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INHIBITING CORROSION DUE TO SULFUR COMPOUNDS

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12 Claims. (Cl. 252—8.55)

This invention relates to a method of inhibiting the corrosive action of soluble sulfur compounds on ferrous metal equipment. More particularly, the invention relates to means for inhibiting the rapid corrosion of well tubing and/or pump rods which has heretofore occurred in wells where the well fluid contains both water and hydrogen sulfide.

Crude oil containing sulfur compounds, particularly sulfides, is produced in many of the major producing areas of the United States. These corrosive sulfides may be either alkali metal sulfides, alkaline earth metal sulfides, and/or acid sulfides, such as hydrogen sulfide. Hydrogen sulfide is very soluble in both fresh and salt water; and, when a well produces both water and a sulfide, the iron and steel equipment in the well is corroded rapidly, due to the active formation of iron sulfide. This corrosion takes place at a pH below about 9, i. e., in both acidic and mildly alkaline sulfide brines. This range embraces virtually all brines produced from oil and gas wells, where the problem is most severe.

In some areas where the production from oil and gas wells contains sulfides, corrosion is so severe that a string of new pump rods may start breaking after as little as 40 days of use, and new tubing may be corroded to perforation in as little as six to eight months. The cost of replacing producing equipment in such wells often renders them uneconomical to operate, long before the producing reservoir has been depleted.

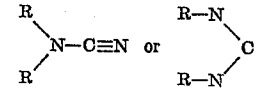
In an effort to reduce the cost of maintaining production and collection equipment, it has heretofore been the practice to treat wells producing corrosive oil-brine mixtures with caustic soda, soda ash, ammonium hydroxide, cyanides, and other alkaline solutions in sufficient proportion to neutralize the acidic sulfur components. These neutralization treatments obviously require the introduction into the well of a very considerable amount of the treating agents, are correspondingly expensive, and have not, in the main, proven satisfactory. The use of insufficient alkali may cause the sulfide corrosion to be even more severe, and the injection of alkaline solutions into wells producing brines carrying calcium and magnesium in solution may cause the deposition of scale which will plug the tubing and working parts of the oil well pump.

Various other treatments, particularly treatments which produce a protective film on the metal parts, have been tried with considerable success. The major difficulty with such treatments appears to be in the frequency at which the treating agent must be added to the well. That is, the film produced appears to be erroded or corroded away so rapidly that the treating agent must be added to the well continuously, or at very short intervals. Also, most of the treating agents do not give adequate protection against corrosion.

It is an object of this invention to provide an improved method of inihibiting corrosion of ferrous metals. Another object of this invention is to provide an improved method of inhibiting sulfide corrosion in oil or gas wells.

Another object of this invention is to provide an improved corrosion inhibitor for sulfide corrosion of ferrous metals in oil and gas wells. A further object of this invention is to provide an improved inhibitor for sulfide corrosion of ferrous metals which will unite with the metal in the presence of a corrosive sulfide and form a protective film that is very stable. Other objects of this invention will become apparent as the description thereof proceeds.

This invention comprises, in brief, the addition of a cyanamide to a corrosive well in which the corrosion is due to a soluble sulfide, the amount of cyanamide being sufficient to form a protective film on the ferrous metal parts in the well. The inhibitor comprises, more specifically, any of a group of compounds such as hydrogen cyanamide, an alkali or alkali earth metal cyanamide, or an alkyl or allyl cyanamide. It also includes the dicyanamides and dicyandiamides. The inhibitor, therefore, includes generally the compound:



in which (>N—C≡N) or (—N=C=N—) is the characteristic cyanamide radical and (R—) is an organic radical, particularly an alkyl, an allyl, or another cyanamide radical, or an inorganic radical, particularly hydrogen, or a metal.

Typical inhibitors of this class include hydrogen, calcium, barium, and magnesium cyanamide, dimethyl, diethyl, di-isopropyl, and diallyl cyanamide. The dimer in which one R in the above inhibitor molecule represents another cyanamide radical is a very desirable inhibitor. The dimer includes the dicyanamide and the dicyandiamide, both of which include the cyanamide radical. Examples are sodium, calcium, barium, and magnesium dicyanamide and hydrogen dicyandiamide. The trimer, however, does not contain the typical cyanamide radical. Melamine, a trimer, for example, appears to be ineffective as a sulfide corrosion inhibitor. The cyanamides which are completely water soluble or miscible with water are preferred, but all of these compounds appear to be sufficiently soluble to provide protection. In some cases, the less water-soluble cyanamides are desirable since they can be placed in the well in large amounts, the low solubility permitting the water to be treated over many weeks or months.

As an example of the effectiveness of the cyanamides to inhibit sulfide corrosion, cleaned 1" x 1" panels of mild steel were weighed and submerged in one liter of a brine having a pH of 6.5 and containing between 800 and 1,000 p. p. m. hydrogen sulfide. The concentration of the inhibitor versus average weight loss for a fourteen-day test is shown in the following table:

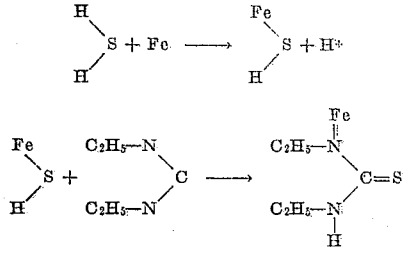
Inhibitor	P. p. m., by Weight	Average Weight Loss in Lbs. Sq. Ft./Yr.
None (control)	0.0	.96
Calcium cyanamide	10	.62
Do	50	.28
Do	100	.10
Do	200	.07
Diallyl cyanamide	10	.50
Do	50	.20
Do	100	.07
Do	200	.05

After noting the weight loss of a number of the panels tested, they were placed back in the brine. Corrosion of the control panel appeared to continue at the same rate; but, after an additional sixty days, no further corrosion of the panels immersed in the cyanamide-inhibited brine was detected. Furthermore, in another series of tests, a number of panels exposed to cyanamide-inhibited brine for fourteen days were, after being cleaned and weighed, immersed in fresh uninhibited brine having the same amount of hydrogen sulfide. At the end of fourteen days, the weight loss of these panels was not detectable, and there was no evidence of corrosion.

Thus, the effect of inhibiting corrosion of ferrous metals with a cyanamide apparently persists. The panels removed from the cyanamide-inhibited brine, in fact, exhibited a film which was firm and tenacious and which apparently protected the metal from attack by the hydrogen sulfide.

While I do not wish to be limited by any theory of operation, it appears that the cyanamide attaches, in a

monomolecular layer, to the iron. This reaction, as represented by diethyl cyanamide, may be as follows:



Thus, it is postulated that the inhibitor unites with and attaches to the iron metal. This theory is borne out by the way the film tenaciously adheres to the metal.

In operation, the cyanamide inhibitor is introduced into a well producing a soluble sulfide. It may be injected by any of a number of methods. For example, the cyanamide may be dissolved in the fluids produced from the well and injected continuously or intermittently into the casing. The solid or liquid inhibitor may be poured into the well or, particularly in wells where the annulus is sealed as in dully completed wells, the solid inhibitor may be incorporated in a stick or ball, by the use of a binder or the like, and dropped into the well.

The amount of inhibitor injected into a well depends upon the hydrogen sulfide concentration, the water production, the frequency of treatment, the solubility of the cyanamide, and the like. As indicated in the above table, the weight loss of the metal decreases as the concentration of the cyanamide inhibitor increases. However, the weight loss at low concentration appeared to be due to the delay in the formation of the protective film. Accordingly, any amount of inhibitor is contemplated, but it is desirable that the concentration during the formation of the film be greater than about 10 p. p. m., based on the weight of the water produced from the well. Due to the many variables, however, it is often preferred that the amount of inhibitor and frequency of treatments be determined by experiment, as by placing coupons in the flow stream and noting the damage due to corrosion or noting the corrosion directly by observation of the iron parts in the well or indirectly by the frequency of failure of the rods, tubing, or other well equipment. The amount of inhibitor and frequency of treatments are then changed, so that the most desirable and economical treatment is obtained.

The cyanamide inhibitors herein disclosed are, generally, non-toxic, are not disagreeable to personnel, do not produce undesirable precipitates in a well or flow line, and are economical to use. They will, as indicated, provide substantially complete protection from sulfide corrosion such as is commonly encountered in oil and gas wells. Furthermore, it will be apparent that the cyanamide inhibitors may be incorporated in corrosion-resistant paints —the solid inhibitors being finely divided as a pigment and the liquid inhibitors being used as or combined with the vehicle. Preferably, such inhibitors are placed in the primer coat, but their use is not so limited.

From the foregoing description in which reference has been made to certain preferred embodiments, it will be apparent that the invention contemplates a wide variety of embodiments. Any such embodiments or modifications which fall within the scope and meaning of the appended claims are considered to be within the spirit and intent of the invention.

I claim:

1. A method of inhibiting corrosion of ferrous metal contacted by water containing a soluble sulfide comprising commingling with said water a sufficient amount of a water-soluble cyanamide to mitigate corrosion of said ferrous metal due to said sulfide.

2. A method of inhibiting corrosion of ferrous metal contacted by water containing a soluble sulfide comprising commingling with said water a sufficient amount of a water-soluble salt of the class which contains the characteristic cyanamide radical $=N-C\equiv N$ to mitigate corrosion of said iron and steel due to said sulfide.

3. A method according to claim 2 in which the amount of said compound is greater than about 10 p. p. m. based on the weight of said water.

4. A method of treating well fluids which contain hydrogen sulfide to inhibit corrosion of ferrous metals in the well comprising commingling with said well fluids a sufficient amount of water-soluble cyanamide to protect said ferrous metals from corrosion due to said hydrogen sulfide.

5. A method according to claim 4 in which said cyanamide is a metal cyanamide.

6. A method according to claim 5 in which said metal is calcium.

7. A method according to claim 4 in which said cyanamide is a dialkyl cyanamide.

8. A method according to claim 4 in which said cyanamide is sodium dicyanamide.

9. A method according to claim 4 in which the amount of said cyanamide is greater than about 10 p. p. m. based on the weight of the water in said well fluids.

10. A method according to claim 4 in which cyanamide is dicyandiamide.

11. A method of inhibiting corrosion of iron and steel contacted by water containing a soluble sulfide comprising commingling with said water a sufficient amount of a water-soluble salt of the class which contains the characteristic cyanamide radical $=N-C\equiv N$ to mitigate corrosion of said iron and steel due to said sulfide.

12. A method of inhibiting corrosion of iron and steel contacted by water containing a soluble sulfide comprising commingling with said water a sufficient amount of a water-soluble salt of the class which contains the characteristic cyanamide radical $-N=C=N-$ to mitigate corrosion of said iron and steel due to said sulfide.

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