CORROSION PREVENTION METHOD

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This invention relates to a method of corrosion inhibition of a ferruginous material, e.g., steel, while in contact with an agitated fluid system of liquid or liquefied gases and an aqueous carbonic acid and/or carbon dioxide. More particularly, the invention applies to corrosion prevention of metal equipment normally used in operating gas-condensate (i.e., light gasoline) wells, whereby such corrosion prevention is effected during the conventional operation of these wells.

In recent years, the problem of preventing corrosion of ferruginous materials in the above-described systems has become quite serious.

It is an object of the present invention to provide an inexpensive and industrially feasible method of corrosion inhibition of ferruginous metals in a system in which an agitated flowing mixture of non-oxidizing gases, a liquefied hydrocarbon phase and an aqueous carbonic acid phase come in contact with such ferruginous metal. It is another object to overcome the disadvantages of prior art practices peculiar to corrosion inhibition as applied in operation of gas-condensate wells. A further object is to provide an inexpensive and industrially feasible corrosion inhibition treatment of iron-containing metals, contacting the above-described system as it occurs in the case of an operating gas-condensate well.

Now, in accordance with the present invention, it has been found that corrosion which is caused by contact of corrosible metal with a system of non-oxidizing gases and an agitated flowing mixture of a liquefied hydrocarbon phase and an aqueous carbonic acid phase can be substantially inhibited by introducing (continuously or intermittently) into this system a minor but corrosion-inhibiting amount of an oil-soluble acidic adduct of an alpha-beta ethylenic polycarboxylic acid (including its anhydride) having not more than 10 carbon atoms per molecule combined with a non-hydroxylated polyunsaturated fatty acid radical having from 8 to 32 carbon atoms at an intermediate point in the carbon atom chain thereof.

Further, in accordance with the present invention, it has been found that additional improvements in corrosion inhibition may be obtained by combining the above oil-soluble product with a water-soluble corrosion inhibitor whereby corrosion due to both the aqueous and oil phases within the oil well are inhibited to an enhanced degree.

The liquefied hydrocarbon phase in gas-condensate wells normally comprises mixtures of light methane, ethane, propane, butane and heavier hydrocarbon condensates up to and including light gasolines having up to about eight carbon atoms. Normally gaseous hydrocarbons are partly liquefied in the well because of the pressures ordinarily existing therein. A typical gas-condensate well produces between twenty and thirty barrels of a liquefied hydrocarbon phase per million cubic feet of gas (MMCF), at typical well-head temperatures and pressures. The temperatures at the bottom of the well usually range from about 85° C. to about 125° C., average temperatures at the well-head being usually in the range from about 45° C. to about 80° C. Pressures in a condensate well usually range from about 100 to about 7,000 pounds per square inch absolute. A typical well may have a bottom-hole pressure of about 2,700 p. s. i. a. and a flowing tubing pressure of about 2,000 p. s. i. a. The pressure increases the ratio of gaseous carbon dioxide (present in condensate wells) which will dissolve in the aqueous phase also present therein. At well-head conditions there is usually a range from about seven to about twenty gallons or higher of liquid water per MMCF of gas produced. This liquid water phase dissolves carbon dioxide, thus providing the aqueous carbonic acid phase. The latter usually has a pH value ranging from about 3.3 to about a pH of 5.5. This aqueous phase may also contain sodium chloride and other electrolytes, the usual amounts of which are well known to the art. The aqueous carbonic acid phase mixed with agitated liquefied hydrocarbon phase and gases is usually distributed throughout the flowing system of the well.

The above-defined polybasic acids or anhydrides are obtained by the condensation of an alpha-beta ethylenic carboxylic acid or anhydride with a polyunsaturated, non-hydroxylated fatty acid containing from eight to 32 carbon atoms, preferably ten to twenty-four carbon atoms, in its carbon chain. The desired polybasic acid or anhydride reactants may be prepared by two different types of reaction. One type of reaction involves the condensation of an alpha-beta ethylenic acid or anhydride with a conjugated, unsaturated, nonhydroxylated fatty acid. The second type of reaction involves the condensation of an alpha-beta ethylenic acid of anhydride with a non-conjugated, unsaturated, nonhydroxylated fatty acid.

It is well known that maleic anhydride and other alpha-beta ethylenic acids or anhydrides with conjugated, unsaturated fatty acids in accordance with Thiele's theory of 1-4 addition. The fatty acid in this case, of course, must contain at least two carbon-to-carbon double bonds and these must be conjugated. This type of reaction has been thoroughly studied by Diels and co-workers, and is often referred to as the "Diels diene synthesis." The products are often called diene synthesis adducts.

Examples of suitable fatty acids which will take part in a Diels condensation include: Geranic acid, laeostearic acid, 10,12-octadecadienoic acid, tung oil fatty acids, etc. Actually, the esters of these acids, such as the triglycerides or the esters of mono- di-, or other polyhydric alcohols may be employed in this condensation in place of the fatty acid itself. Examples of other types of adducts include: methyl-10,12-octadecadienoate, glycolidelaostearate, octacica oil, tung oil, dehydrated conjugated castor oil, ethyl dehydrogeranate and the like. The esters (i.e., glycerides) of polyhydric alcohols may form adducts with the polybasic acid in any proportion up to about one mol of the latter for each fatty acid radical. The most effective adducts comprise those in which each ester molecule contains at least one fatty acid radical in adduct form with the polybasic acid.

The alpha-beta ethylenic carboxylic acids or anhydrides which are suitable for use in the aforementioned Diels diene synthesis for preparation of the present products are those containing less than ten carbon atoms and are exemplified by crotonic acid, maleic acid, fumaric acid, citraconic acid, glutaric acid, acrylic acid, maleic anhydride, and citraconic anhydride.

Polybasic acids or anhydrides contemplated as reactants for production of this new class of compounds are also obtained by the condensation of an alpha-beta ethylenic acid, or anhydride with an unsaturated, non-conjugated, non-hydroxylated fatty acid containing from ten to twenty-four carbon atoms in the carbon chain. It has been shown by Clocker, U. S. Patents 2,188,882 to 2,188,892 inclusive, and Bickford et al., Oil and Soap,
February 1942, page 23 et seq., that such condensations may be brought about by heating the reactants to a suitable elevated temperature, usually above 200° C. and sometimes at temperatures above 300° C. The products formed are also acids or anhydrides, since the reaction does not appear to involve the destruction of these groups. The alpha-beta ethylenic acids or anhydrides which are suitable for use in the aforementioned condensation with non-conjugated, unsaturated, non-hydroxylated fatty acids are those containing less than ten carbon atoms and are exemplified by crotonic acid, maleic acid, fumaric acid, citraconic acid, glutaric acid, acrylic acid, maleic anhydride, and citraconic anhydride. Reference herein and in the claims to alpha-beta unsaturated acids is intended to include the anhydrides corresponding to such acids. Actually they are recognized as being functionally equivalent in condensations of the kinds herein contemplated.

Suitable non-conjugated, unsaturated, non-hydroxylated fatty acids for use in condensation reactions with the above-mentioned alpha-beta ethylenic acids are those containing from ten to twenty-four carbon atoms in their carbon chains, and include undecylenic acid, oleic acid, elaidic acid, linoleic acid, linolenic acid, etc. Oil is also frequently derived from a glyceride containing, in esterified form, a large proportion of non-conjugated, unsaturated, non-hydroxylated fatty acid. Examples of such glycerides are olive oil, corn oil, cottonseed oil, linseed oil, rapeseed oil, perilla oil, cranberry seed oil, menhaden oil, cod oil, whale oil, heat boiled linseed oil, etc.

It is not known just how the present class of inhibitors act to prevent corrosion of steel under the conditions employed in the present invention. Their effectiveness is surprising in view of the turbulence of flow in the system and the low concentrations of inhibitor (less than about 1 wt. percent, based on the liquefied hydrocarbon phase) which are effective, relative to the much higher concentrations of carbonic acid and other corroding components in the system. Also, these inhibitors are soluble in the liquefied hydrocarbon phase; so it would seem that they would be dissolved and swept away by the turbulent flow of this phase, leaving the surface of the metal open to attack by the swiftly churning aqueous carbonic acid present.

The present agents may be introduced into wells in various ways. For example, tubing of relatively small diameter may be run down to the center of the production tube of such a well to approximately the bottom end thereof, and a solution of the present agent may be pumped through the small diameter tubing so as to enter the well at or near the bottom of the well tube; the rising turbulent flow will then carry the injected agent up through the tube. Obviously, the corrosion inhibitors may be added or introduced into the wells by other means or methods depending, in part, on whether the wells are operated through the casings or through tubing disposed in such casings. Also, it is clear that the inhibitors may be introduced into the top of the well and allowed to flow down, or may be forced to any given point or points in the well, at which the inhibitor can then come in contact with the turbulent up-flowing fluid mixture which, as stated, would cause metal corrosion but for the presence of the corrosion inhibitors of this invention.

The employment of the present agents is best effected by having them in solution in a liquid hydrocarbon readily miscible with the liquefied hydrocarbon phase of the well, and then introducing the hydrocarbon solution to a condensate well as above-described. Any organic solvent which is substantially non-reactive with the agent(s) under the conditions employed (e.g., such solvents as esters, alcohols, ketones, etc.), may be used for preparing an inhibitor solution, although it is preferable to employ light gasolines or normally liquid or liquefied condensates from the well to be treated. In the alternative, a suitable crude oil or crude oil fraction (whether refined or not) is also efficacious as a means of forming a fluid solution which can be flowed or forced into these condensate wells. In some cases it is advantageous to use a more or less concentrated solution or dispersion (up to about 50 wt. percent of the agent) in a suitable fluid medium such as diesel oil. The amount of solvent in the inhibitor solution is so small, relative to the volume of liquid in the system treated therewith, that it does not materially affect the normal operation of the well.

The subject additives may be combined as noted hereinbefore with certain water-soluble corrosion inhibitors such as the alkali metal chromates or dichromates, e.g., sodium chromate; the alkali metal arsenates, e.g., potassium arsenite and the alkali metal phosphates, e.g., di-potassium hydrogen phosphate. By this means corrosion inhibitors are present in both the hydrocarbon phase and the water phase present in the well. Hence, corrosion due to components contained in either one of these phases is substantially inhibited for a longer period of time.

In the operation of an oil well the oil is pumped back to the surface in which the sucker rods move against the sides of the well tubing. It will be apparent that the possibility for wear is always present under such circumstances. In the past it has been common practice to replace tubing frequently during the replacement of corroded sucker rods. However, when the oil well is properly inhibited against corrosion of the sucker rods, the problem of tubing wear due to lack of proper lubrication between the sucker rods and the tubing becomes increasingly evident. In addition to the corrosion inhibiting function of the subject additives the latter have been found to possess an unexpected benefit with respect to enhancing the lubrication of products being pumped through the oil well. This can be demonstrated by testing oil compositions with and without the subject additives. A standard four-ball test is employed, the conditions being 80° C., 7 kg. load and a speed of 600 R. P. M. The balls were one-half inch (diameter) SKF steel ball bearings having Rockwell “C” hardness of 60–65. Under these conditions the test oil, which was a lubricating oil having a SAE 10 viscosity, developed a scar diameter of 0.67 mm. Modification of the lubricating oil with 0.05% of the said inhibitor oil preparation is described hereinafter, reduced the scar diameter to 0.43 mm.

Still further improvements in the lubrication benefits of the subject additives may be made by sulfurizing the same, using the well-known methods and agents for introducing sulfur and the extreme pressure agents and lubricants, such as sulfur, phosphorus sulfides or sulfur chlorides. It is preferred that the sulfur content of the resulting sulfurized additives be between 0.5% and 10% by weight.

In providing the proper degree of corrosion resistant it is preferred that the additives be present in the well in proportions between about 0.001% and 1% based on the hydrocarbon phase and still more preferably in amounts between 0.025% and 0.1%.

For the purpose of illustration, references will now be made to the following examples, it being understood that there is no intention of limiting the invention to the specific conditions and reactants disclosed therein. In these examples steel plates (9% inch wide, 5% inches long, and blasted cold rolled steel strips) were placed in simple bottles. Liquids saturated with carbon dioxide and having the following composition were added: 50 cc. of kerosene plus 10 cc. of distilled water containing 3% sodium chloride, 0.1% calcium chloride, 0.03% magnesium chloride and 0.1% acetic acid. The bottles were closed and rotated
end over end at 60 R. P. M. for a period of 17-24 hours. The concentration of the adducts given in the table below are based upon the kerosene weight. The test temperature was 180° F. At the end of this time the corrosion rate was measured for each of the steel plates. The result of the technique is given below.

Adducts were formed between maleic anhydride and each one of the following oils: crude oleic acid, sardine oil, linseed oil and soy bean oil. In preparing the adducts 200 parts by weight of the oil were diluted with an equal weight of petroleum fuel oil to which 20 parts by weight of maleic anhydride were added. The mixture was heated for 150 minutes at a temperature between about 220° and about 235° C. The product was hydrolyzed with 300 parts by weight of water and washed with 200 parts by weight of water. In order to purify the product it was then extracted with kerosene. Using the test method described above the effectiveness of each of the individual inhibitors was found to be as follows:

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Wt. Percent Concentration</th>
<th>Corrosion Rate, Alts per yr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>Oleic acid adduct</td>
<td>0.05</td>
<td>9</td>
</tr>
<tr>
<td>Do</td>
<td>0.01</td>
<td>5</td>
</tr>
<tr>
<td>Sardine oil adduct</td>
<td>0.02</td>
<td>7</td>
</tr>
<tr>
<td>Do</td>
<td>0.01</td>
<td>3</td>
</tr>
<tr>
<td>Soybean oil adduct</td>
<td>0.009</td>
<td>4</td>
</tr>
<tr>
<td>Do</td>
<td>0.01</td>
<td>2</td>
</tr>
<tr>
<td>Linseed oil adduct</td>
<td>0.01</td>
<td>3</td>
</tr>
<tr>
<td>Do</td>
<td>0.01</td>
<td>2</td>
</tr>
</tbody>
</table>

I claim as my invention:

1. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corroding well parts, which method includes the step of mixing with said system an additive radical, radicals present in said adduct being glyceride radicals.

2. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corroding well parts, which method includes the step of mixing with said system an additive radical, radicals present in said adduct being glyceride radicals.

3. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corroding well parts, which method includes the step of mixing with said system an additive radical, radicals present in said adduct being glyceride radicals.

4. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corroding well parts, which method includes the step of mixing with said system an additive radical, radicals present in said adduct being glyceride radicals.

5. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corroding well parts, which method includes the step of mixing with said system an additive radical, radicals present in said adduct being glyceride radicals.
least one non-hydroxylated polyethylene fatty acid radical, having from 8 to 32 carbon atoms, of a fatty acid glyceride any ester radicals present in said adducts being glyceride radicals.

7. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 55° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corrotable well parts, which method includes the step of mixing with said system an amount between about 0.001% and about 1% by weight of the hydrocarbon phase of an acidic adduct of an alpha-beta ethylenic polycarboxylic acid having no more than 10 carbon atoms per molecule, combined at an intermediate point in the carbon atom chain of at least one fatty acid radical per molecule of sardine oil glycerides any ester radicals present in said adduct being glyceride radicals.

8. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corrotable well parts, which method includes the step of mixing with said system an amount between about 0.001% and about 1% by weight of the hydrocarbon phase of an acidic adduct of an alpha-beta ethylenic polycarboxylic acid having no more than 10 carbon atoms per molecule, combined at an intermediate point in the carbon atom chain of oleic acid any ester radicals present in said adduct being glyceride radicals.

9. The method of treating a hydrocarbon-containing system in its natural state in a well for the purpose of inhibiting corrosion by aqueous carboxylic acid of well metal parts, said system comprising a non-oxidizing gas phase, a liquefied normally gaseous hydrocarbon phase and a minor amount of aqueous carboxylic acid, which system in a state of agitated flow at a temperature of between about 45° C. and about 125° C. and under a pressure of between about 100 and 7000 pounds per square inch absolute, comes in contact with corrotable well parts, which method includes the step of mixing with said system an amount between about 0.001% and about 1% by weight of the hydrocarbon phase of an acidic adduct of an alpha-beta ethylenic polycarboxylic acid having no more than 10 carbon atoms per molecule, combined at an intermediate point in the carbon atom chain of oleic acid any ester radicals present in said adduct being glyceride radicals.

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