustrates that when the ferrocyanide ion and the borate ion are both present in solution in the brine, the corrosion of the test specimen is inhibited much more effectively than can be accounted for by the additive corrosion-inhibiting effects of the separate ions. Thus, when a concentration of approximately 14 p.p.m. of the ferrocyanide ion together with a concentration of approximately 56 p.p.m. of the borate ion is present simultaneously in solution in the brine, approximately 92.5% corrosion inhibition is obtained. As noted from the graphs of the effectiveness of the separate ions when used alone, the borate ion at this concentration has a negligible corrosion-inhibiting effect, and the ferrocyanide ion at this concentration is only 42.5% effective. Thus, the effectiveness of the combined ions in solution at these concentrations is over twice that of the ions used alone.

The synergistic effect of the combination is clearly indicated by these particular tests throughout a range of concentrations of from less than 5 p.p.m. to approximately 70 p.p.m. of the ferrocyanide ion in solution and for a concentration of the borate ion in solution above 5 p.p.m. for the conditions under which the data plotted in the graphs were obtained. Effective corrosion inhibition can be obtained with a concentration of the water-soluble ferrocyanide ion in solution in the range of 5 to 140 p.p.m. together with the water-soluble borate ion in solution in the range of 5 to 140 p.p.m. The preferred ranges for most effective corrosion inhibition at the minimum total concentration of the respective ions in solution are 7 to 100 p.pm. of the ferrocyanide ion and at least 10 p.p.m. of the borate ion.

When the method of this invention is applied to ferrous metal surfaces, a very adherent and tough layer or film of noncorrosive material is deposited on them. During the tests described hereinabove, the film produced on the test specimen lasted several days after the injection of the inhibitor into the brine of the test cell was stopped. In treating oil wells, batch injection of a water-soluble ferrocyanide ion into a well, the fluids of which contained a water-soluble borate, proved to be satisfactory for continuously protecting the ferrous metal apparatus in the well from the effects of the corrosive well fluids.

The following data are presented as a further exemplification of the corrosion-inhibiting effects of the composition of this invention when ratios of components, other than those plotted on the graph of FIG. 2, are used. These data were obtained in the same apparatus and with conditions of operation comparable to those explained heretofore.

Sodium ferrocyanide was used as the source of the ferrocyanide ion and sodium tetraborate as the source of the borate ion.

It is apparent from the above data that the synergistic effect achieved by the method of this invention is not adversely affected by the presence in solution of the various alkali and alkaline earth metal ions, nor of the ammonium ion.

In the evaluation tests and field use of this invention, neither the ferrocyanide alone nor the borate alone provided effective corrosion inhibition of the ferrous metal surfaces at the concentrations used. However, by making these ions simultaneously available in solution at these same concentrations, the corrosion of the ferrous metal surfaces exposed to the inhibited corrosive fluid was greatly reduced. This improvement in the effectiveness of the combined ions is not predictable from the action of the component ions taken alone or from their known chemical behavior.

This invention, therefore, provides a method for protecting metal surfaces from the action of corrosive fluids by intermixing in solution in these fluids relatively low concentrations of ferrocyanide ion and borate ion. Particularly, the method and composition of this invention is 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. A corrosion-inhibiting composition consisting essentially of a water-soluble ferrocyanide and a water-soluble borate, said water-soluble ferrocyanide being present in an amount to produce a concentration of ferrocyanide ion in aqueous solution of 5 p.p.m. to 140 p.p.m. and said water-soluble borate being present in an amount to produce a concentration of borate ion in aqueous solution of 5 p.p.m. to 140 p.p.m.

2. A corrosion-inhibiting composition for inhibiting the effect of a corrosive aqueous fluid on a metal surface comprising a mixture of a water-soluble ferrocyanide and a water-soluble borate, said ferrocyanide being present in said composition in an amount to produce in said aqueous fluid a concentration of ferrocyanide ion of 5 p.p.m. to 140 p.p.m. and said borate being present in said composition in an amount to produce in said aqueous fluid a concentration of borate ion of 5 p.p.m. to 140 p.p.m.

3. A corrosion-inhibiting composition consisting essentially of sodium ferrocyanide decahydrate and a sodium tetraborate decahydrate, said sodium ferrocyanate decahydrate being present in the range of substantially 3% to 95% by weight of said composition, said composition being capable of dissolving in water to produce in solution a concentration of ferrocyanide ion of not less than substantially 5 p.p.m. and a concentration of borate ion of not less than substantially 5 p.p.m.

4. A corrosion-inhibiting composition comprising an aqueous solution of a mixture of sodium ferrocyanide decahydrate and sodium tetraborate decahydrate, said sodium ferrocyanide decahydrate being present in the range of substantially 0.2% to 35% by weight of said composition, said soduim tetraborate decahydrate being present in the range of substantially 0.8% to 4% by weight of said composition.

5. The method of inhibiting corrosion of ferrous metal apparatus in an oil well having a temperature above about 145° F. and 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 a 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.

6. The method of inhibiting corrosion of ferrous metal surfaces in contact with an oil field brine which comprises incorporating with said brine so that both are present at the same time a water-soluble ferrocyanide in an amount sufficient to produce in solution a concentration of ferrocyanide ion in the range of 5 p.p.m. to 140 p.p.m. and a water-soluble borate in an amount sufficient to produce in solution a concentration of borate ion in the range of 5 p.p.m. to 140 p.p.m.

7. The method of inhibiting corrosion of ferrous metal surfaces in an oil well having a temperature above about 145° F. which is producing fluids comprising crude oil and brine and in which said brine contains in solution carbon dioxide and at least 5 p.p.m. of borate calculated as BO_3 ion which comprises combining with the borate-containing brine in the well a water-soluble ferrocyanide in an amount sufficient to produce a concentration of ferrocyanide ion in solution in said brine in the range of 5 p.p.m. to 140 p.p.m.

8. The method of inhibiting corrosion of ferrous metal surfaces in an oil well having a temperature above about 145° F. and containing fluids including crude oil and brine which comprises introducing into said fluids an aqueous solution of a ferrocyanide and a borate in an amount sufficient to produce a concentration of ferrocyanide ion in said fluids of not less than 5 p.p.m. and a concentration of borate ion calculated as BO_3 ion in said fluids of not less than 5 p.p.m.

9. 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 5.5 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., and an aqueous solution of a salt of boric acid in an amount to produce a concentration of borate ion in said fluids of not less than 5 p.p.m.

10. A method of inhibiting corrosion of ferrous metal surfaces in contact with an oil field brine in an oil well which comprises determining the presence and concentration of any borate ion which may be in said brine, adding to said brine a water-soluble borate in an amount sufficient based upon the borate ion concentration of said brine to bring the concentration of borate ion in said brine at least into the range of 5 p.p.m. to 140 p.p.m. and adding to said brine sufficient water-soluble ferrocyanide to produce a concentration of ferrocyanide ion in the range of 5 p.p.m. to 140 p.p.m.

11. The method of inhibiting corrosion of ferrous metal apparatus in an oil well having a temperature above about 145° F. and containing fluids comprising crude oil and brine and in which said brine contains in solution borate ion in the range of 5 p.p.m. to 140 p.p.m. which comprises combining with the borate-containing brine in the well a water-soluble ferrocyanide in an amount sufficient to produce a concentration of ferrocyanide ion in said brine in the range of 5 p.p.m. to 50 p.p.m.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,127,932 April 7, 1964

Frederic W. Schremp et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 14, for "this" read -- the --; column 6, line 61, for "71" read -- 7 --; column 7, line 52, for "ferrocyanate" read -- ferrocyanide --; line 72, for "a", first occurrence, read -- the --.

Signed and sealed this 4th day of August 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

UNITED STATES PATENT OFFICE

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