

# UNITED STATES PATENT OFFICE

2,614,980

## PROCESS FOR INHIBITING CORROSION IN OIL WELLS

Melba L. Lytle, Houston, Tex., assignor, by mesne assignments, to Standard Oil Development Company, Elizabeth, N. J., a corporation of Delaware

No Drawing. Application April 3, 1950,  
Serial No. 153,767

10 Claims. (Cl. 252—8.55)

1

This invention relates to a method of inhibiting the corrosiveness to corrodible ferrous metal surfaces of corrosive fluids containing hydrogen sulfide. More particularly, the invention relates to means for inhibiting the corrosivity of sulfide-containing, subsurface formation fluids to the corrodible conduits and attendant equipment through which the fluids are flowed and processed.

Crude oil containing soluble sulfides is often produced from subsurface formations and corrosion of conduits and attendant equipment is especially severe in those instances in which brine is produced along with the sour crude. Corrosive sulfide brines may include alkali metal sulfides, alkaline earth metal sulfides, acid sulfides such as hydrogen sulfide, and/or organic sulfides. Those brines containing hydrogen sulfide are especially corrosive to iron and steel equipment, the sulfides attacking the metal to form iron sulfide. Since these corrosive substances occur in or are introduced into the fluids originating in the subsurface formations, corrosion may occur throughout the conduits and attendant equipment through which the fluids from the subsurface formations are flowed and produced. In other cases the corrosion may be more or less localized to a limited portion of the conduits through which the fluids from the subsurface formations are produced. In any case, corrosion of the conduits and/or attendant equipment may be so severe as to require replacement of either or of both. Such replacements can be, and often are, extremely expensive. The expense involved is not limited merely to the cost of replacing the corroded equipment but may also involve killing the well in order to make repairs and to replace the corroded equipment. Not only is the cost of killing the well high, but there is a marked loss in revenues due to having a well off production and to the necessity of having to maintain additional wells and sources of supply to meet production requirements during the period when the well is off production for repairs as a result of the corrosion. Corrosion may, on occasion, be so severe as to result in failure of the equipment in which event the well may flow wild. Enormous losses are incurred in such an eventuality.

The main object of the present invention is to provide a method of substantially eliminating or inhibiting the corrosive action of subsurface fluids containing sulfides to conduits and attendant equipment through which the fluids are produced from the subsurface formations in which they originate.

2

According to the present invention the corrosivity to corrodible ferrous metal surfaces by corrosive subsurface fluids including hydrogen sulfide is eliminated or substantially reduced by incorporating in the corrosive fluids a corrosion inhibiting amount of a fatty derivative of an alkyl or an alkanol amine. This fatty derivative is prepared by reacting a fatty material selected from the class of fatty oils and fatty acids and an alkyl or alkanol amine at a temperature in the range of 300° to 550° F. in the presence of an alkaline reacting catalyst. Alkali metal hydroxides or carbonates, or mixtures thereof, may be suitably employed as an alkaline reacting catalyst.

Fatty acids which may suitably be used as the fatty material in the aforementioned reaction include those fatty acids having at least 12 and no more than 26 carbon atoms per molecule. As examples of such acids, mention may be made of oleic, ricinoleic, linoleic, linolenic, licanic, eleostearic, arachidonic, clupanodonic, lauric, myristic, arachidic, stearic, palmitic, etc. The fatty oils which may be employed are those from which fatty acids having from 12 to 26 carbon atoms in the molecule can be derived. Fatty oils which have been found to produce especially effective agents include tung oil, China-wood oil, oiticica oil, chaulmoogra oil, cottonseed oil, menhaden oil, linseed oil, castor oil, and the like. It will be understood, of course, that mixtures of individual members of the aforementioned class of oils or mixtures of the individual members of the aforementioned class of acids or mixtures including both oils and acids may be employed as the fatty material from which the corrosion inhibiting agent of the present invention is produced.

Various alkyl and/or alkanol amines may suitably be employed in the aforementioned reaction to produce the corrosion inhibiting reaction product of the present invention. Examples of alkanol amines which may be employed include triethanol amine, di-n-propanol amine, di-isopropanol amine, tri-n-propanol amine, tri-isopropanol amine, di-n-butanol amine, di-isobutanol amine, di-tert. butanol amine, tri-n-butanol amine, tri-isobutanol amine, tri-tert. butanol amine, etc. Examples of alkyl amines which may be employed include triethyl amine, di-n-propyl amine, di-isopropyl amine, di-n-butyl amine, di-isobutyl amine, di-tert. butyl amine, tri-n-propyl amine, tri-isopropyl amine, tri-n-butyl amine, tri-isobutyl amine, tri-tert. butyl amine, tri-amyl amine (and its isomeric

3

forms), tri-hexyl amine (and its isomeric forms), etc. Rather than containing only alkanol or alkyl groups, the amines employed may contain both alkanol and alkyl groups. Examples of such alkyl-alkanol amines include di-ethyl,ethanol amine; ethyl,di-ethanol amine; ethyl,di-n-propanol amine; di-ethyl,n-propanol amine; ethyl,di-isopropanol amine; di-ethyl,isopropanol amine; n-propyl,di-ethanol amine; isopropyl,di-ethanol amine; di-n-propyl,ethanol amine; di-isopropyl,ethanol amine; ethyl,di-butanol amine; etc. While the amines employed preferably contain a total of between 6 and 18 carbon atoms in the alkyl and/or alkanol side chains, they may contain an even larger number of carbon atoms in the side chains. It will be understood, of course, that mixtures of the aforementioned amines may suitably be employed. Polymers of these amines, such as the polymers of tri-ethanol amine, may also be employed.

When the fatty derivatives of the present invention are prepared from a fatty oil, it is preferable that the fatty oil be present in the initial reaction mixture in a weight ratio of from about 1:1 to about 5:1 as compared to the alkyl or alkanol amine. When the fatty derivative is prepared from a fatty acid, the fatty acid is preferably present in the initial reaction mixture in a weight ratio of from about 0.5:1 to about 3:1 as compared to the amine.

The effectiveness as a corrosion inhibiting agent of the reaction product of fatty oils and/or fatty acids with alkyl amines and/or alkanol amines depends upon the temperature at which the reaction is conducted. If the reaction is conducted at a temperature below about 300° F., the resulting reaction product possesses little, any, effectiveness as a corrosion inhibiting agent for well fluids containing hydrogen sulfide. On the other hand, if the reaction is conducted at a temperature in excess of about 550° F., the reaction product obtained tends to be of very high solidification point and of low solubility in the corrosive media. The particular temperature selected will depend to some extent upon the particular fatty oil or acid employed and upon the particular amine employed. For example, when the corrosion inhibiting agent is prepared from tri-ethanol amine and either tung oil, oiticica oil, chaulmoogra oil, or cottonseed oil in the presence of sodium hydroxide, a reaction temperature maintained for 1½ to 4 hours in the range of 400° to 475° F. results in a product of especially desirable inhibition properties.

The extent of reaction, in addition to depending upon reaction temperature, also depends upon the time during which the reaction is permitted to continue. Ordinarily, an effective agent may be prepared when the reactants are reacted for a period of time in the range of from ½ to 5 hours, although the preferred time is in the range of 1½ to 4 hours.

As hereinbefore mentioned, an alkaline reacting catalyst such as alkali metal hydroxides or carbonates or mixtures thereof is employed. Examples of such materials are sodium hydroxide or sodium carbonate. The alkaline reacting catalyst concentrations ordinarily need not exceed about 3 per cent by weight of the reactants although considerably lower concentrations may be successfully employed. For example, a concentration of 0.5 per cent by weight of sodium hydroxide or sodium carbonate based upon the weight of the reactants has been found sufficient to promote the reaction. As a matter of

4

fact, as little as about 0.05 per cent of sodium hydroxide based upon the weight of the reactants has been found sufficient. Of course, mixtures of sodium hydroxide and sodium carbonate may be employed.

On completion of the reaction, the reaction product is allowed to cool and may be incorporated as such in the corrosive fluid to be treated or may be first dissolved in a suitable solvent such, for example, as an aromatic solvent or kerosene, and the solution incorporated in the corrosive fluid.

The amount of fatty derivatives of the present invention employed to inhibit the corrosion of ferrous metal surfaces by well fluid mixtures including moisture and hydrogen sulfide may be varied over a relatively wide range. However, it has been found that amounts within the range of 0.005 per cent to 0.1 per cent by volume of the fluid mixture give satisfactory results. Ordinarily, an amount within the range of 0.005 per cent to 0.01 per cent by volume will be sufficient.

The following examples will illustrate the effectiveness of the corrosion inhibitors hereinbefore described in inhibiting the corrosivity of a corrosive well fluid including hydrogen sulfide to corrodible ferrous metal surfaces.

#### EXAMPLE I

40 parts by weight of triethanol amine, 52 parts by weight of tung oil, and 2 parts by weight of sodium hydroxide were heated together at 445° to 465° F. for a period of about 5 hours. In order to test the effectiveness of the reaction product thus formed, 0.01 volume per cent and 0.005 volume per cent were added to two different samples of a 50:50 mixture of West Texas crude oil and West Texas brine, the mixture being saturated with hydrogen sulfide. Mild carbon steel coupons were immersed 31 times per minute for a period of 14 days in each of these samples. The extent of the corrosion inhibition obtained was compared with results obtained when similar coupons were exposed under identical conditions to a hydrogen sulfide saturated 50:50 mixture of West Texas crude oil and West Texas brine, no corrosion inhibitor being present. The comparative results obtained are shown in Table I below.

Table I

Inhibitor	Conc. of Inhibitor, Vol. Per cent	Corrosion Rate of Coupons, In./Yr.	Percent Reduction Over Blank
None		0.0093	
Reaction Product of Triethanolamine, Tung Oil and Sodium Hydroxide	0.01	0.0006	94
Do	0.005	0.0004	96

#### EXAMPLE II

60 grams of cottonseed oil, 38 grams of tri-ethanol amine, and 0.5 gram of sodium hydroxide were heated together at a temperature of 410° to 443° F. for a period of more than 1 but less than 2 hours. In order to test the effectiveness of the reaction product thus formed, it was incorporated in a 50:50 mixture of West Texas crude oil and West Texas brine saturated with hydrogen sulfide, the concentration of the reaction product in the mixture being 0.01 volume per cent of the mixture. A mild carbon steel coupon was suspended in a sealed glass tube containing 100 cc. of the oil-brine mixture and the coupon was immersed in the mixture 31 times per minute for a

5

period of 14 days. The extent of the corrosion inhibition obtained was compared with the results obtained when similar coupons were exposed under identical conditions to a hydrogen sulfide saturated 50:50 mixture of West Texas crude oil and salt water brine containing no inhibitor. The results obtained are shown in the following Table II below:

Table II

Inhibitor	Conc. of Inhibitor, Vol. Percent	Corrosion Rate of Coupons, In./Yr.	Percent Reduction Over Blank
None		0.0232	
Reaction Product of Cottonseed Oil, Triethanolamine, and Sodium Hydroxide	0.01	0.0002	99

<sup>1</sup> Average of seven determinations.

## EXAMPLE III

60 grams of cottonseed oil, 38 grams of triethanol amine, 0.5 gram of sodium hydroxide, and 2 grams of sodium carbonate were heated together at a temperature of 410° F. to 443° F. for a period of time greater than 1 hour but less than 2 hours. To test the effectiveness of this reaction product as a corrosion inhibitor, it was incorporated in two different samples of a 50:50 mixture of West Texas crude oil and West Texas brine saturated with hydrogen sulfide, the concentration of the reaction product in the mixture being 0.005 and 0.01 volume per cent of the mixture, respectively. The extent of corrosion inhibition obtained was compared with the results obtained when similar coupons were exposed under identical conditions to a similar hydrogen sulfide saturated West Texas crude oil-West Texas brine mixture containing no inhibitor. The results obtained are shown in Table III below.

Table III

Inhibitor	Conc. of Inhibitor, Vol. Percent	Corrosion Rate of Coupons, In./Yr.	Percent Reduction Over Blank
None		0.0232	
Reaction Product of Cottonseed Oil, Triethanolamine, Sodium Hydroxide, and Sodium Carbonate	0.01	0.0001	99
Do	0.005	0.0036	85

<sup>1</sup> Average of seven determinations.

## EXAMPLE IV

35 grams of tung oil, 30 grams of tri-amylamine, and 2 grams of sodium hydroxide were heated together at a temperature of 392° to 432° F. for a period of 2 hours. The resulting reaction product, when cooled, solidified at a temperature of 244° F. The effectiveness of this reaction product as an inhibitor was tested in a laboratory by using a concentration of 0.01, 0.005, and 0.001 weight percent in a 50:50 mixture of West Texas crude oil and West Texas brine which was saturated with hydrogen sulfide. 100 cc. of the oil-brine mixture containing the aforementioned amounts of reaction product was placed in a glass tube and a mild carbon steel coupon was then suspended in the tube. The coupon was immersed in the brine-oil mixture 31 times per minute for a period of 14 days. The extent of the corrosion inhibition obtained was compared with the results obtained when similar coupons were exposed under identical conditions

6

to a hydrogen sulfide saturated 50:50 mixture of West Texas crude oil and West Texas brine, this mixture containing no inhibitor. The results obtained are shown in Table IV below.

Table IV

Inhibitor	Conc. of Inhibitor, Wt. Percent	Corrosion Rate of Coupons, In./Yr.	Percent Reduction Over Blank
None		0.0344	
Reaction Product of Tung Oil, Triamylamine, and Sodium Hydroxide	0.01	0.0015	96
Do	0.005	0.0111	68
Do	0.001	0.0306	11

## EXAMPLE V

47 grams of tung oil, 47 grams of triethanol amine, and 2 grams of sodium hydroxide were heated together at a temperature of 400°-428° F. for a period of 3¼ hours. The reaction product obtained, when tested in a concentration of 0.01 volume per cent of a 50:50 West Texas crude oil-West Texas brine mixture by the procedure outlined in Example II, reduced the corrosion of the mixture by 95%.

## EXAMPLE VI

58 grams of oiticica oil, 40 grams of triethanol amine, and 2 grams of sodium carbonate were heated together at a temperature of 385°-403° F. for a period of 4 hours. The reaction product, when tested in a concentration of 0.01 and 0.005 volume percent of a 50:50 West Texas crude oil-West Texas brine mixture in the manner outlined in Example II, reduced corrosion by 95%.

## EXAMPLE VII

60 grams of chaulmoogra oil, 38 grams of triethanol amine, and 2 grams of sodium hydroxide were heated together at a temperature of 426°-438° F. for a period of 1 hour. This reaction product, when tested in a concentration of 0.01 volume percent of a 50:50 West Texas crude oil-West Texas brine mixture in the manner outlined in Example II, reduced corrosion by 95%.

## EXAMPLE VIII

60 grams of menhaden oil, 39 grams of triethanol amine, 0.5 gram of sodium hydroxide, and 2 grams of sodium carbonate were heated together at a temperature of 404°-438° F. for a period of 1½ hours. The reaction product, when tested in a concentration of 0.01 volume percent of a 50:50 West Texas crude oil-West Texas brine mixture in the manner outlined in Example II, reduced corrosion by 95%.

## EXAMPLE IX

70 grams of linoleic acid and 35 grams of triethanol amine were heated together at a temperature range of from 340° to 378° F. for a period of 30 minutes, no catalyst being employed. This reaction product, when tested in a concentration of 0.01 volume percent of a 50:50 West Texas crude oil-West Texas brine mixture in the manner outlined in Example II, reduced corrosion by 95%. (0.005 volume percent gave 90% reduction.)

## EXAMPLE X

70 grams of oleic acid and 37 grams of triethanol amine were heated together at a temperature range from 400° to 422° F. for a period of 1 hour, no catalyst being employed. This reaction product, when tested in a concentration of

0.01 volume percent of a 50:50 West Texas crude oil-West Texas brine mixture in the manner outlined in Example III, reduced corrosion by 95%.

#### EXAMPLE XI

58 grams of tung oil, 40 grams of tri-isopropanol amine, and 2 grams of anhydrous sodium carbonate were heated together at a temperature of 410°-421° F. for a period of 1½ hours. The reaction product thus formed, when tested in a concentration of 0.01 volume percent of a West Texas crude oil-West Texas brine mixture in the manner outlined in Example II, reduced corrosion by 95%.

#### EXAMPLE XII

A sample of tri-hydroxyethyl amine stearate obtained from a commercial source, when tested as an inhibitor for a 50:50 West Texas crude oil-West Texas brine mixture, gave a reduction in corrosion rate of 30%. This same commercial product, when heated at a temperature of 400° to 440° F. for a period of approximately 1 hour, reduced the corrosivity of the aforesaid brine-oil mixture by 95%.

The nature and objects of the present invention having been fully described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. A method for reducing the corrosiveness to corrodible ferrous metal of a corrosive petroliferous well fluid including moisture and hydrogen sulfide which comprises introducing into said fluid a corrosion inhibiting amount of the reaction product of a fatty material selected from the group consisting of fatty acids having no less than 12 and no more than 26 carbon atoms per molecule and a fatty oil containing fatty acid radicals having no less than 12 and no more than 26 carbon atoms with an amine selected from the group consisting of alkyl and alkanol amines having a total of no less than 6 and no more than 18 carbon atoms per molecule, the reaction product being formed at a temperature in the range of 300° to 550° F. and in the presence of an alkaline reacting catalyst selected from the group consisting of alkali metal hydroxide and alkali metal carbonate, the weight ratio of fatty material to amine being in the range of 0.5:1.0 to about 5.0:1.0.

2. A method for reducing the corrosiveness to corrodible ferrous metal of a corrosive petroliferous well fluid including moisture and hydrogen sulfide which comprises introducing into said fluid a corrosion inhibiting amount of the reaction product formed by reacting tung oil and tri-ethanol amine for a period of from ½ to 5 hours at a temperature in the range of 300° to 550° F. in the presence of an alkaline reacting catalyst selected from the group consisting of alkali metal hydroxide and alkali metal carbonate, the weight ratio of tung oil to tri-ethanol amine being in the range of 1:1 to about 5:1.

3. A method for reducing the corrosiveness to corrodible ferrous metal of a corrosive petroliferous well fluid including moisture and hydrogen sulfide which comprises introducing into said fluid a corrosion inhibiting amount of the reaction product formed by reacting tung oil with tri-amyl amine for a period of from ½ to 5 hours

at a temperature in the range of 300° to 550° F. in the presence of an alkaline reacting catalyst selected from the group consisting of alkali metal hydroxide and alkali metal carbonate, the weight ratio of tung oil to tri-amyl amine being in the range of 1:1 to about 5:1.

4. A method for reducing the corrosiveness to corrodible ferrous metal of a corrosive petroliferous well fluid including moisture and hydrogen sulfide which comprises introducing into said fluid a corrosion inhibiting amount of the reaction product formed by reacting menhaden oil with triethanol amine for a period of from ½ to 5 hours at a temperature in the range of 300° to 550° F. in the presence of an alkaline reacting catalyst selected from the group consisting of alkali metal hydroxide and alkali metal carbonate, the weight ratio of menhaden oil to tri-ethanol amine being in the range of 1:1 to about 5:1.

5. A method in accordance with claim 1 in which the reaction product is added to the corrosive well fluid in an amount in the range of 0.005% to 0.1% by volume of the fluid.

6. A method in accordance with claim 2 in which the reaction product is added to the corrosive well fluid in an amount in the range of 0.005% to 0.1% by volume of the fluid.

7. A method in accordance with claim 3 in which the reaction product is added to the corrosive well fluid in an amount in the range of 0.005% to 0.1% by volume of the fluid.

8. A method in accordance with claim 4 in which the reaction product is added to the corrosive well fluid in an amount in the range of 0.005% to 0.1% by volume of the fluid.

9. A method for reducing the corrosiveness to corrodible ferrous metal of a corrosive petroliferous well fluid including moisture and hydrogen sulfide which comprises introducing into said fluid a corrosion inhibiting amount of the reaction product formed by reacting cottonseed oil with triethanol amine for a period of from ½ to 5 hours at a temperature in the range of 300° to 550° F. in the presence of an alkaline reacting catalyst selected from the group consisting of alkali metal hydroxide and alkali metal carbonate, the weight ratio of cottonseed oil to tri-ethanol amine being in the range of 1:1 to about 5:1.

10. A method in accordance with claim 9 in which the reaction product is added to the corrosive well fluid in an amount in the range of 0.005% to 0.1% by volume of the fluid.

MELBA L. LYTTLE.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
1,992,689	Cox	Feb. 26, 1935
2,366,013	Duncan	Dec. 26, 1944
2,416,552	Valko	Feb. 25, 1947
2,460,259	Kahler	Jan. 25, 1949
2,466,517	Blair	Apr. 5, 1949
2,470,965	Woods	May 25, 1949

#### OTHER REFERENCES

"Alkaterge," Bulletin, November 8, 1948, Commercial Solvents Corp.