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METHOD OF PREVENTING CORROSION OF
CORROSIVE FLUID TO FERROUS METALS

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The present invention is directed to a method for reducing the corrosiveness of a corrosive fluid to a ferrous metal exposed thereto. More specifically, the invention is directed to reducing the corrosiveness of ferrous metal surfaces exposed to gaseous corrosive fluids in a confined space.

The present invention may be described briefly as involving a method of reducing the corrosiveness of a corrosive fluid including hydrocarbon, moisture and an acidic gas selected from the group consisting of hydrogen sulfide and carbon dioxide to a corrodible ferrous metal surface exposed in a confined space to said corrosive fluid, the method comprising introducing into the confined space an amount of urea and urease sufficient to inhibit the corrosivity of the corrosive fluid to the ferrous metal.

The ferrous metal equipment employed to confined spaces, such as oil and gas storage and stock tanks and the annuli of oil and gas wells, are susceptible to corrosion by virtue of the fact that such ferrous metals surfaces are exposed to corrosive fluid such as gases including hydrocarbon, moisture, and as an acidic gas, such as hydrogen sulfide and/or carbon dioxide. This corrosion by the corrosive fluids if not controlled or reduced to a marked degree will ultimately result in the destruction of the ferrous metal surface. For example, stock tanks which contain crude oil and brines, such as produced from wells in the West Texas area, usually have a vapor space or atmosphere above them containing hydrocarbon, moisture, and acidic gas which may include either hydrogen sulfide or carbon dioxide or both of them. The ferrous metal surfaces of the stock tanks may corrode rapidly and be destroyed by the corrosive fluid in the vapor space.

In the annuli of oil wells, for example especially a pumping well producing through a tubing string, the outer annulus of such well may have a corrosive atmosphere or a confined space filled with a corrosive gaseous fluid which will attack the exposed ferrous metal surfaces. This atmosphere or the gas filling such space may include hydrocarbon, moisture, hydrogen sulfide, carbon dioxide, and other vaporous constituents originating from the producing formation or injected into the well. If the corrosion of the ferrous metal surfaces exposed to the corrosive fluid is not reduced or controlled, the well may be destroyed or require expensive working over.

In accordance with my invention the corrosivity of such corrosive well fluid may be substantially reduced by introducing into the confined space in which the corrosive fluid is enclosed a corrosion inhibiting amount of urea and the enzyme urease. The corrosion inhibiting amounts employed may vary depending on the amount of corrosive materials in the corrosive fluid and should be selected to provide a sufficient amount to neutralize the corrosive effects of the corrosive fluid. Ordinarily, an amount of urea in the range from one to ten pounds per 1000 square feet of metal exposed to the corrosive fluid may be sufficient. Satisfactory results may be obtained with an amount of urea in the range from one to five pounds per

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1000 square feet of exposed metal. An amount of the enzyme urease should be provided to react or hydrolyze the urea and this amount ordinarily will range from 0.5% to 20% based on the urea. Good results may be obtained with 1%.

The urea is hydrolyzed by the enzyme urease to produce ammonia in the confined space or in the vaporous atmosphere where the corrosive fluid exists.

The urea and urease may be introduced into such confined spaced or into annular spaces of oil and/or gas wells either separately or together. It is convenient and desirable to introduce the urea and urease as aqueous solutions. For example, a solution of urea and urease may be prepared in an aqueous medium and introduced into an annular space of an oil well or separate solutions of the urea and urease may be provided and separately introduced into an annular space of a well. By adjusting the concentration of the enzyme urease and the urea, the two materials may be mixed just before introduction into the well. The urea and urease solution may be introduced into an oil or gas well by means of a lubricator or by pouring the solution or solutions into an annular space if the well is produced by pumping.

It is within the scope and purview of my invention to use an aqueous alcoholic solution for the urea and urease to decrease the specific gravity of the solution and to provide the compounds above the liquid hydrocarbons in the annular space.

Hydrolysis of the urea by the enzyme urease produces ammonia and carbon dioxide. For example, one mole of urea may be hydrolyzed to produce two moles of ammonia and one mole of carbon dioxide. While carbon dioxide in the presence of moisture is quite corrosive, a sufficient amount of ammonia is produced in the hydrolysis of urea to offset the corrosive effects of the carbon dioxide produced by hydrolysis of urea and also to overcome the corrosive effects of carbon dioxide which may be present in the corrosive fluid.

However, the carbon dioxide produced by hydrolysis of the urea may be neutralized, if desired, by buffering of the solutions employed with phosphates or sodium hydroxide and other media. It is desirable to maintain buffered solutions at a pH of 7 or below so as not to reduce the activity of the enzyme.

The urease may be obtained from extracts of soy bean and jack bean meals. It is also available from micrococcus ureae, a bacteria.

As stated before, the present invention may be practiced by introducing or injecting the urea and urease simultaneously or separately into the space confined by the ferrous metals exposed to the corrosive fluid. This may be accomplished by pumping the solutions separately or together into the confined space or by pouring the solutions into the space. The urea and urease react rapidly to release ammonia and carbon dioxide, the latter being neutralized by a buffer in the solution or neutralized by the in situ formed ammonia which is produced in sufficient quantities to inhibit the corrosivity of the corrosive fluid and also to neutralize the carbon dioxide produced in the hydrolysis reaction.

The invention will be further illustrated by the following examples:

10 volumes of corrosive brine from an oil well was drawn into each of 4 tubes. The brine was introduced into the tubes in such a manner that it would not wet steel coupons, each of which had an area of 6¼ square inches, which were placed in the upper portion of the tubes while maintained in an up-right position, the brine being in the lower section of the tubes below the lower ends of the coupons. The area of the glass tubes was about 31 square inches each. Equal volumes of carbon dioxide, hydrogen sulfide and methane were introduced

into the evacuated tubes containing brine until the pressure was equalized at atmospheric pressure. 5 volumes of an aqueous solution containing 1 gram of urea and 0.01 gram of urease was injected into each of two of the tubes, the other two tubes being used as controls. Following the introduction of the urea and urease into the two tubes, all 4 tubes were sealed. The four tubes were then placed in a container to which sufficient water was added to bring the water level up to the level of the brine in the tubes. This water bath was then heated to a temperature in the range between 145° and 148° F. and then allowed to cool to room temperature to cause condensation of water vapor on the steel coupons. The heating cycle was performed 6 times during a 14-day test period. Observations during the test cycles indicated that less water condensed on the steel coupons exposed to vapors from the brine solution to which the urea and urease was introduced than condensed on the control coupons exposed to the brine solution where no urea and urease were employed. At the conclusion of the test the seals were broken and a strong odor of ammonia was noted from the tubes into which the urea and urease were introduced. The steel coupons were weighed before and after the runs to determine the metal loss due to corrosion by the corrosive fluid. The results of these runs, in which the corrosion rates of the metal coupons are presented in inches per year, are shown in the following table:

Table

	Corrosion Rate of Coupons, in./yr.			
	A	B	Average	Percent Reduction
Control.....	0.0015	0.0027	0.0021	85
Urea-Urease.....	0.0004	0.0001	0.0003	

It will be seen that the average reduction in corrosion of the metal coupons for the fluid inhibited by urea and urease is 85%.

The practice of the present invention is quite advantageous since it is unnecessary to employ liquid ammonia under high pressure such as has been necessary heretofore where it was desirable to control corrosiveness of corrosive fluids in a vapor space such as the annuli of oil and/or gas wells or of storage and/or stock tanks. As stated before, the urea and urease may be formed into an aqueous solution or aqueous solutions and the solutions introduced together or separately into the space exposed to corrosion.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method of reducing the corrosiveness of a corrosive fluid including hydrocarbon, moisture, and an acidic gas selected from the group consisting of hydrogen sulfide and carbon dioxide to a corrodible ferrous metal exposed in a confined space to said corrosive fluid which comprises introducing into said confined space an amount of urea in the range from 1 to 10 pounds per 1000 square feet of ferrous metal exposed to the corrosive fluid and urease in an amount in the range from 0.5% to 20% based on the urea sufficient to inhibit the corrosivity of said corrosive fluid to said metal.
2. A method in accordance with claim 1 in which the urea and urease are introduced into said space in an aqueous solution.
3. A method in accordance with claim 1 in which the

urea and urease are separately introduced into said space in separate aqueous solutions.

4. A method of reducing the corrosiveness of a corrosive fluid including hydrocarbon, moisture, and an acidic gas selected from the group consisting of hydrogen sulfide and carbon dioxide to a ferrous metal tank exposed to and confining said corrosive fluid which comprises introducing into the corrosive fluid confined in said tank an aqueous solution containing a sufficient amount of urea in the range from 1 to 10 pounds per 1000 square feet of ferrous metal exposed to said corrosive fluid and urease in an amount in the range from 0.5% to 20% based on the urea to inhibit the corrosivity of said corrosive fluid to said ferrous metal equipment.

5. A method for reducing the corrosiveness of a corrosive fluid including hydrocarbon, moisture and an acidic gas selected from the group consisting of hydrogen sulfide and carbon dioxide to ferrous metal equipment exposed to and confining said corrosive fluid which comprises introducing into said equipment an amount of urea in the range from one to ten pounds per 1000 square feet of ferrous metal exposed to the corrosive fluid and an amount of urease in the range from 0.5% to 20% based on the urea to inhibit the corrosivity of said corrosive fluid to said ferrous metal equipment.

6. A method of preventing corrosion of ferrous metal well equipment exposed to a gaseous corrosive fluid including hydrocarbon, moisture, and an acidic gas selected from the group consisting of hydrogen sulfide and carbon dioxide which comprises introducing urea in an amount in the range from 1 to 10 pounds per 1000 square feet of ferrous metal exposed to said corrosive fluid and urease in an amount in the range from 0.5 to 20% based on the urea into the annular space in said well equipment containing said corrosive fluid sufficient to inhibit the corrosivity of said corrosive fluid to said ferrous metal equipment.

7. A method of preventing corrosion of ferrous metal well equipment exposed to a gaseous corrosive fluid including hydrocarbon, moisture, and an acidic gas selected from the group consisting of hydrogen sulfide and carbon dioxide which comprises separately introducing into an annular space in said well equipment containing said corrosive fluid urea in an amount in the range from one to ten pounds per 1000 square feet of ferrous metal surface exposed to the corrosive fluid and an amount of urease in the range from 0.5% to 20% based on the urea.

8. A method in accordance with claim 6 in which the urea is introduced in an amount in the range from one to five pounds per 1000 square feet of exposed ferrous metal and the urease is in an amount of 10% based on the urea.

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