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OIL WELL INHIBITOR

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This invention relates to the prevention of corrosion of metal equipment in producing oil wells. More particularly, the invention relates to the protection of steel casings, steel tubing, and other metal well equipment from the deleterious effects of corrosive formation liquids.

In the production of oil, corrosion of steel and other metal well equipment is caused by the action of certain types of sulfur-bearing waters, aqueous carbonic acid, and natural brines. Corrosive sulfide brines include alkali and alkaline earth metal sulfides and hydrogen sulfide. Hydrogen sulfide is very soluble in water, brines, and petroleum oil forming corrosive solutions which cause deterioration of well and surface equipment. This corrosion takes place in both acidic and alkaline brines having a pH below about 8, which includes practically all natural well brines.

It is common practice to introduce an inhibitor at the wellhead into the annular space between the casing and the tubing in a well extending into a producing formation. The liquid inhibitors which have been used are expected to flow to a producing zone in the well to mix with the corrosive liquids flowing therefrom and then will flow up through the tubing to the surface.

In gas lift wells in particular and in some pumping and flowing wells, however, a considerable column of oil and water or brine may stand in the annular space between casing and production tubing. In such wells the conventional inhibitors will be rather ineffective in extending protection from corrosion throughout the well. We have found that two additional requirements must be met to insure effective placement of the inhibitor. First, the density of the inhibitor must be greater than that of the liquids contained in the annular space, and second it must not be appreciably soluble in oil.

It is a principal object of this invention, therefore, to provide a method of inhibiting corrosion in producing oil wells in which the corrosion inhibitor is weighted with a liquid to make it fall more readily through any liquid column to a producing zone in a well.

A further object of the invention is to render oil-soluble inhibitors sufficiently limited in solubility so as to pass readily through the oil layer floating upon a column of brine without appreciable dissolution by providing a liquid solubility-limiting-weighting agent in combination with the corrosion inhibitor.

A still further object of this invention is to provide improved weighted corrosion inhibiting compositions for use in producing oil wells.

Other objects of the invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various

ways in which the principles of the invention may be employed.

It has been found that various liquids comprising polyhydroxy compounds can be added to iron corrosion inhibitors to impart the desired weight and retard the oil solubility without deleterious effect on the action of the inhibitor or the well system.

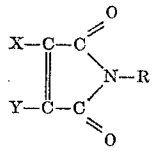
Broadly stated, our invention comprises a method of inhibiting corrosion in oil wells which consists in weighting an iron corrosion inhibitor with a liquid to provide a composition which when added at the wellhead will drop readily through any bore-standing oil and aqueous column diffusing in part with the aqueous phase and arrive in substantial quantity at a producing zone or well bottom to commingle with corrosive liquids produced therefrom.

The liquid weighting agents which are useful for the practice of this invention must possess the following properties: They must be substantially insoluble in oil so as not to be appreciably dissipated upon passage through an oil column standing in a well. They must be at least partially water soluble to permit some diffusion of the inhibitor into the corrosive brines standing in the well. The weighting liquids employed must be compatible with the inhibitor and capable of forming a solution or a stable form of suspension with the inhibitor. They must have a specific gravity greater than that of the corrosive brine column in the well. The actual specific gravity of the weighting liquid used is dependent upon two variables. One, the concentration of the weighting liquid which may be used in the corrosion inhibiting composition and, two, the density of the brine column in the well. As to the latter that varies with different wells. For example, the densities of brine solutions from wells located in south Texas and Ceres Pool Field may run as high as about 1.05 and about 1.18, respectively. It, therefore, follows that if the inhibiting solution is to be used in south Texas a density of about 1.06 would be sufficient while an inhibiting solution having a density of about 1.2 may be required if it is to be used in the Ceres Pool Field. The foregoing values are maximum and as a rule an inhibiting composition the density of which is greater than 1.01 will be suitable for use in most wells. Generally, the specific gravity of the weighting liquid should be within the range of about 1.1 to about 1.45. The weighting agents must be non-reactive with the inhibitor, and the solution, colloidal solution or stable suspension or dispersion resulting from the admixture of weighting agent and inhibitor must be capable of remaining largely intact during its passage through the oil layer and into the brine column. Such a composition we designate as a "homogeny" and as so used herein and in the appended claims includes true and colloidal solutions and stable dispersions and suspensions.

Materials which have been found to be especially suitable for use as weighting agents for the purposes of this invention include the polyhydroxy compounds such as ethylene glycol and glycerine, aqueous solutions, preferably concentrated of sugars such as sucrose, glucose, molasses, and mixtures thereof. When these materials are mixed in proper proportions with a corrosion inhibitor, the mixture solubilizes to form a liquid which is not appreciably miscible with oil and has a density great enough to penetrate the oil-brine interface and fall through the column of salt water beneath the oil undergoing only partial dissolution therewith.

Various known iron corrosion inhibitors may be employed. They may be of the nitrogen chain or ring type, salts of petroleum sulfonic acids, and the like. One useful inhibitor is a primary high molecular weight amine derived from rosin by reaction with ammonia followed

by hydrogenation to form an amine. Similar amines prepared from modified (hydrogenated and dehydrogenated) rosins are likewise useful. Such products are available from Hercules Powder Company under the trademark brank name "Rosin Amine." A group of quaternary ammonium salts which are effective inhibitors are the dialkyl dimethyl ammonium chlorides wherein the alkyl groups contain from 8 to 18 carbon atoms. One such material is manufactured by the Chemical Division of Armour and Company and sold under the trade name "Arquad 2C." Still another useful nitrogen type inhibitor is a condensation product of oleic acid and aminoethylethanolamine available as "Amine 220" from Carbide and Carbon Chemicals Company. Typical nitrogen ring type inhibitors include acridine and derivatives, pyrrole and derivatives, and morpholine and derivatives. Especially effective nitrogen ring inhibitors are the N-aliphatic pyrrolinediones represented by the formula:



where X and Y are members from the class consisting of hydrogen, halogen, and simple hydrocarbon groups and R is an aliphatic group, such as disclosed in U. S. Patent No. 2,466,530 issued to C. M. Blair and W. F. Gross, and are available under the brand name 'Kontol–118" which has a density of 0.957 at 60° F. from the Tretolite Company. The aliphatic radical contains at least 7 and not more than 32 carbon atoms. The flash point, fire point, pour point, and viscosity are 165° F., 225° F., —20° F. and 477 SSU at 100° F. respectively. It is soluble in oil but insoluble in water.

Another class of inhibitors which are useful as inhibitors in the practice of this invention are the organic sulfonates. For example, there are the salts of the mahogany or petroleum sulfonic acids, particularly the oil-soluble salts of the aromatic sulfonic acids from petroleum. Many of the aromatic sulfonic acids have cycloalkyl (i. e., naphthenic) groups in the side chains attached to the aromatic nucleus. The mahogany acids also include non-aromatic sulfonic acids produced in conventional sulfuric acid refining of lubricating oil distillates, and from refining operations using fuming sulfuric acid in the manufacture of petrolatum. The industrial production of oil-soluble mahogany sulfonates from petroleum is well understood in the art and is fully described elsewhere in the literature. Another group of effective sulfonate inhibitors are the synthesized organic sulfonates, which include the sulfonated alkaryl compounds such as sodium polydodecylbenzene sulfonate. Sodium polydodecylbenzene sulfonate is an article of commerce which is the sodium salt of polydodecylbenzene sulfonic acid. This sulfonic acid is prepared by sulfonating polydodecylbenzene. Polydodecylbenzene, also known as "Neolene–400" bottoms, is described in U. S. Patent 2,671,757 issued March 9, 1954, to Thomas G. Wisherd, filed March 31, 1951.

The following specific examples are illustrative of this invention, in which parts given unless otherwise stated are parts by volume. Various compositions are shown for use with brines of varying density.

Example I

A solution was made up by mixing equal parts of a commercial N-aliphatic pyrrolinedione inhibitor (Kontol–118) and ethylene glycol. This solution had a specific gravity of 1.042 which was sufficient to enable the inhibitor to penetrate an oil layer, oil-brine interface, and through a brine column standing in the well.

Example II

Still another solution contained 25 parts of the commercial N-aliphatic pyrrolinedione inhibitor (Kontol) and 75 parts of ethylene glycol. The density of this mixture was 1.06.

Example III

Inhibitor solutions made of oil-soluble salts of sulfonated hydrocarbons may be made as follows: Twenty-five parts of sodium polydodecylbenzene sulfonate was added to 25 parts of an aqueous sugar solution having a sucrose concentration of 600 grams per liter. This mixture was thoroughly stirred and to it was added 10 parts of ethylene glycol. The final mixture was a clear transparent solution, the specific gravity of which was approximately 1.06 and possessed a viscosity approximately that of 30 S. A. E. oil. The solution when dropped into an oil well did not dissolve appreciably in the oil layer and dispersed only slowly as it fell through the brine column.

The relative quantities of the liquid weighting agent and inhibitor to be used are dependent upon the specific gravities of the inhibitors and of the formation liquids through which it is desired to introduce the inhibitors, the requirement being that the specific gravity of the resulting inhibitor mixture be sufficient to cause it to fall through the oil layer, to penetrate the oil-brine interface, to diffuse throughout the brine, and to fall in sufficient quantity to the bottom or a production zone of a well. It is apparent that these proportions can be readily determined to provide the precise formulation of the weighted composition primarily by specific gravity measurements. Where the sugar solutions are used, in order to attain sufficient increase in specific gravity of the inhibitor, it is desirable that the concentration of sugar be relatively high. The weighted inhibitor is introduced into the well in amounts to maintain a concentration of from about 1 to 10,000 parts of the inhibitor component per million parts of corrosive well liquids.

It is apparent that many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof. The examples given are by way of illustration only and the invention is limited only by the terms of the appended claims.

We claim:

1. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising a substantially oil insoluble water dispersible homogeny having a specific gravity greater than 1.01 comprising a liquid iron corrosion inhibitor which has a specific gravity of less than 1.0 and an organic polyhydroxy compound having the specific gravity of more than 1.1.

2. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising a substantially oil-insoluble, water-dispersing homogeny, having a specific gravity greater than 1.01, comprising a liquid iron corrosion inhibitor which has a specific gravity of less than 1.0 and ethylene glycol.

3. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising a substantially oil-insoluble, water-dispersing homogeny, having a specific gravity greater than 1.01, comprising a liquid iron corrosion inhibitor which has a specific gravity of less than 1.0 and glycerine.

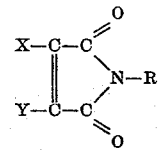
4. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising a substantially oil-insoluble, water-dispersing homogeny, having a specific

gravity greater than 1.01, comprising a liquid iron corrosion inhibitor which has a specific gravity of less than 1.0 and a concentrated aqueous solution of sugar.

5. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising an iron corrosion inhibitor having incorporated therewith, as a weighting agent, a polyhydroxy compound in an amount sufficient to increase the specific gravity of the inhibitor above that of the corrosive liquids to enable the inhibitor to fall readily through the liquid column to a producing zone and to diffuse at least partially throughout said liquid column.

6. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising a substantially oil-insoluble water-dispersible homogeny having a specific gravity greater than 1.01 comprising sodium polydodecylbenzene sulfonate and an organic polyhydroxy compound having the specific gravity of more than 1.1.

7. A method of treating oil wells containing a column of corrosive formation liquids which comprises the addition thereto of a weighted corrosion inhibiting composition said composition comprising a substantially oil-insoluble water-dispersible homogeny having a specific gravity greater than 1.01 comprising N-aliphatic pyrrolinedione represented by the general formula:



where X and Y are members selected from the group consisting of hydrogen, halogen, and simple hydrocarbon groups, and R is an aliphatic group containing 18 carbon atoms.

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