METHOD OF PROTECTING METAL SURFACES AGAINST HYDROGEN SULFIDE CORROSION

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1. This invention relates to a method of protecting underground metal equipment against corrosion by hydrogen sulfide, and relates particularly to the prevention of hydrogen sulfide corrosion of the metal parts buried in oil wells drawing sour crudes.

It is an object of the invention to protect oil well casings and tubing against hydrogen sulfide corrosion.

It is a second object of the invention to protect the sucker rods and pumping machinery of an oil well against corrosion by hydrogen sulfide.

It is a third object of the invention to improve upon the efficiency and economy of oil well drilling and operation by reducing the extent of hydrogen sulfide corrosion occurring in the casing, tubing, and machinery in the well.

Other objects and advantages of the invention will in part be obvious, and in part appear hereinafter.

We have discovered that hydrogen sulfide corrosion of the metal parts buried in an oil well can be prevented to a substantial degree by depositing on those metal parts protective films of certain related chemical compounds and materials which are either adsorbed on the metal surfaces or react with the metal surfaces to lay thereon a protective coating impermeable to hydrogen sulfide, or resistant to its corrosive action. In brief, the method of protecting metal surfaces in the oil well comprises injecting into the annual space between the casing and the tubing of the well a solution of a particular compound to contact the casing wall and tubing and pumping it from the well together with crude oil and brine, thereby effectively contacting those surfaces of the well which not only are contacted by fluids drawn from the well, but are exposed to vapors of water, hydrogen sulfide and other corrosive media occurring in wells. The injection of the protective compound is accomplished from the surface in a manner such that the casing of the well is contacted with the compound as it descends to the bottom.

The invention involves the discovery that cyclic nitrogen compounds containing a tertiary nitrogen in which the nitrogen is present in the ring, typified by pyridine bases, such as pyridine, quinolone, isoquinolone, alkyl derivatives thereof, and mineral acid salts thereof, are effective media for protecting metal surfaces against corrosive action of hydrogen sulfide in wells.

Many oil fields, for example fields found in west Texas, some in Michigan, Kansas, and Oklahoma, are characterized by the fact that they produce very sour crudes which contain a relatively high proportion of sulfur compounds, and, accordingly, the pumping of the well is accompanied by the evolution of considerable quantities of hydrogen sulfide with its consequent corrosive effect on the well tubing, casing and machinery. The corrosion by hydrogen sulfide is greatly accentuated in the presence of moisture, and as much as moisture is practically always present in an oil well, the corrosion conditions become ideal for the destruction of the metal parts. In many cases experience has shown that the tubing and the sucker rods in the well can be so badly weakened in a period of about thirty days as to break off and require "fishing" in order to remove broken parts for replacement.

As the flow of oil from a well diminishes, the quantity of brine drawn therefrom increases. Since the well will usually give hydrogen sulfide in addition to other sulfur compounds, together with crude oil, the increasing quantity of brine in combination with the hydrogen sulfide aggravates the corrosion problem in the well. In due course, as the flow of brine increases, the aggravation of the corrosion attributable to the hydrogen sulfide in the well and enhanced by an increased quantity of brine can hasten the time when it becomes uneconomical to pump the well to strip it further of oil.

In the journal of "Petroleum Technology" for January, 1946, the American Institute of Mining and Metallurgical Engineers, Technical, Publication 1970, there appears a good summary and description of the problem of hydrogen sulfide corrosion in oil wells, with a solution devised by the authors P. L. Menaub and T. H. Dunn. Their solution consisted simply in preserving the metal parts against hydrogen sulfide corrosion by injecting a corrosion inhibitor consisting essentially of an aqueous solution of formaldehyde into the well in quantities sufficient to deposit a protective film on the well parts. The quantity of corrosion inhibitor needed is related to the rate of withdrawal of crude and brine from the oil well, and roughly, is quoted by the authors as be-
We have discovered a group of other compounds which are very effective protective agents against hydrogen sulfide corrosion and include such compounds as pyridine, quinoline, methyl pyridines, methyl quinolines, and their salts, which, when placed in alkaline solution and used in the well in the ratio of about 1 gallon of 25 per cent aqueous or alcoholic solution per 100 barrels of brine, are effective in substantially completely arresting hydrogen sulfide corrosion of the metal parts in the well. Use of the solution in the quantity indicated represents a ratio of about 1 part of active inhibiting agent to 10,000 parts of brine. Related materials such as hydrochlorides, sulfates, and other salts of the bases are generally about as effective as the tertiary bases themselves in preventing the oil well corrosion.

A typical composition applied to an oil well according to our invention for protecting against hydrogen sulfide corrosion, involves injecting into an oil well 1 quart of pyridine per 100 barrels of brine. By so doing, the pyridine can be applied to the well in aliquot portions during a day to maintain an effective concentration in the well. The compositions and method of practicing the invention and the possibilities for its application will be more readily understood by consideration of the following examples giving some experimental data:

### Example I

In an experimental test run in which the protective value of the inhibiting solution for steel exposed to corrosive conditions essentially duplicating those found in a well was measured, the following procedure was carried out: A high-carbon steel rod 1/4 inch in diameter and 4 inches long was cleaned, sandblasted, weighed, and placed in a large test tube. To the tube there were then added 3 cc. of oil well brine and 20 cc. crude oil, after which 2 cc. of a solution made up of 0.5 gram of pyridine in 50 cc. of benzene was added. The system was freed of air by freezing the liquid contents of the tube and evacuating, after which the contents were rewarmed and saturated with hydrogen sulfide. The tube was sealed and allowed to remain at room temperature for a period of 64 days, after which it was opened and the specimen cleaned by washing with acetone and water, and dipping in acid to remove surface sulfides. A determination of weight loss was made as a measure of the protective value of the pyridine as a corrosion inhibitor. The pyridine in the ratio of 1 part of the inhibitor to 1,000 parts of brine and oil held the corrosion down to a weight loss of about 0.0012 gram in 64 days.

### Example II

A similar test was carried out with 2 cc. of a quinoline solution made up of 0.5 gram of quinoline in 50 cc. of benzene in which the inhibitor was present in the system in a quantity of 1 part to 1,000 parts of oil and brine, and it was found that after a period of 64 days the weight loss was only 0.00125 gram.

### Example III

Quinoline in 10 per cent ethyl alcohol solution was added to a test tube containing a steel sample and oil well brine in amount sufficient to establish a ratio of 1 part of quinoline to 1,000 parts of brine by weight. The tube contents were saturated with hydrogen sulfide, the tube sealed and allowed to stand for 31 days. Upon expiration of the period, the tube was opened and the sample cleaned as indicated above. The weight loss determined was only 0.004 gram.

### Example IV

Pyridine was added to a test tube containing a steel sample and oil well brine in amount sufficient to establish a ratio of 1 part of pyridine to 1,000 parts of brine by weight. The tube contents were saturated with hydrogen sulfide, the tube sealed and allowed to stand for 30 days. Upon expiration of the period, the tube was opened and the sample cleaned as indicated above. The weight loss determined was only 0.0005 gram.

### Example V

Similar tests were carried out with pyridine and quinoline hydrochlorides and it was found that corrosion was materially reduced by amounts comparable to those cases where the tertiary bases were used, when the inhibitor was present in the system in the amount of about 1 part per 1,000.

### Example VI

Denaturing grade pyridine was tested for its efficacy as an inhibitor according to the procedure outlined. It was found that 1 part of the pyridine in 1,000 parts of the hydrogen sulfide-brine system reduced the corrosion rate of the steel sample to the point where a weight loss of only 0.0016 gram in 30 days occurred.

Denaturing pyridine is a technical grade commonly used for denaturing alcohol.

### Example VII

Blank tests were conducted under conditions duplicating those of the previous specific examples with the inhibiting material left out of the system. In each case it was found that the rate of corrosion of the steel by hydrogen sulfide exceeded 0.05 to 0.1 gram in 30 days.

When the protective materials are employed to reduce the rate of corrosion of the parts of a well under actual producing conditions, the experimental tests and the results are duplicated by injecting periodically an amount of the protective material or solution thereof to supply the inhibitor in a ratio of about 1 part per 1,000 to 10,000 of brine produced from the well. The protective material can be injected into the well as an aqueous alkaline, alcoholic, or alkaline alcoholic solution in concentrations which make for convenience in handling and economy in the quantity of material used. In general, it will be found advantageous to use the inhibitor in about 3 to 15 or 20 per cent solution in the solvent carrier.

It has been found that when the inhibitor is injected into the well in the recommended proportions, that shutdowns of the well normally necessitated by corrosion of the parts within the well structure are materially reduced with the consequent improvement in the economy and efficiency of operation of the well.

Since certain changes may be made in carrying out the method described without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method of protecting metal equipment
in oil wells against hydrogen sulfide and brine corrosion comprising continually introducing into said wells during production of oil and brine therefrom compounds selected from the group consisting of pyridine, quinoline, their methyl derivatives and their mineral acid salts, in an amount of about 1 part of said compounds per 1,000 to 10,000 parts of brine produced from the well, and withdrawing oil and brine from the well mixed with said compounds.

2. Method in accordance with claim 1 in which the compound is pyridine.

3. Method in accordance with claim 1 in which the compound is denaturing pyridine.

4. Method in accordance with claim 1 in which the compound is quinoline.

5. Method in accordance with claim 1 in which the compound is quinoline hydrochloride.

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