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CORROSION INHIBITION AND CORROSION INHIBITED HYDROCARBON

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My invention relates to the inhibition of corrosion, particularly the corrosion of iron and steel when in contact with petroleum hydrocarbons.

It is well known that rust frequently occurs in pipe lines, storage tanks and other equipment because of traces of moisture which inevitably are present in petroleum distillates. For example, although gasoline as it leaves the refinery is usually free of occluded moisture it might contain as much as 0.005 to 0.01 percent of dissolved moisture. Part of this dissolved moisture separates when the gasoline is chilled, and settles as a separate liquid phase beneath the main body of gasoline. Water can also enter gasoline systems along with air through partially filled tanks provided with breather devices. As such a tank cools, for example, at night, its contents contract and moisture-laden air is drawn in. This moisture condenses on the walls of the tanks, settles to the bottom and dried air is expelled when the contents of the tank again warm up, as from the heat of the sun the next day. Repetition of this cycle eventually leaves an appreciable amount of moisture at the bottom of the tank.

Rust that forms permanently injures expensive equipment and there is additional loss in terms of replacement costs of such equipment and operating time lost during such replacement. For example, where rust forms on interior surfaces of product pipe lines which are used for the transportation of light petroleum distillates such as gasoline, kerosene and home heating oil, and no effort is made to prevent the rust, this formation of rust can reduce the carrying capacity of the lines by more than 12 percent in one year. In addition to the decrease in life of rusted equipment such as storage tanks, there is also the danger of trouble in engine operation from failure of fuel carrying equipment and the likelihood of rust particles clogging carburetors or injecting devices for motors and burners, for example.

Another area in which iron and steel are subjected to corrosion is in the production of petroleum from wells. Some degree of corrosion takes place in the metallic equipment of practically all oil wells and in certain environments corrosion reaches costly proportions. The casing, tubing, sucker rods, and lead lines are particularly subject to corrosive effects. The sucker rods and sucker rod boxes which operate under heavy cyclic load conditions are especially susceptible to failure through corrosion fatigue. As a result of corrosion, costs may be greatly increased because of the necessity of pulling tubing and sucker rods for repair or replacement. Indirect costs in terms of production losses dur-

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ing shut-down for repair or replacement of rods, tubing and other equipment can also prove to be considerable.

In accordance with my invention, I have discovered that the corrosion of iron and steel which normally takes place when iron and steel are in contact with a petroleum hydrocarbon can be prevented or substantially retarded or inhibited by including in the petroleum hydrocarbon a small amount of an ammonium or amine salt of an alpha-sulfoalkyl acid of the formula $RCH(SO_2OH)COOH$, where R is an alkyl group having from 6 to 20 carbon atoms, and preferably from 14 to 18 carbon atoms. Mixtures of such salts can also be employed in accordance with my invention. Alpha-sulfoalkyl acids can be obtained by the sulfonation with sulfur trioxide of the corresponding carboxylic acids in accordance with procedures which are known in the art. Among the alpha-sulfoalkyl acids which can be thus prepared are: alpha-sulfodecanoic acid, alpha-sulfolauric acid, alpha-sulfomyristic acid and alpha-sulfopalmitic acid, alpha-sulfostearic acid and alpha-sulfobehenic acid. The salts which are utilized as corrosion inhibitors in accordance with my invention can be prepared in the way in which salts are normally prepared in the art by reaction of ammonia or an amine and an acid. It will be noted that the alpha-sulfoalkyl acids described above are dibasic acids. With ammonia or an amine, neutralization occurs first at the sulfonic acid group, which is the stronger acid group, and subsequently at the carboxyl group. Both the mono-salts (those in which only the sulfonic acid group has been neutralized) and the di-salts (those in which both the sulfonic acid group and the carboxyl group have been neutralized) are useful inhibitors according to my invention.

Any of a wide variety of amines can be employed in preparing the alpha-sulfoalkyl acid salts which I use as corrosion inhibitors. Thus, the amines can be primary, secondary or tertiary. The amines can be derived from animal or vegetable fats and oils or rosin. Aromatic and other ring compounds containing a nitrogen atom capable of reacting with an acid can also be employed in preparing the corrosion inhibitors. Likewise, heterocyclic compounds containing nitrogen such as morpholine or pyridine, are useful, as are polyamines.

Suitable amines for use in preparing the corrosion inhibitors include:

Primary amines: methylamine, isopropyl amine, 2-amino-butane, tertiary butyl amine, 2-amino-4-methylpentane, various amyl, hexyl, heptyl, octyl and higher homologous primary amines where the amine group is attached to a secondary or tertiary carbon atom; cyclopentyl amine, alkylated cyclopentyl amines, cyclohexyl amine, mono-methyl cyclohexylamines, dimethyl cyclohexylamines, trimethyl cyclohexylamines, other alkylated cyclohexylamines, bornyl amine, fenchyl amine, cyclo-terpenyl amines, pinyl amine, benzylamine, betaphenyl-ethylamine, alkylated benzylamine, tetrahydro betanaphthylamine, allyl amine, beta-methyl allylamine, betachloroallylamine, and their homologs and analogs.

Secondary amines: di-methyl-, di-ethyl-, di-n-propyl-, di-isopropyl-, di-butyl-amines; various secondary amines derived from amyl, hexyl, heptyl, octyl, and higher homologous alkyl groups; methyl isobutyl amines, N-methyl N-tertiary-butylamine, N-alkyl N-cyclohexyl amine, N-alkyl N-bornyl amine, di-bornyl amine,

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N-methyl N-cycloterpenyl amine, N-isopropyl N-(1-methyl amine, N-alkyl N-benzyl amines and their homologs and analogs; dicyclopentyl amine, dicyclohexyl amine, alkylated dicyclohexyl amines; dibenzylamine, di-(beta phenyl ethyl) amine; piperidine, piperazine, alkylated piperidines or piperazines; alkylated and unalkylated oxazines such as morpholine and 2,4,4,6-tetramethyl tetrahydro-1,3-oxadiazine; alkylated 1,3-thiazolines such as 2,4,4,6-tetramethyl tetrahydro-3-thiazoline.

Secondary amine type derivatives of alkylene diamines such as:



wherein R_1 and R_3 may be like or different aliphatic, alicyclic, aralkyl, alkarylalkyl, heterocyclic, terpenic radicals, and wherein R_2 is an alkylene or cycloalkylene radical. These R_1 and R_3 radicals for instance, may be hydrogen, isopropenyl, butyl, cyclohexyl, benzyl, and/or bornyl radicals. The R_2 radical is preferably an ethylene, propylene or tetramethylene radical.

Tertiary amines: trimethylamine, triethylamine, tri-n-propylamine, tri-isopropylamine, tributylamine, higher homologous and isomeric trialkylamines, variously N-substituted tertiary amines having different organic radicals on the amino nitrogen atom, e.g., alkyl, alicyclic, bornyl, fenchyl, aralkyl, and like homologs and analogs; and tertiary amine type derivatives of alkylene diamines.

The precise amount of the alpha-sulfoalkyl acid salt admixed with the petroleum hydrocarbon will depend upon the particular petroleum hydrocarbon and also upon other factors. Generally, however, the amount of salt employed as the corrosion inhibitor will be within the range from 0.25 to 25 pounds per 1000 barrels of the petroleum hydrocarbon. Where the petroleum hydrocarbon is a petroleum distillate having a viscosity not exceeding that of gas oil, such as gasoline, kerosene and home heating oil, the amount of salt used as the corrosion inhibitor will preferably be within the range from 0.25 to 5 pounds per 1000 barrels. On the other hand, when the salt is used as a corrosion inhibitor in an oil well, the amount of salt utilized will preferably be within the range from 1 to 25 pounds per 1000 barrels of well fluid, that is, crude oil and any brine associated with the crude.

The following example illustrates various embodiments which fall within the scope of my invention.

EXAMPLE

In order to prepare mono-(di-butylamine) alpha-sulfo-palmitic acid, 0.05 gram mole of alpha-sulfoalpalmitic acid was weighed into a beaker equipped with a stirrer and a thermometer. About 20 grams of isopropanol-benzene (75-25 volume ratio) mixture was used as a solvent for the acid. To hasten solution, the mixture was heated to about 100° F. with stirring, until all of the acid had been dissolved. The solution was then allowed to cool to room temperature.

0.05 gram mole of di-butylamine in a separate beaker was poured slowly with stirring into the acid solution which was placed in a cold water bath. Addition of the amine took about 30 seconds. The temperature was not allowed to rise over about 120° F., being controlled by the use of the bath. The reaction was essentially complete after about 10 minutes of stirring. A brown solid mass which was soluble in benzene and soluble in isopropanol was obtained after the solvent was stripped off using a vacuum.

The di-salts, in which both the sulfonic acid group and carboxyl group are neutralized, can be prepared in an analogous manner. Often, it is possible to prepare di-salts of 100 percent active ingredient by direct mixing

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of the acid and amine (liquid) without using a solvent. An example of this is as follows:

Di-(di-n-butylamine) alpha-sulfoalpalmitate was prepared by adding 0.2 mole (25.8 g.) di-n-butylamine to 0.1 mole alpha-sulfoalpalmitic acid (34.0 g.). The reaction was carried out in the same equipment as above. An excess (5 g.) of amine was added to insure complete reaction. The mixture was heated under vacuum to remove the excess. The resulting product is a clear, straw-colored, very viscous mass. It is soluble in benzene.

Table I sets forth the names and characteristics of other salts which have been prepared and which are useful corrosion inhibitors in accordance with my invention.

Table I

Compound	Percent Active Ingredient	Remarks
Di-morpholine alphasulfostearate.	190	White powder. Soluble in alcohol - benzene mixture. Water soluble.
Mono - morpholine alphasulfostearic acid.	180	Clear yellow "jelly." Soluble in alcohol-benzene mixture, water soluble. Water soluble (cloudy).
Mono-ammonium alpha-sulfoalpalmitic acid.	189	
N-tallow morpholine alphasulfostearic acid.	100	Slightly soluble in isopropanol. Soluble in benzene-isopropanol mixture. Cloudy dispersion in water.
N-aminopropyl morpholine alphasulfostearic acid.	100	White waxy power, benzene-soluble.
Dimethyl hydroxenated tallow - amine alpha - sulfoalpalmitic acid.	100	Tan solid. Insoluble in diesel oil. Soluble in benzene.
Methyl di-hydroxenated tallow-amine alpha sulfoalpalmitic acid.	100	Hard, waxy, tan solid. Insoluble in diesel oil. Soluble in benzene.
Di-(di-2-ethyl hexyl amine) alpha sulfoalpalmitate.	100	Clear, dark red-brown viscous mass. Soluble in isopropanol, benzene.
Mono - (di - 2 - ethyl hexyl amine) - alpha-sulfoalpalmitic acid.	178	Clear, dark, red-brown liquid. Water, benzene and isopropanol soluble.

¹ Balance is isopropanol.

Each of the eleven salts described above was tested for effectiveness in inhibiting corrosion by a modified ASTM D-665 turbine oil rust test. Procedure A for distilled water was used, but the test was shortened to four hours and the temperature of the test was reduced to 100° F. Thus, a freshly ground rust test coupon consisting of a 1/2 inch diameter by 5 1/2 inches long mild steel rod was suspended in a 400 ml. breaker equipped with a stirrer and placed in a temperature control bath capable of maintaining the temperature at 100° F. ± 1° F. The gasoline or diesel fuel to be tested (350 ml.) was added and stirred for 30 minutes while containing the rust inhibitor to precoat the test specimen. Part (50 ml.) of the gasoline or diesel fuel was then removed and 30 cc. of distilled water was added, and the mixture stirred for 3 1/2 hours. At the end of this time, the coupon was removed, dried with solvents, inspected and rated according to the following table:

Rating:	Percent of surface rusted
A -----	None
B++ -----	0 to 0.25
B+ -----	0.25 to 5
B -----	5 to 25
C -----	25 to 50
D -----	50 to 75
E -----	75 to 100

Table II sets forth the minimum concentration of ammonium or amine salt in points per 1000 barrels of gasoline or diesel fuel required to give a B++ rating.

in the test. Table II also sets forth comparative results obtained with various commercial corrosion inhibitors.

Table II

Inhibitor	Minimum Concentration, #/1,000 Bbls. for B++ Ratings	
	Gasoline	Diesel Fuel
A. Mono-salts: ¹		
Morpholine alpha-sulfostearic acid.....	0.75	0.75
Ammonium alpha-sulfopalmitic acid.....	0.75	0.75
N-tallow morpholine alpha-sulfostearic acid.....	0.75	1
Mono-(dimethyl hydrogenated tallow amine) alpha-sulfopalmitic acid.....	4.5	2.25
(Methyl dihydrogenated tallow amine) alpha-sulfopalmitic acid.....	0.4	2.25
N-aminopropyl morpholine alpha-sulfostearic acid.....	3.75	0.4
Mono-(di-n-butylamine) alpha-sulfopalmitic acid.....	0.4	1.5
Mono-(di-2-ethyl hexylamine) alpha-sulfopalmitic acid.....	0.75	2.25
B. Di-Salts: ¹		
Di-morpholine alpha-sulfostearate.....	2	1
Di-(di-2-ethylhexyl amine) alpha sulfopalmitate.....	1	2
Di-(di-n-butylamine) alpha-sulfopalmitate.....	0.5	2
C. Commercial Inhibitors ²:		
A (10% active ingredient).....	20	12
B (50% active ingredient).....	6	2
C (35% active ingredient).....	9	8
D (35% active ingredient).....	8	6
E (35% active ingredient).....	4	6

¹ 100% active ingredient basis.

² As received basis.

When the ammonium or amine salts of the alpha-sulfoalkyl acids are utilized as corrosion inhibitors for the purpose of preventing corrosion in oil wells, the inhibitor is added to the well fluids by conventional methods, usually by merely injecting the desired amount of inhibitor down the annulus between the production tubing and the casing. The resulting crude produced from the well, after separation of any brine by conventional methods, displays favorable corrosion inhibiting properties when transported through connecting pipe lines to the refinery.

I claim:

1. A method for prevention of the corrosion of iron and steel in contact with a liquid petroleum hydrocarbon containing moisture which comprises admixing with the petroleum hydrocarbon an amount effective to substantially inhibit the corrosion of a salt of an acid of the formula $RCH(SO_2OH)COOH$, the said salt being selected from the group consisting of ammonium and amine salts, the said salt being selected from the group consisting of those in which only the sulfonic acid group has been neutralized and those in which both the sulfonic acid group and the carboxyl group have been neutralized, R being an alkyl radical containing from 6 to 20 carbon atoms.

2. The method of claim 1 wherein the amount of said salt is within the range from 0.25 to 25 pounds per 1000 barrels of said liquid petroleum hydrocarbon.

3. The method of claim 1 wherein said liquid petroleum hydrocarbon is a petroleum distillate having a viscosity not exceeding that of gas oil.

4. A method for the prevention of the corrosion of iron and steel in contact with gasoline containing moisture which comprises admixing with the gasoline from 0.25 to 5 pounds per 1000 barrels of gasoline of a salt of an acid of the formula $RCH(SO_2OH)COOH$, the said salt being selected from the group consisting of ammonium and amine salts, the said salt being selected from the group consisting of those in which only the sulfonic acid group has been neutralized and those in which both the sulfonic acid group and the carboxyl group have been neutralized, R being an alkyl radical containing from 6 to 20 carbon atoms.

5. The method of claim 4 wherein said salt is ammonium alpha-sulfopalmitic acid.

6. The method of claim 4 wherein said salt is (methyl dihydrogenated tallow amine) alpha-sulfopalmitic acid.

7. The method of claim 4 wherein said salt is mono-(di-n-butylamine) alpha-sulfopalmitic acid.

8. The method of claim 4 wherein said salt is mono-(di-2-ethyl hexylamine) alpha-sulfopalmitic acid.

9. The method of claim 4 wherein said salt is di-(di-n-butyl amine) alpha-sulfopalmitate.

10. A liquid petroleum hydrocarbon containing moisture having admixed therewith an amount effective to substantially inhibit the corrosion of iron and steel of a salt of an acid of the formula $RCH(SO_2OH)COOH$, the said salt being selected from the group consisting of ammonium and amine salts, the said salt being selected from the group consisting of those in which only the sulfonic acid group has been neutralized and those in which both the sulfonic acid group and the carboxyl group have been neutralized, R being an alkyl radical containing from 6 to 20 carbon atoms.

11. The liquid petroleum hydrocarbon composition of claim 10 wherein the amount of said salt is within the range from 0.25 to 25 pounds per 1000 barrels of said liquid petroleum hydrocarbon.

12. The liquid petroleum hydrocarbon composition of claim 10 wherein said liquid petroleum hydrocarbon is a petroleum distillate having a viscosity not exceeding that of gas oil.

13. Gasoline containing moisture having admixed therewith as a corrosion inhibitor from 0.25 to 5 pounds per 1000 barrels of gasoline of a salt of an acid of the formula $RCH(SO_2OH)COOH$, the said salt being selected from the group consisting of ammonium and amine salts, the said salt being selected from the group consisting of those in which only the sulfonic acid group has been neutralized and those in which both the sulfonic acid group and the carboxyl group have been neutralized, R being an alkyl radical containing from 6 to 20 carbon atoms.

14. The gasoline composition of claim 13 wherein said salt is ammonium alpha-sulfopalmitic acid.

15. The gasoline composition of claim 13 wherein said salt is (methyl dihydrogenated tallow amine) alpha-sulfopalmitic acid.

16. The gasoline composition of claim 13 wherein said salt is mono-(di-n-butylamine) alpha-sulfopalmitic acid.

17. The gasoline composition of claim 13 wherein said salt is mono-(di-2-ethyl hexylamine) alpha-sulfopalmitic acid.

18. The gasoline composition of claim 13 wherein said salt is di-(di-n-butyl amine) alpha-sulfopalmitate.

19. In the production of oil from wells wherein a stream of well fluid is withdrawn from an oil well in contact with iron or steel surfaces, the method of reducing the corrosive effect of said well fluid upon the iron or steel surfaces which comprises introducing into the stream of well fluid an amount effective to substantially inhibit said corrosive effect of a salt of an acid of the formula $RCH(SO_2OH)COOH$, the said salt being selected from the group consisting of ammonium and amine salts, the said salt being selected from the group consisting of those in which only the sulfonic acid group has been neutralized and those in which both the sulfonic acid group and the carboxyl group have been neutralized, R being an alkyl radical containing from 6 to 20 carbon atoms.

20. The method of claim 19 wherein the amount of said salt is within the range from 1 to 25 pounds per 1000 barrels of said well fluid.

21. The method of claim 20 wherein said salt is ammonium alpha-sulfopalmitic acid.

22. The method of claim 20 wherein said salt is (methyl dihydrogenated tallow amine) alpha-sulfopalmitic acid.

23. The method of claim 20 wherein said salt is mono-(di-n-butylamine) alpha-sulfopalmitic acid.

24. The method of claim 20 wherein said salt is mono-
(di-2-ethyl hexylamine) alpha-sulfopalmitic acid.
25. The method of claim 20 wherein said salt is di-(di-
n-butyl amine) alpha-sulfopalmitate.

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