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METHOD FOR INHIBITING OIL WELL CORROSION

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6 Claims. (Cl. 252—8.55)

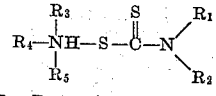
This invention relates to a method for inhibiting the corrosion of ferrous metals constituting the flow lines of producing oil wells. More particularly, the invention relates to a method for preventing corrosion of ferrous metals in a producing oil well delivering a production stream comprising crude oil, brine consisting mainly of aqueous sodium chloride and commonly containing small amounts of other inorganic salts, and carbon dioxide.

Corrosion of ferrous metal surfaces in contact with the production streams of producing oil wells has long been recognized as a serious operating problem by petroleum producers. Considerable effort has been directed to this problem and several methods of reducing corrosion rates and thereby reducing the frequency of replacement of well tubing, sucker rods, etc. have been proposed. In the present state of the art it appears that the attack upon any given corrosion problem must of necessity be in a very considerable degree empirical. For example, corrosion inhibitors which have been found effective in the acid media of pickling baths cannot be expected to exhibit an equivalent inhibiting effect in a different corrosive environment. Inhibitors which are effective in one corrosive environment not only may be valueless, but frequently operate to accelerate corrosion, in a different environment.

The particular corrosive environment with which the present invention is concerned is one in which corrosion by direct acid attack upon the ferrous metal is a minor factor in producing the total corrosion with which the producer is confronted. The essential features of this corrosive environment include a ferrous metal in contact with oil, brine, and gas containing carbon dioxide, gas liquid interfaces in contact with the metal, and areas of turbulent liquid flow in contact with the metal surfaces. If the only corrosion experienced were that attributable to direct acid attack, there would be no corrosion problem because corrosion at the low rate produced by this cause alone could be accepted, since other operating factors would then be controlling in fixing equipment life and breakdown frequency. When a ferrous metal is exposed to the oil well production effluent under quiescent conditions where there is no movement through the liquid or of free gas bubbles through the liquid, the corrosion rate observed is usually less than 25% of that observed under actual producing conditions which include turbulent motion of the liquid in contact with the metal and the presence of minute gas bubbles which contact the metal. In laboratory apparatus it is found that the corrosion rate due to quiescent brine saturated with carbon dioxide gas is increased three and one-half fold when either the condition of liquid turbulence or finely divided gas bubbles moving through the liquid is superimposed on the presence of the carbon dioxide saturated brine.

It is an object of this invention to provide a method for inhibiting corrosion of ferrous metal tubing, and the like, in producing oil wells delivering a production stream comprising crude oil, brine, and carbon dioxide gas.

It has been found that the corrosion of ferrous metals in this environment can be inhibited by introducing a compound of the formula:



in which R_1, R_2, R_3, R_4 and R_5 are materials of the group of alkyl radicals containing 1 to 8 carbon atoms, and hydrogen, at least one of R_1 and R_2 being one of said alkyl groups, into the bottom of the well, the amount of said compound being from 0.05% to 0.001% by weight based on the produced water. The presence of either a hydroxyl group or an amino group in one or more of the alkyl groups does not reduce the inhibiting efficiency of the compounds and, in some instances, appears to enhance it. Further cycloalkyl and heterocycloalkyl radicals may replace the alkyl radicals without adverse effect.

The alkyl radicals in the formula shown above are preferably selected to give a product having appreciable water solubility. In general, this property is exhibited by the compound if the total number of carbon atoms in the alkyl groups does not exceed 20. The compounds above described exhibit oil-water distribution coefficients such that the water phase will contain a sufficient amount of the material to effectively inhibit corrosion when the material is introduced into a producing well in the amounts indicated. The inhibiting materials described are introduced into the well bottom in amounts ranging from 0.001% to 0.05% based on the produced water. In an average well amounts ranging from 0.03 to 0.01% based on the produced water are preferred.

The inhibitor can be introduced into the well by periodic lubrication or by continuous or intermittent pumping. Ordinarily, the inhibitor is introduced into the annulus between the casing and the tubing. When the introduction of the inhibitor is intermittent, the period between injections preferably should not exceed 48 hours.

A number of the inhibitors above described was tested in laboratory apparatus in which iron coupons were contacted with a turbulent stream of oil well brine saturated with carbon dioxide gas and containing carbon dioxide gas bubbles. The corrosion rate was measured by determining the amount of hydrogen evolved at the iron surface during the corrosion process (A Hydrogen Evolution Method for Evaluation of Corrosion Inhibitors for Oil Wells, Corrosion, 8, 234 (1952)). Corrosion rates were determined without any inhibitor present and then with inhibitor present, and the percentage reduction in the

corrosion rate was calculated. The results are shown in the following table.

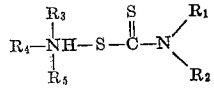
Table

Formula	Percent Inhibition (at 50 p. p. m.)	Solubility in	
		Water	Oil
$C_2H_5NHCS_2NH_3C_2H_5$	78	high	insoluble.
$C_4H_9NHCS_2NH_3C_4H_9$	85	do	Do.
$C_8H_{17}NHCS_2NH_3C_8H_{17}$	95	moderate	low.
$(C_2H_5)_2NCS_2NH_2(C_4H_9)_2$	82	do	Do.
$(C_3H_7)_2NCS_2NH_2(C_3H_7)_2$	87	do	Do.
$(C_4H_9)_2NCS_2NH_2(C_4H_9)_2$	88	low	moderate.
$C_2H_5NHCS_2NH_2(C_4H_9)_2$	88	moderate	Do.
$C_2H_5NHCS_2NH_2(C_8H_{17})_2$	75	low	high.
$(C_2H_5)_2NCS_2NH_3C_4H_9$	88	high	low.
$(C_2H_5)_2NCS_2NH_3C_8H_{17}$	94	do	Do.
$(C_2H_5)_2NCS_2NH_2(C_4H_9)_2$	92	low	moderate.
$(C_2H_5)_2NCS_2NH_2(C_8H_{17})_2$	75	do	high.
$(HOCH_2CH_2)_2NCS_2NH_2(CH_2CH_2OH)_2$	81	high	insoluble.
$H_2NCH_2CH_2NHCS_2NH_3CH_2CH_2NH_2$	82	do	Do.

The corrosion rate of a producing well delivering a production stream consisting essentially of crude oil, brine, and carbon dioxide and having an average daily production of 40 barrels of water was determined by the Thiocyanate Colorometric Method (Scott's Standard Method of Chemical Analysis, 5th ed., Van Nostrand, 1939, page 486). After normal corrosion rate of the well had been determined, the well was treated by introducing 2 gallons per day of a solution of the monobutyl-amine salt of monobutyldithiocarbamic acid into the well. The quantity of the amine salt contained in the solution was equivalent to 60 parts per million based on the daily water production. After the well had been under treatment for a period of 44 days, the corrosion rate was observed to be approximately 8% of the normal corrosion rate.

I claim:

1. A process for inhibiting corrosion of ferrous metal tubing in an oil well delivering a production stream comprising crude oil, water, and carbon dioxide which comprises introducing a compound of the formula



in which R_1, R_2, R_3, R_4 and R_5 are materials of the group consisting of alkyl radicals containing 1 to 8 carbon atoms, and hydrogen, at least one of R_1 and R_2 being one of said alkyl groups, into the bottom of the well, the amount of said compound being from 0.05% to 0.001% by weight based on the produced water.

2. The method as defined in claim 1, wherein the total number of carbon atoms in the alkyl groups is in the range from 2 to 20.

3. A process for inhibiting corrosion of ferrous metal tubing in an oil well delivering a production stream comprising crude oil, water, and carbon dioxide which comprises introducing a water-soluble salt of a primary amine and a dialkyl dithiocarbamic acid, the amine containing from 1 to 8 carbon atoms per molecule and each alkyl group of the acid containing from 1 to 8 carbon atoms, into the bottom of the well, the amount of said salt being from 0.05% to 0.001% by weight based on the produced water.

4. A process for inhibiting corrosion of ferrous metal tubing in an oil well delivering a production stream comprising crude oil, water, and carbon dioxide which comprises introducing a water-soluble salt of a primary amine and a monoalkyl dithiocarbamic acid, the amine containing from 1 to 8 carbon atoms per molecule and the alkyl group of the acid containing from 1 to 8 carbon atoms, into the bottom of the well, the amount of said salt being from 0.05% to 0.001% by weight based on the produced water.

5. A process for inhibiting corrosion of ferrous metal tubing in an oil well delivering a production stream comprising crude oil, water, and carbon dioxide which comprises introducing a water-soluble salt of a secondary amine and a dialkyl dithiocarbamic acid, the amine containing from 1 to 8 carbon atoms in each of its alkyl groups and each alkyl group of the acid containing from 1 to 8 carbon atoms into the bottom of the well, the amount of said salt being from 0.05% to 0.001% by weight based on the produced water.

6. A process for inhibiting corrosion of ferrous metal tubing in an oil well delivering a production stream comprising crude oil, water, and carbon dioxide which comprises introducing a water-soluble salt of a secondary amine and a monoalkyl dithiocarbamic acid, each alkyl group of the amine and the alkyl group of the acid containing from 1 to 8 carbon atoms into the bottom of the well, the amount of said salt being from 0.05% to 0.001% by weight based on the produced water.

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