United States Patent Office 3,712,863 Patented Jan. 23, 1973

3,712,863

WELL TREATING FLUID AND CORROSION INHIBITOR

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No Drawing. Division of application Ser. No. 88,168, Nov. 9, 1970, which is a continuation of application Ser. No. 770,130, Oct. 23, 1968, which is a continuation-in-part of application Ser. No. 634,967, May 1, 1967, which in turn is a continuation-in-part of application Ser. No. 528,764, Feb. 21, 1966, all now abandoned. This application Feb. 23, 1971, Ser. No. 118,171

Int. Cl. C23f *11/00*

U.S. Cl. 252—8.55 E 6 Claims

ABSTRACT OF THE DISCLOSURE

An iron corrosion inhibitor is coupled to a weighting material to produce a liquid formulation which will fall through oil in well annulus without separation but after it has fallen through water beneath the oil the inhibitor will separate from the weighting material and float back to the oil-water interface where it can enter well tubing ports. The inhibitor includes carboxlyic acid, e.g. petroleum wax oxidate, type inhibitor reacted with amine type corrosion inhibitor and dispersed in an organic solvent system. Sulfonic acid may be used to disperse the water insoluble amines. The weighting material is water soluble metal salt including zinc chloride. Usually an alcohol is the coupling agent.

This application is a division of prior application Ser. No. 88,168 filed Nov. 9, 1970, which was a continuation of our prior application Ser. No. 770,130 filed Oct. 23, 1968, which was a continuation-in-part of our prior application Ser. No. 634,967 filed May 1, 1967, which was a continuation-in-part of our prior application Ser. No. 528,764 filed Feb. 21, 1966, all now abandoned.

This invention pertains to treatment of well pipes to prevent corrosion.

It is known to protect well pipes against corrosion by means of organic corrosion inhibitors including carboxylic acids (e.g. mono-, di-, and tri-carboxylic acids) and ammoniacal compounds (e.g. amines, diamines, imidazolines, amine polymers, amidoamines, oxazolines). Such organic inhibitors are disclosed, for example, in U.S. Pats. 2,466,517; 2,466,530; 2,468,163; 2,598,213; 2,599,385; and 2,756,211.

In the use of such organic inhibitors it is customary, as disclosed in the aforesaid U.S. patents, to arrange that the inhibitor reach the bottom of the well so that the full length of the well pipe is contacted by and protected with the inhibitor. To this end, in order to avoid the use of pumping equipment which represents over 50% of the cost of the usual treatment job, it has been proposed to add to the inhibitor a weighting material to carry it quickly by gravity to the bottom of the well. Some difficulty may be experienced with known weighting materials. Stick type weighted inhibitors tend to hang up in couplings and thus fail to reach bottom. Solid weighting materials also tend to clog up chokes when delivered into the well fluid. Some weighting materials are undesirable because they will poison the catalysts used at the refineries. Certain inhibitor-weighting material emulsions tend also to create oil-water-emulsions of the well fluid necessitating extra expense to treat and break the well fluid emulsion.

According to the present invention a weighted, corrosion inhibiting, treating fluid is provided which is free of the above mentioned disadvantages.

The treating fluid embodying the present invention is especially useful in connection with pumping wells having fluid communication between the tubing and annulus. In such wells there is usually an oil-water interface near the bottom of the well adjacent the ports in the tubing that place the annulus in communication with the tubing. The treating fluid of the present invention has the special property that after being dumped into the annulus it will fall through the oil without separation but after it has fallen through the water the inhibitor will separate from the weighting material and float back to the oil-water interface. At the interface the inhibitor is close to the tubing ports through which it enters the tubing and quickly diffuses into the tubing fluid.

Briefly, according to the invention, an organic inhibitor formulation, including carboxylic acid and ammoniacal compound, dispersed in a solvent system, is weighted with a primarily aqueous solution of metal salt, the foregoing formulation and weighting material being bound together by suitable coupling agent tending to prevent separation of the inhibitor formulation and weighting material.

The inhibitor formulation will have a density in the range of 7 to 8 lb./gal., usually from 7.5 to 8.2 lb./gal. This is a density comparable to that of oil, usually about 7 to 8 lb./gal., ranging from 6.5 lb./gal. for gasoline and kerosene up to 8.3 for naphtha, but is less than that of water, fresh water having a density of 8.33 lb./gal. at room temperature and salt water ranging in density up to over 9 lb./gal.

The weighting material will have a density in the range of 16–18 lb./gal. In order to provide a treating fluid having a desired density higher than the density of the inhibitor formulation, the necessary amount of the weighting material is added to the inhibitor formulation. Preferably the treating fluid will have a density in the range of 8.2 to about 12 lb./gal., the lower end of the range representing treating fluids denser than the anticipated oil in the well but intended to float at the oil water interface, the upper end of the range representing treating fluids intended to fall quickly through the water as well as the oil, followed by release of the inhibitor formulation which then floats back up to the oil-water interface.

The following is an example of the composition by weight of a treating fluid that has been used successfully:

Material	Possible range, percent	Example I composition, percent
1. Petroleum wax oxidate, 75% to 95% strength (Texaco TX-3650 acid)	3-25	7.9
2. Crude N-hydroxyethylethylene diamine, 75% to 95% strength (Jefferson Chemical Co., Amine AL-1)	0.5-30	2.5
3. Mixed di- and tri-aminoethyl glyoxalidine, 75% to 95% strength (Textilana, PR7475)	0.5-20	1.3
4. Dodecyl benzene sulfonic acid, 99% strength	0.5-20	0.9
5. Residue bottoms from production of butyl alcohol, 100% strength	0.0-30	18.7
6. Calcium chloride (solid, commercially pure)	1.0-20	8.6
7. Zinc chloride (solid, commercially pure)	10.0-60	43.1
8. Water	10.0-50	14.6
9. Isopropyl alcohol, 99% strength	1.0-25	2.5

Items 1, 2 and 3 will be recognized as the carboxylic acid and the ammoniacal compounds constituting the inhibitor. Item 1 reacts with items 2 and 3. Item 4 reacts with 2 and/or 3 to form dispersions. Item 5 is the organic solvent system in which the inhibitors are dispersed. Items 6–8 constitute the weighting material. Item 9 is the primary coupling agent. It is to be appreciated that many of the other items assist in coupling the inhibitor formulation to the weighting material.

As noted in the left hand column of the above chart, the composition of the treating material can be varied considerably using the particular constituents there named. In addition, other constituents can be substituted, as will next be discussed.

For the inhibitor formulation, any of the variety of organic inhibitors previously mentioned may be used. The inhibitor component of the treating fluid functions by forming a persistent film over the metal to be protected, thereby keeping the metal out of contact with the corroding substance. Any suitable solvent for the inhibitor may be used, e.g. alcohol, naphtha, water. Dispersing agents that are suitable include:

(a) Sulfonates;

(b) Oxalkylated alkyl phenols; and

(c) Polyols and esterified polyols from 1,000 to 20,000 molecular weight.

For the weighting material the soluble salts of a large number of metals are available, e.g. such salts of magnesium, calcium, strontium, barium, aluminum, tin, lead, copper, zinc, cadmium, manganese sodium, potassium, iron, cobalt, and nickel. The salt should be soluble in water or other polar solvent. Desirable factors involved in the choice of particular metal salts are high density, high water solubility, low cost, good coupleability to the inhibitor formulation, and lack of undesirable side effects such as corrosion production.

The weighting material will be recognized as similar in composition to packer fluids used in controlling excess formation pressure in wells and the subject treating material may be considered to comprise an organic corrosion inhibitor coupled to such packer fluid serving in this case as a weighting material. A preferred formulation for the weighting material per se is as follows:

EXAMPLE II

Material		Pounds
Item number:		
1	Water	99
2	Calcium chloride	58
3	Zinc chloride	292
4	Hydrochloric acid	4

In preparing the weighting material of Example II a suitable method is to add the calcium chloride to the water and mix until a clear solution is obtained. Then add the zinc chloride and hydrochloric acid to the previous mixture and mix until a clear solution is obtained. The same procedure is applicable to other weighting material compositions within the scope of the invention.

The primary coupling agent for coupling the inhibitor formulation to the weighting material will usually be one of the alcohols. It is also to be borne in mind that the components selected for the inhibitor formulation and the weighting material may assist in the coupling thereof. In Example I the zinc of the weighting material tends to couple with the amine component of the inhibitor formulation. Also, the sulfonic acid dispersant functions as a coupler by reacting with the non-water soluble amines to render them more water soluble. The chlorides of the weighting material also assist in coupling the inhibitor to the weighting agent.

The following is a general method for preparing the well treating fluid according to the invention:

(1) Put solvent system in mixing tank.

(2) Add organic (carboxylic) acid, mix well.

(3) Add ammoniacal compounds and mix well.

(4) Add dispersant and mix well until entire contents of tank are homogeneous.

(5) Add premixed salt solution (weighting material) and mix well.

The resultant treating material is a stable liquid product that does not separate in storage. Furthermore, it can fall through thousands of feet of oil without separating. After falling through a few thousand feet of water, however, the intermingling and complexing of the inhibitor

formulation with the weighting material is broken and the organic and/or metal-organic portion of the treating fluid is released from the remainder which is principally, though not altogether, the aqueous salt solution.

The treating fluid of the present invention is easily used. A lubricator is connected to the tubing of flowing wells or to the casing of pumping wells. The treating fluid is introduced into the lubricator and the lubricator closed to atmosphere. The lubricator is then opened to the well, pressure in the well and lubricator equalizes, and the treating fluid falls into the well. The inhibitor component of the treating fluid adheres to and forms a protective film over the well pipe as it falls through the oil or gas to the water at the bottom of the well, and continues to coat the pipe after contact with the water, releases the inhibitor component from the weighting material.

The length of protection obtained with the treating fluid of the invention is about the same as that obtained with other film persistent corrosion inhibitors. The treating fluid of Example I was used successfully in a well in the Eugene Island field in Louisiana. In this case the well still had satisfactory corrosion protection ten months after treatment.

The following is given as another example of the composition by weight of a treating material embodying the invention and currently in use:

EXAMPLE III

Material		Pounds
Item number:		
1	Water	53
2	Isopropyl alcohol	89
3	Petroleum wax oxidate, 75% to 95% strength (same as in Example I).	53
4	Crude N hydroxyethyethylene diamine, 75% to 95% strength (same as Example I).	16
5	Mixed di- and tri-aminoethyl glyoxalidines, 75% to 95% strength (same as in Example I).	8
6	Dodecylbenzene sulfonic acid	6
7	Water	99
8	Calcium chloride	58
9	Zinc chloride	292
10	Hydrogen chloride (37% acid)	4

In preparing the treating fluid of Example III, the isopropyl alcohol and water are mixed five minutes to provide the solvent system. Then the organic corrosion inhibitors (wax oxidate, diamine, and glyoxalidine-items 3, 4, and 5) are added to the solvent system and mixed for 30 minutes. Next, the sulfonic acid dispersant is added and mixed for 45 minutes. With the mixer running slowly, the premixed and cooled (below 130 deg. F., preferably to room temperature) weighting material (items 7–10) are added. The addition of the weighting material is accomplished slowly enough so that time is allowed for the heat of reaction to be dissipated, the temperature never being allowed to exceed 130 deg. F., for if the mix get too hot, the resultant product will not be stable and will separate.

In mixing the weighting material for Example III the calcium chloride is mixed with the water (item 7) until a clear solution is obtained. The zinc chloride and hydrochloric acid are then added and the mixing continued until a clear solution is obtained. Then the mixture is cooled to preferably 75 deg. F. before adding to the inhibitor formulation.

An embodiment of the present invention has the following physical properties:

Specific gravity—1.38
Density (lb./gal.)—11.5
Viscosity—300 cps. at 75° F.
Flash point (closed cup)—170° F.
Pour point—28° F.

This material is especially recommended for use in the following situations:

(1) To treat gas wells by means of pumping, pouring, or lubricating the inhibitor down the tubing. Gas wells that are not adapted to squeeze type treatments because of

reservoir characteristics can be treated with this material. Examples of the latter type of wells are those that require extremely high pressure to displace the inhibitor into the formation and wells in which a squeeze type treatment may tend to kill the flow from the well.

(2) To treat the annular area of dual and triple and other multiple completed wells.

(3) To treat high fluid level pumping wells.

The treatment fluid of the invention possesses the unique property that when it is immersed in water or brine, the weighting material will slowly diffuse into the water and release the inhibitor concentrate. The inhibitor concentrate will then rise to the oil water interface. It will also enter the tubing perforations, if the well is a producing, pumping well. The treating fluid does not contain any organic halides, arsenic, or other substance that would be detrimental to oil refineries. The treating material can be made to have densities in the range from about 7.5 to about 12 pounds per gallon.

Although in the preferred embodiments of the invention heretofore described the weighting material metal salts have been described as being in an aqueous or other polar solution prior to addition thereof to the inhibitor formulation, it is also possible to add the salts directly to the inhibitor formulation and then add the polar solvent.

That being claimed is:

1. A weighted liquid corrosion inhibitor formulation consisting essentially of:

(1) a corrosion inhibiting mixture of an imidazoline corrosion inhibitor and a petroleum wax oxidate,

(2) an aqueous solution of zinc chloride to provide a density in the range of 8.2 to about 12 pounds per gallon,

(3) a water soluble alcohol as a coupling agent to prevent separation of said corrosion inhibiting mixture and said aqueous solution.

2. Formulation according to claim 1 additionally including a dispersing agent.

3. Formulation according to claim 2 wherein said dispersing agent includes dodecyl benzene sulfonic acid.

4. Formulation according to claim 2 wherein said aqueous solution includes also calcium chloride in minor proportion to said zinc chloride.

5. A weighted liquid corrosion inhibitor formulation consisting essentially of:

(1) a corrosion inhibiting mixture of an imidazoline corrosion inhibitor and a petroleum wax oxidate,

(2) an aqueous solution of zinc chloride to provide a density in the range of 8.2 to about 12 pounds per gallon,

(3) isopropyl alcohol as a coupling agent to prevent separation of said corrosion inhibiting mixture and said aqueous solution.

6. Formulation according to claim 5 additionally including dodecyl benzene sulfonic acid as a dispersing agent and wherein said aqueous solution includes also calcium chloride in minor proportion to said zinc chloride.

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U.S. Cl. X.R.

21—2.5, 2.7; 166—310; 252—389