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2,822,330

WEIGHTED CORROSION INHIBITOR

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10 Claims. (Cl. 252—8.55)

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 and carbon dioxide are very soluble in water and brines and in addition hydrogen sulfide is soluble in petroleum oil thus forming corrosive solutions which cause deterioration of well and surface equipment. This corrosion takes place in 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 agent and a 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.

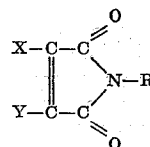
The foregoing objects are attained by a process which broadly stated comprises a method of inhibiting corrosion in oil wells which comprises the addition to the annular space between the casing and the tubing of a producing oil well a liquid corrosion inhibiting composition comprising an oil soluble corrosion inhibitor, an immiscibilizing agent for the corrosion inhibitor and a mutual solvent for the inhibitor and the immiscibilizing

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agent. The mutual solvent must have a specific gravity so that the final composition has a specific gravity greater than 1.01. Based on the weight of the composition, the inhibitor, immiscibilizing agent, and solvent may vary from 20 to 70, 5 to 25, and 5 to 75 percent respectively.

Before proceeding with specific examples illustrating our invention it may be well to indicate in general the nature of the materials required in the process.

The oil soluble corrosion inhibitors which are useful for the practice of this invention are iron corrosion inhibitors and in general they may be of the nitrogen chain or ring type, high molecular weight carboxylic acid, sulfonic acids and various salts of these acids with alkali metals, alkaline earth metals, ammonia, amines, and alkanolamines. Various alkyl pyrimidines are also suitable in the process of this invention. Nitrogen ring type inhibitors may be used also. Specific nitrogen ring type 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. 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 S. S. U. at 100° F. respectively. It is soluble in oil but insoluble in water. Among the high molecular weight carboxylic acids suitable in the process of this invention are high molecular weight polycarboxylic acids. Especially suited are polycarboxylic acids obtained by polymerization of unsaturated acids in accordance with a method such as is described in the Journal of the American Oil Chemists Society, 24, 65 (1947). Thus, raw materials containing linoleic acid on treatment by this method yield mixtures of dimers, trimers, and higher polymers of linoleic acid. Such a polymer mixture that may be utilized in the process of this invention is available commercially under the trade designation M-461-R, dimer acids. It has the following properties:

Neutral equivalent	290-310
Iodine value	80-95
Dimer content	percent ca. 85
Trimer and higher	do ca. 12

Another suitable polymerized unsaturated acid is available commercially under the trade designation D-85 dimer acid. It has the following properties:

Acid value	94-116
Iodine value	44-50
Molecular weight	ca. 750

Suitable sulfonic acids for the process of this invention include various petroleum sulfonic acids known as mahogany sulfonic acids obtained by the sulfonation of high molecular weight petroleum fractions. Other satisfactory sulfonic acids are those obtained by the sulfonation of alkyl aromatic hydrocarbons obtained by the alkylation of aromatic hydrocarbons with alkyl alkylating agents having more than nine carbon atoms, as, for example, haloparaffins, olefins as from dehydrohalogenated haloparaffins, polyolefins such as polypropylene, alkylsulfates, aliphatic alcohols, and others. Specific suitable sulfonic acids are those obtained by sulfonating alkyl aromatic

hydrocarbons known in the art as dodecylbenzene, post-dodecylbenzene, and diwaxbenzene. Dodecylbenzene is obtainable under the trade name of Neolene 400. Physical properties of Neolene 400 are as follows:

Specific gravity at 16° C.	0.8742
Average molecular weight	232
A. S. T. M., D-158 Engler:	
I. B. P.	° F. 535
5	° F. 545
10	° F. 550
50	° F. 560
90	° F. 580
97	° F. 592
F. B. P.	° F. 603
Refractive index at 20° C.	1.4885
Viscosity at 20° C.	14
Bromine number	0.16

Postdodecylbenzene is a mixture of monoalkylbenzene and dialkylbenzenes in the approximate ratio of 2:3. Its typical physical properties are as follows:

Specific gravity at 38° C.	0.8649
Average molecular weight	365
Percent sulfonatable	88
A. S. T. M., D-158 Engler:	
I. B. P.	° F. 647
5	° F. 682
50	° F. 715
90	° F. 760
95	° F. 775
F. B. P.	° F. 779
Refractive index at 23° C.	1.4900
Viscosity at:	
-10° C.	centipoises 2800
20° C.	do 280
40° C.	do 78
80° C.	do 18
Aniline point	° C. 69
Pour point	° F. -25

Although the sulfonic acids may be used, the salts formed by neutralizing these acids with alkaline materials are preferred. As stated above, about 20 to 70 percent or even less corrosion inhibitor may be present in the liquid corrosion inhibiting composition for use in oil wells and inhibition of corrosion be obtained, it is desirable that the concentration be about 50 to 70 percent in order for maximum inhibition of corrosion.

Suitable solvents for use in the process of this invention are inert solvents which have a boiling point sufficiently high that they will not boil at the temperature and pressure encountered in the well bore. As mentioned above, they should have a specific gravity sufficiently high that when they are added to the inhibitor composition the resultant specific gravity of the mixture will be greater than 1.01 preferably greater than 1.05. In general the solvent will have a specific gravity greater than 1.1. Although unhalogenated compounds satisfying the above requirements may be used, preferred solvents are halogenated hydrocarbons including, for example, the following: Monochlorobenzene, dichlorobenzene, trichlorobenzene, methylene chloride, chloroform, carbon tetrachloride, the dichloroethanes, the trichloroethanes, trichloroethylenes, the chloro and polychloropropanes, the chloro and polychlorobutanes, and the chloro and polychloro derivatives of higher members of this homologous series. Other suitable solvents include cyclohexyl chloride and methyl chloroacetate. The amount of solvent used in the liquid corrosion inhibiting composition for use in oil wells may be varied from 5 percent or less to about 75 percent. The minimum amount of solvent that may be used is that amount which will bring the specific gravity of the composition to at least 1.01. A greater amount of solvent would be used to reduce viscosity of the composition where viscous inhibitors and/or immiscibilizing agents are used to that viscosity at which the composition will flow to the

bottom of the well. Also, more solvent would be used in the composition where the atmospheric temperatures are low in order that the composition may be readily transferred by pouring.

The immiscibilizing agent is a nonionic surface active compound soluble in the mixture of corrosion inhibiting compound and solvent and which agent by reason of its hydrophylic nature reduces the solubility of the liquid corrosion inhibiting composition in petroleum oil and which agent assists in the dispersion of the corrosion inhibiting compound under the turbulent conditions at the bottom of the well. Nonionics that may be used are those having certain definite balance between the hydrophylic and lipophylic portion of the molecule. This balance may be expressed by the HLB value of the molecule which may be determined in accordance with the methods taught by W. C. Griffin in Journal of Cosmetic Chemists, vol. II, No. 4, 1954. Thus:

$$HLB = 20 \left(1 - \frac{S}{A} \right)$$

where:

HLB=hydrophile—lipophile balance

S=saponification number of the nonionic

A=acid number of the fatty acid portion of the nonionic,

or:

$$HLB = \frac{E}{5}$$

where:

E=weight percentage of the hydrophilic portion of the nonionic.

Nonionics that may be used in the process of this invention have HLB values of from 10 to 17, however, the preferred range is from 13.5 to 15.5. To obtain this range of HLB values the hydrophilic portion of the nonionic molecule may be from 50 to 85 percent of the nonionic molecule.

Different types of nonionic surface active compounds that may be used are as follows:

Type of Nonionic Compound:	Prepared in Accordance with U. S. Patent—
1. Polyoxyalkylene ethers of fatty alcohols.	1,970,578, Schoeller et al., August 21, 1934. 2,425,755, Roberts, August 19, 1947. 1,970,578. 2,457,139, Fife et al., December 28, 1948.
2. Polyoxyalkylene esters of fatty acids.	2,542,607, Nevison et al., February 20, 1951. 2,559,583, Barker, July 10, 1951. 2,422,486, Johnston, June 17, 1947.
3. Polyoxyalkylene ethers of polyhydroxy alkyl esters of fatty acids.	1,970,578. 2,085,706, Schoeller et al., June 29, 1937.
4. Polyoxyalkylene ethers of alkyl phenols.	2,522,447, Harris, September 12, 1950.
5. Polyoxyalkylene ethers of alkyl naphthols.	1,970,578. 2,085,706.
6. Polyoxyalkylene thioethers of fatty mercaptans.	2,522,446, Harris, September 12, 1950.
7. Polyoxyalkylene derivatives of fatty acid amides.	2,565,986, Olin, September 28, 1951. 1,970,578. 2,085,706.
8. Polyoxyalkylene derivatives of fatty acid alkylol amides.	2,559,584, Barker, July 10, 1951. 2,470,081, Thurston et al., May 10, 1949.
9. Polyoxyalkylene derivatives of amines.	2,174,762, Schuette et al., October 3, 1939.
10. Polyethylene imide derivatives of fatty acids.	2,510,284, Haggard, June 6, 1950. 2,222,208, Ulrich, November 19, 1940.
11. Polyoxyalkylene derivatives of oxazolines.	2,636,038, Brandner, April 21, 1953.

Nonionic surface active compounds selected from the above list and having HLB values in the preferred range for use in the process of this invention are known by their trade names as Atlas G-1441, Atlas G-2079, Atlas G-2144, Atlas G-3720, Atlas G-3915, Atlas G-3920, Tweens 60, 65, 80, and 85.

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Atlas G-1441 is a polyoxyethylene sorbitol lanolin derivative having an HLB value of 14.

Atlas G-2079 is a polyoxyethylene monopalmitate having an HLB value of 15.5 and a general formula:



where x = about 20.

Atlas G-2144 is a polyoxyethylene mono-oleate having an HLB value of 15.1 and a general formula:



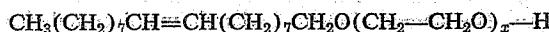
where x = about 20.

Atlas G-3720 is a polyoxyethylene monostearyl ether having an HLB value of 15.3 and a general formula:



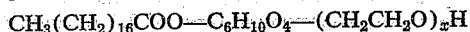
where x = about 20.

Atlas G-3915 and Atlas G-3920 are polyoxyethylene monooleyl ethers having HLB values of 15.3 and 15.4, respectively, and the general formula:



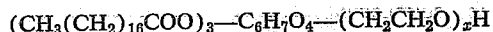
where x = about 19 to 20.

Tween 60 is a polyoxyethylene sorbitan monostearate having an HLB value of 14.9 and the general formula:



where x = about 15.5.

Tween 65 is a polyoxyethylene sorbitan tristearate having an HLB value of 10.5 and a general formula:



where x = about 18.

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mild carbon steel test coupon subject to corrosion conditions in the presence of 50 p. p. m. of inhibitor composition by comparing the weight loss of a similar test coupon when subject to corrosion conditions in the absence of the inhibitor composition. A large mouth bottle of about 250 ml. capacity was charged with 150 ml. of Arbuckle brine and 50 ml. of Arbuckle oil containing the corrosion inhibitor composition being tested. The bottle was agitated to distribute the corrosion inhibitor between the two phases, a weighed 1-inch by 3-inch 10-20 mild carbon steel coupon inserted, and the bottle stopper fitted on. Carbon dioxide was bubbled through the solution at a rate of about 12 ml. per second. After about 160 hours, the coupon was removed from the bottle, descaled by scrubbing with a nylon bristle brush and a cleaning powder, weighed and its loss in weight determined. The same technique was followed to obtain a blank in the absence of corrosion inhibitor. The percent protection was calculated as follows:

$$P. C. P. = \frac{(Wb_i - Wb_f) - (Wc_i - Wc_f)}{(Wb_i - Wb_f)} \times 100$$

where:

P. C. P. = Percent protection afforded by inhibitor.

Wb_i = Initial weight of coupon subjected to test in the absence of inhibitor.

Wb_f = Final weight of coupon subjected to test in the absence of inhibitor.

Wc_i = Initial weight of coupon subjected to test in the presence of inhibitor.

Wc_f = Final weight of coupon subjected to test in the presence of inhibitor.

Protection afforded by various inhibitor compositions

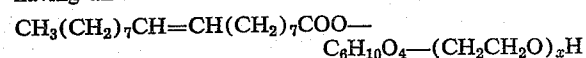
[50 p. p. m. corrosion inhibiting composition in 3 parts of Arbuckle brine and 1 part of Arbuckle oil and a carbon dioxide environment for 160 hours.]

Experiment No.	Corrosion Inhibiting Composition					
	Corrosion Inhibitor	Parts Per 100 Parts of Composition	Immiscibilizing Agent	Parts Per 100 Parts of Composition	Solvent	Parts Per 100 Parts of Composition
1	D-85	65	Tween 80	15	Dichlorobenzene	20
2	PDBSO ₂ Na ¹	65	do	15	do	20
3	PDBSO ₂ Ca	65	do	15	do	20
4	Imidazole/PDBSO ₂ ²	65	do	15	do	20
5	D-85	65	Tween 65	15	do	20
6	D-85	65	Tween 85	15	do	20
7	D-85	65	Tween 60	15	do	20
8	D-85	65	Tween 80	15	CCl ₄	20
9	D-85	65	do	15	Trichloroethylene	20
10	D-85	70	do	25	Dichlorobenzene	5
11	D-85	50	do	20	do	30
12	D-85	40	do	10	do	50
13	D-85	20	do	5	do	75
14	M-461-R	65	do	15	do	20

¹ Sodium postdodecylbenzene sulfonate.

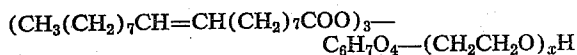
² Postdodecylbenzene sulfonic acid.

Tween 80 is a polyoxyethylene sorbitan mono-oleate having an HLB value of 15.0 and the general formula:



where x = about 16.

Tween 85 is a polyoxyethylene sorbitan trioleate having an HLB value of 11 and a general formula:



where x = about 20.

The following specific examples are illustrative of this invention in which parts given are parts by weight.

EXAMPLE 1

The efficiencies of the various corrosion inhibitors were compared by determining the percent protection given a

EXAMPLE 2

Example 1 was repeated with the exception a hydrogen sulfide environment was maintained for 160 hours rather than a carbon dioxide environment. The results obtained were very similar to those obtained in Example 1.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

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 an oil soluble iron

corrosion inhibitor, an oil immiscibilizing agent for said corrosion inhibitor said immiscibilizing agent is a non-ionic surface active compound having a hydrophile-lipophile balance (HLB) value of from 10 to 17 as determined by the following formula:

$$HLB = 20 \left(1 - \frac{S}{A} \right)$$

wherein:

S =saponification number of the nonionic

A =acid number of the fatty acid portion of the nonionic

and a mutual solvent having a specific gravity of more than 1.1 for said inhibitor and said immiscibilizing agent in an amount sufficient to increase the specific gravity of the inhibitor composition above that of the corrosive liquids to enable the inhibitor composition to fall readily through the liquid column to the producing zone and diffuse at least partially throughout said liquid column.

2. The method of claim 1 wherein the amount of said iron corrosion inhibitor, said oil immiscibilizing agent and said mutual solvent based upon the total weight of the corrosion inhibiting composition varies from 20 to 70 percent, 5 to 25 percent, and 5 to 75 percent respectively.

3. The method of claim 1 wherein the amount of said iron corrosion inhibitor, said oil immiscibilizing agent and said mutual solvent based upon the total weight of the corrosion inhibiting composition varies from 50 to 70 percent, 5 to 25 percent, and 5 to 75 percent respectively.

4. The method of claim 1 wherein said immiscibilizing agent is a nonionic surface active compound having a hydrophile-lipophile balance within the range of 13.5 to 15.5.

5. The method of claim 1 wherein the immiscibilizing agent is a polyoxyethylene sorbitan mono-oleate.

6. The method of claim 1 wherein the immiscibilizing agent is a polyoxyethylene sorbitan monostearate.

7. The method of claim 1 wherein the oil soluble iron corrosion inhibitor is a polymerized unsaturated acid having the following properties: acid value 94-116, iodine value 44-50, and molecular weight ca. 750.

8. The method of claim 1 wherein the oil soluble iron corrosion inhibitor is a polymerized unsaturated acid having the following properties: neutral equivalent 290-310, iodine value 80-95, dimer content ca. 85%, and trimer and higher content ca. 12%.

9. The method of claim 1 wherein the oil soluble iron corrosion inhibitor is sodium postdodecylbenzene sulfonate wherein said sodium postdodecylbenzene sulfonate is the sodium salt of the sulfonic acid produced by sulfonating a mixture of monoalkylbenzene and dialkylben-

zenes in the approximate ratio of 2:3 having the following physical properties:

Specific gravity at 38° C.	0.8649
Average molecular weight	365
Percent sulfonatable	88

A. S. T. M., D-158 Engler:

I. B. P.	° F.	647
5	° F.	682
50	° F.	715
90	° F.	760
95	° F.	775
F. B. P.	° F.	779

Refractive index at 23° C. 1.4900

Viscosity at:

-10° C.	centipoises	2800
20° C.	do.	280
40° C.	do.	78
80° C.	do.	18

Aniline point. ° C. 69

Pour point. ° F. -25

10. The method of claim 1 wherein the oil soluble iron corrosion inhibitor is calcium postdodecylbenzene sulfonate wherein said calcium postdodecylbenzene sulfonate is the calcium salt of the sulfonic acid produced by sulfonating a mixture of monoalkylbenzene and dialkylbenzenes in the approximate ratio of 2:3 having the following physical properties:

Specific gravity at 38° C.	0.8649
Average molecular weight	365
Percent sulfonatable	88

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80° C.	do.	18

Aniline point. ° C. 69

Pour point. ° F. -25

References Cited in the file of this patent

UNITED STATES PATENTS

2,466,530	Blair et al.	Apr. 5, 1949
2,649,415	Sundberg et al.	Aug. 18, 1953
2,671,757	Wisherd	Mar. 9, 1954