

UNITED STATES PATENT OFFICE

2,493,462

INHIBITING CORROSION IN WELLS

Paul L. Menaul, Tulsa, Okla., assignor to Stanolind Oil and Gas Company, Tulsa, Okla., a corporation of Delaware

No Drawing. Application December 28, 1946, Serial No. 719,117

15 Claims. (Cl. 252—8.55)

1

This invention relates to a method of inhibiting corrosion and more particularly to a method of, and a corrosion inhibitor for, preventing or reducing corrosion of metal parts, such as flow lines, wellhead equipment, rods, tubing, etc., used in connection with petroleum wells.

The well corrosion encountered in producing wells presents a major problem in maintenance of equipment. The inspection and replacement of tubing and wellhead equipment, including the cost of work-over jobs is an important factor in the economy evaluation of fields which produce corrosive well fluids. Therefore, much work has been and is being done to remedy the particularly vicious corrosion encountered in high pressure wells of the gas-condensate type.

I have discovered that there are organic acids present in many highly corrosive well fluids, particularly in the well water or brine withdrawn from high-pressure distillate wells. While the origin of these organic acids is not known, it is probably in the buried vegetation of past geologic ages. Their presence in distillate well production is assumed to be due to the fact that the corrosive organic acids are volatile at temperatures encountered in deep distillate wells plus the fact that they are highly soluble in the water. At lower temperatures such as are encountered near the wellhead these acids may precipitate or coprecipitate with water on the cold metal parts causing the severe corrosion.

Rapid corrosion also occurs when crude oil containing soluble sulfides is produced and the corrosion of oil field equipment is especially severe in areas where brines are associated with the sour crudes. These corrosive sulfide brines are believed to include alkali sulfides, alkaline earth metal sulfide, and acid sulfide such as hydrogen sulfide. It has been found that sulfide corrosion occurs in both acidic sulfide brines and in alkaline sulfide brines with a pH below 9. Neutralization of acidic component does not inhibit corrosion because the salts are readily hydrolyzed to bases and volatile acids which may condense on the cold metal parts.

It is, therefore, an object of this invention to provide a method for inhibiting corrosion in wells due, for example, to organic acids or sulfides. It is a further object of this invention to provide an inhibitor for such corrosion and a method by which it may be introduced into the well in such a manner that it will inhibit corrosion by the produced well fluids for a substantial period of time. A further object to provide such an in-

2

hibitor that will not form harmful solid reaction products or corrosive compounds when dispersed in the well fluids. Other objects and advantages will be apparent from the following description of examples of my process and inhibitor.

Organic acids which I have identified are acids of aliphatic hydrocarbons, such as formic, acetic, propionic, butyric, valeric, etc. In one sample of well water they were found to be in a concentration of about 250 parts per million. The actual concentration was probably higher because of the difficulty in quantitatively recovering these acids from such dilute solutions. In order to ascertain the possible corrosive effects of these acids, a liter of solution of acids (0.5%) which were extracted from well fluids was compared with a similar solution of propionic acid and one of caproic. The solution of well acids had a pH of 4.9 while the other solutions were 4.5. The following table will indicate the relative corrosion of mild steel panels at 150° F. when exposed to the above-mentioned synthetic and actual solutions:

Solution	pH	Loss in mg./in. ² /day
Propionic acid.....	4.5	12.1
Caproic acid.....	4.5	9.9
Acids extracted from well water.....	4.9	7.4

A second comparison was made between a dilute solution of the well acids compared to that of propionic acid by noting their respective effect on mild steel panels at a temperature of 150° F. and at an exposure of 12 hours. The results are set forth in the following table:

Solution	Percent	Concentration of Iron in Solution (P. P. M.)
Propionic acid.....	0.1	383
Acids extracted from well water.....	0.1	320

Known treating agents have been introduced into the distillate wells and in some cases favorable results were obtained from the point of inhibiting corrosion but serious scale formation has resulted from the treating agent or from a reaction product of the treating agent, and the dissolved contents of the well fluids. As a consequence of such scale formation production is reduced and shutdowns result. For example, it has been found that the injection of ammonium hydroxide in the corrosive condensate wells will

prevent corrosion. True condensate production contains no appreciable amount of calcium or scale forming elements and the neutralization with ammonium hydroxide does not produce a scale. However, some wells classed as corrosive condensate wells also produce a formation water which is very acidic and high in calcium content.

Thus, by treating well fluids containing these organic acids to reduce the acidity of the solution or neutralize them, the corrosive properties of the well fluids are substantially reduced but if formation water high in calcium content is also produced there is a scale formation.

Bone oil is a by-product of the manufacture of bone charcoal and is a complex mixture including pyridine and quinoline, together with a tar fraction which is insoluble in well fluids. If the entire bone oil fraction were employed as the corrosion inhibiting agent, the insoluble tar fraction tends to form an amorphous precipitate in the bottom of the well and this precipitate would adversely affect production by tending to plug the well pores. I have found that a very useful corrosion inhibitor can be obtained by extracting a quantity of bone oil with at least an equal quantity of a hydrocarbon such as kerosene to produce an extract of the soluble constituents. Ethyl alcohol is not a suitable extractant because bone oil is completely soluble therein. Some residue is obtained with carbon tetrachloride and with benzene but extraction with heptane produced the largest amount of an insoluble precipitate. A particularly desirable way to produce the precipitate-free inhibitor is to first dissolve the bone oil in a portion of the produced well fluids, thereby introducing into the well only that portion of the bone oil which is soluble in the particular well fluids to be encountered.

The extent of corrosion is indicated by the concentration of iron in the well effluent or produced water. It has been found that the corrosion can be materially reduced or inhibited by adding to the well an extract of about 1 gallon of bone oil to about ten barrels of acidic brine produced. For example, in one well producing about twenty barrels of oil per day and twenty barrels of water per day having a pH of approximately 5.7, the introduction of an extract of about one gallon of bone oil per day was adequate to inhibit corrosion completely. It is contemplated, however, that in general an extract of between about 0.25 gallon and about 1.5 gallons of bone oil per day will effectively inhibit corrosion and maintain the iron content of the produced well fluids below about twenty-five parts per million.

A comparison of the inhibiting power of bone oil compared with the same concentrations of selected constituents of commercial bone oil under the same conditions has clearly demonstrated that the known constituents of commercial bone oil including acetonitrile, quinoline, pyridine, triethylamine and aniline, do not have an inhibiting power which even approaches that of commercial bone oil or extracts of bone oil. To demonstrate this fact a series of tests were conducted which consisted in exposing a mild steel panel of 2 square inches surface area, to 5 liters of deaerated solution of acetic acid in a concentration of 600 P. P. M. acetic acid to which the inhibitor was added in a concentration of 500 P. P. M., the panels were immersed in the solutions for three days (73 hrs.) at 160° F. Nearly

complete inhibition was obtained with bone oil whereas the percent inhibition with the separate constituents ranged as low as zero and averaged less than 30 percent as effective as the bone oil.

The mechanism by which this complex mixture of bone oil, or an extract from which the insoluble tar has been removed, effectively inhibits corrosion is not entirely understood. Nevertheless, I have found that great advantage can be obtained by the addition of my inhibiting agent to acidic brines before they contact the metal parts associated with a well. This treatment counteracts almost completely the normal corrosive tendency of acidic brines even under elevated temperature conditions.

In practicing my improved method, as for example, in inhibiting the corrosion in a high pressure distillate well wherein organic acids are found in the well fluids, I introduce into the well, preferably at the bottom of the well below the mouth of the tubing from which the well fluids are withdrawn, a quantity of the treating material sufficient to inhibit the corrosive action of the organic acids produced. If desired, the segregated or confined quantity of the material can be disposed in the well for the controlled release of the treating agent over a substantial period of time, thus continually preventing corrosion of the metal parts with which the well fluids come into contact.

To effect the introduction of a treating agent at the base of the well in my preferred manner, and particularly where the well is producing and a packer set between the tubing and the casing prevents a communication from the surface with the bottom of the well, I may introduce into the well hole a receptacle for the treating agent which may be positioned and retrieved from the base of the well by the customary running and retrieving tool. This receptacle, if the treating agent is a liquid, for example bone oil, may comprise a metal bottle having an automatically operated valve means in the opening thereof and a pressure-equalizing tube for permitting the well fluids to flow in behind the treating agent which flows from the bottle against the pressure within the well when the valve is open. By selecting the proper size of orifice on the bottle, the flow of treating agent can be controlled. Where the temperatures of the well are sufficiently high to vaporize the contents of the bottle, the treating agent will be discharged at a continuous rate into the well fluids over a period of time determined by the quantity of material that the bottle will contain. The vapors of the treating agent may, however, be then absorbed by the well fluids.

The preferred embodiment of my invention described herein is for the purpose of illustration only and is not intended to limit the scope of the invention defined by the appended claims, since it is apparent that the principles of my invention may be applied generally by those skilled in the art in view of the foregoing description.

I claim:

1. The method inhibiting the tendency of corrosive brines containing low-boiling organic acids to attack metal surfaces which comprises the step of mixing with said brines a small amount of bone oil.

2. The method of protecting ferrous metals from attack by aqueous fluids having organic acids dissolved therein which comprises the step

of dispersing a small amount of bone oil in the aqueous fluids.

3. The method of treating organic acid-containing well fluids to inhibit its tendency to cause corrosion which includes the step of mixing with the well fluids being produced a small amount of bone oil.

4. The method of inhibiting corrosion in wells wherein well fluids containing organic acids are produced, the step which comprises treating the well fluids with bone oil.

5. The method of inhibiting corrosion of metals in wells due to acidic brine containing organic acids produced from the well, comprising the step of commingling bone oil with the well fluids in the ratio of about one gallon of bone oil to ten barrels of acidic brine produced.

6. The method of inhibiting corrosion of ferrous metals by well fluids containing organic acids and brine which comprises supplying to well fluids in a lower region of a producing well a minor quantity of bone oil said quantity being substantially proportional to the volume of brine produced.

7. The method of inhibiting the tendency of corrosive hydrocarbon well fluids containing organic acids to attack metal surfaces which comprises the steps of introducing a small amount of bone oil near the base of the well at spaced intervals of time while producing said well, said amount being substantially proportional to the volume of brine produced.

8. The method of inhibiting the normal tendency of organic acids in a corrosive mixture of dissimilar fluids to attack metal surfaces which comprises the step of adding to said mixture a small amount of bone oil which is dispersed in at least one of said dissimilar fluids.

9. The method of treating organic acid-containing well fluids to inhibit their tendency to cause corrosion which includes the step of dispersing in said well fluids a small amount of bone oil soluble in hydrocarbons.

10. The method of inhibiting corrosion of ferrous metals in distillate wells due to water-soluble organic acids, the steps which comprise dissolving bone oil in a kerosene fraction and dispersing the dissolved bone oil in the well fluids at a low point in the well from which they are produced.

11. The method of inhibiting the attack of ferrous metals by normally corrosive aqueous fluids containing water-soluble organic acids and produced with a major proportion of hydrocarbon fluids which comprises dispersing in the fluids a small amount of bone oil soluble in said hydrocarbon fluids.

12. The method of producing a distillate well fluid which is normally corrosive due to acidic brine containing organic acids, the steps which

comprise segregating a small quantity of distillate well fluid, dissolving a small amount of bone oil in said well fluid, and dispersing said dissolved bone oil in a lower region of said well, said small amount of bone oil being proportioned to the quantity of acidic brine produced.

13. In the method of inhibiting the attack of ferrous metals by normally corrosive, non-aqueous and aqueous well fluids containing water-soluble organic acidic material wherein corrosion is evidenced at the surface by the iron content of the aqueous well fluids produced, the steps which comprise dispersing in the well fluids a small amount of a bone oil fraction soluble in the non-aqueous well fluids produced by said well, said small amount being sufficient to maintain the iron content of the aqueous well fluids below about 50 parts per million.

14. A corrosion inhibitor for wells producing mixtures of aqueous and non-aqueous well fluids containing organic acidic materials comprising a light hydrocarbon fraction having dissolved therein an extract of commercial bone oil obtained by treating said bone oil with a portion of the produced well fluids.

15. A corrosion-inhibited well fluid produced from a high-pressure distillate well comprising a mixture of aqueous and non-aqueous liquids containing organic acidic materials and an added corrosion inhibiting composition, which composition is soluble in said well fluids and which consists essentially of a light hydrocarbon having dissolved therein an extract of bone oil which is substantially free from substances precipitable by said well fluid.

PAUL L. MENAUL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,248,302	Foster	Nov. 27, 1917
1,678,775	Gravell	July 31, 1928
1,873,084	Walker	Aug. 23, 1932
1,877,504	Grebe et al.	Sept. 13, 1932
1,988,823	Winning et al.	Jan. 22, 1935
2,225,695	Henderson	Dec. 24, 1940
2,357,559	Smith	Sept. 5, 1944
2,441,848	Sexton	May 18, 1948
2,441,849	Sexton et al.	May 18, 1948

OTHER REFERENCES

Bannister et al.: An X-Ray Study of Diamonds, article in *Mineralogical Magazine*, vol. 26, 1943, pages 315-321.

Condensate Corrosion, article in *The Oil Weekly*, May 6, 1946, page 32.