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3,382,179

CORROSION INHIBITOR COMPOSITION

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6 Claims. (Cl. 252-148)

ABSTRACT OF THE DISCLOSURE

A metal corrosion inhibitor for use with aqueous acids, comprising specified amounts of an acetylenic alcohol or sulfide, an amine or nitrogen base compound, and an oxyalkylated naphthenic acid and optionally a solubilizer or diluent.

The present invention relates to inhibition of corrosion and especially to new and useful compositions which may be employed in acid solutions to decrease or inhibit the corrosion of metal in contact with the acid solutions.

The present invention is particularly useful in the acidizing or treating of earth formations and wells traversed by a bore hole.

Many various types and compositions have been employed for the inhibition of corrosion of metal surfaces. Most have been employed with varying degrees of success. A particular failing of most prior art corrosion inhibiting compositions is that they cease to be effective after relatively short periods of time or break down under high temperature conditions, that is temperature of 175° F. or higher.

It is therefore a primary object of the present invention to provide a new and improved composition for inhibiting the corrosion of metal surfaces in contact with acid solutions, which is effective for relatively long periods of time and at relatively high temperatures.

Another object of the present invention is to provide a corrosion inhibiting composition which is effective in acid solutions at both low and high temperatures.

Another object of the present invention is to provide a new improved composition which may be added to acids, especially hydrochloric acid which will substantially inhibit the corrosion effect of the acids on metal surfaces, especially on steel and other ferrous metals, in contact with the acids.

Still another object of the present invention is to provide a new and improved corrosion inhibiting composition which may be employed in acidizing solutions used in well treating and which will effectively inhibit the corrosive action of the acid on underground well equipment.

Other objects and advantages of the present invention will become readily apparent from a reading of the description of the invention hereinafter.

It has been discovered that a synergistic blend of an acetylenic alcohol or alcohols, an amine or nitrogen compound, and an ethylene oxide derivative of naphthenic acids in particular amounts of each, provides a composition having superior corrosion inhibiting properties when added in small quantities to an acid solution.

In some instances, it may be desired to add a suitable diluent or solubilizer.

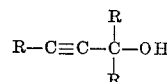
In the preferred form of the invention, two or more acetylenic alcohols, each having an ethynyl hydrogen on the acetylenic group, are employed as the acetylenic alcohol component.

Some examples of acetylenic alcohols or compounds

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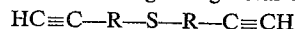
which may be employed in the present invention are: hexynol, dimethyl hexynol, dimethyl hexynediol, dimethyl hexanediol, dimethyl octynediol, methyl butynol, methyl pentynol, ethynyl cyclohexanol, 2-ethyl hexanol, phenyl butynol, and ditertiary acetylenic glycol.

Other acetylenic compounds which can be employed in accordance with the present invention are for example methylbutynol, methylpentynol, butynediol, 1-ethynyl-cyclohexanol, 3-methyl-1-nonyn-3-ol, 2-methyl-3-butyn-2-ol, also 1-propyn-3-ol, 1-butyn-3-ol, 1-pentyn-3-ol, 1-heptyn-3-ol, 1-octyn-3-ol, 1-nonyl-3-ol, 1-decyn-3-ol, 1-(2,4,6-trimethyl-3-cyclohexenyl)-3-propyne-1-ol, and in general acetylenic compounds having the formula



wherein R is hydrogen, alkyl, phenyl, substituted phenyl or hydroxyalkyl radical, and the alpha R's may be joined together to form a cyclohexyl ring.

Acetylenic sulfides having the general formula



can also be employed in the present invention. Examples of these are dipropargyl sulfide, bis (1-methyl-2-propynyl) sulfide and bis (2-ethynyl-2-propyl) sulfide.

The nitrogen or ammonia base compounds that can be employed in accordance with the present invention are those amines such as mono, di and trialkyl amines having from 2 to 6 carbon atoms in each alkyl moiety as well as the 6 membered N-heterocyclic amines, for example alkyl pyridines and mixtures thereof. This includes such amines as ethylamine, diethylamine, triethylamine, propylamine, dipropylamine, tripropylamine, mono, di and tributylamine, mono, di and tripropylamine, mono, di and trihexylamine and isomers of these such as isopropylamine, tertiarybutylamine etc. This also includes alkyl pyridines having from 1 to 5 nuclear alkyl substituents per pyridine moiety, said alkyl substituents having from 1 to 12 carbon atoms and preferably those having an average of 6 carbon atoms per pyridine moiety, such as a mixture of high-boiling tertiary-nitrogen-heterocyclic compounds such as Alkyl Pyridine HB, Reilly HAP (High Alkyl Pyridines) or Reilly 10-20 base.

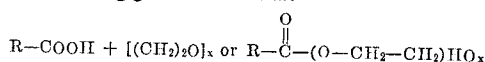
Ethylene oxide derivatives of naphthenic acids suitable for use can vary from 12% to 60% by volume of the inhibitor blend and can vary in composition in the following manner:

Ethylene oxide (percent by weight):	Naphthenic acids (percent by weight)
25	75
35	65
50	50
65	35
75	25
85	15

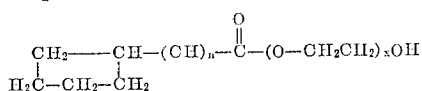
Mixed ethylene oxide-propylene oxide derivatives of naphthenic acids are also suitable.

Naphthenic acids may be defined as monobasic carboxylic acids of the general formula RCOOH , wherein R is a naphthenic radical. This is a radical derived principally from cyclopentane or a homolog of cyclopentane, and in some cases a bicyclic cyclopentane derivative.

A preferred ethylene oxide derivative of naphthenic acid has the following general formula:



A more specific derivative is:



In the above formula, $n=1$ to 20 and x =moles of ethylene oxide or propylene oxide and may vary from about 25%–85% by weight. Additionally, propylene oxide and ethylene oxide can be reacted with a naphthenic acid at the same time to provide a mixed ethylene oxide, propylene oxide composition.

Suitable diluents are diacetone alcohol, mesityl oxide, acetone, alcohols (ethanol, isopropanol, N-propanol, etc.), aromatic solvents, other acid soluble organic solvents or water.

On a basis of a volume of 100%, a preferred composition of the present invention is comprised as follows:

Acetylenic compound—31% to 85% by volume

Ethylene oxide derivative—12% to 60% by volume

Nitrogen or ammonia base compound—3%–9% by volume based on the active acetylenics present in the blend.

A solubilizer or diluent may be added to the above preferred compositions in a concentration of about 5%–50% of the total volume.

Another preferred composition of the present invention, may be expressed by the formula

$$X+Y+Z=100\%$$

wherein

X =Acetylenic compound—31% to 85% by volume

Y =Oxide derivative of naphthenic acid—12% to 60% by volume

Z =Nitrogen or ammonia base compound—(.03–.09) (X) (A) by volume

wherein A =percent active ingredients or activity of the acetylenic compound.

An effective composition or preferred blend, especially at high temperatures, was found to be as follows:

Chemical	Parts by Volume	Percent by Volume	Percent by Weight
Crude Propargyl Alcohol.....	4.0	54.50	54.7
Oxyethylated Naphthenic Acid.....	1.5	20.44	21.8
High Alkyl Pyridines (Reilly HAP).....	0.34	4.63	5.0
Ethyl Octynol.....	1.5	20.44	18.5

A crude propargyl alcohol with about 75% active ingredients, with the remainder being non-aqueous reaction products resulting from the production of propargyl alcohol is particularly preferred. Pure or 100% propargyl alcohol may be used, but it is more expensive than the crude propargyl alcohol.

Hexynol in lieu of ethyl octynol also gives superior results in the blend.

High Alkyl Pyridines (Reilly HAP) (assumed to be 100%) can be substituted with a less active percent of alkyl pyridines by increasing the amount to be added to the blend, while staying within the concentration range of from 3 to 9% by volume based on the active acetylenics present in the blend. Other sources of suitable nitrogen compounds can be obtained elsewhere. Reilly 10–20 base and Alkyl Pyridines HB are examples of other commercial products which can be used.

A number of laboratory tests were conducted wherein the preferred blend of this invention, compound X, was compared with a prior art corrosion inhibitor, compound A, prepared in accordance with the teachings of U.S. Patent No. 3,107,221 and consisting of 2 parts acetylenic alcohols and 1 part Alkyl Pyridines HB, by volume.

Procedure

In these tests, the acid solutions were mixed by diluting 20° Bé. HCl with water to the desired concentrations.

The acid solutions were then titrated with a standard base solution to ascertain the exact acid concentration. The various acid solutions were prepared in advance in sufficient quantities to complete an entire series of tests with the same batch of acid.

Corrosion coupons of J-55 steel were ordered in sufficient quantities to complete a series of tests on the same batch of coupons. The coupons were cleaned as follows: pickled in an uninhibited 10% HCl acid solution for 10 minutes, neutralized in a 10% solution of sodium bicarbonate, scrubbed by hand with a fine wire brush and a detergent containing a pumice, rinsed, dipped in acetone to remove the excess water and then dipped in alcohol and allowed to dry. They were then weighed to the nearest milligram and stored in a desiccator until time for use.

Tests were conducted at various temperatures.

The acid solution was poured into glass bottles in sufficient quantity to approximate the specific acid volume-to coupon surface area ratio that was desired. The quantity of acid used was dependent upon the surface area of the coupon to be tested. In most of the tests, a 25 cc./in.² acid volume to coupon surface area ratio was used.

After the desired amount of acid was poured into the bottles, the inhibitor was added with a hypodermic syringe and the resulting solution was stirred with a glass rod. The inhibited acid solution was then placed in a water bath which had been set at a predetermined temperature and allowed to preheat for 20 minutes. After which time, the coupons were placed in the preheated inhibited acid solutions. The coupons were left in the acid solutions for the specified test time, then removed, neutralized, recleaned, rinsed, dipped in acetone then alcohol, allowed to dry, then reweighed.

The loss in weight in grams was multiplied times a calculated factor to convert the loss in weight to lbs./ft.²/24 hrs. The factor was calculated as follows:

$$\frac{144 \frac{\text{in.}^2}{\text{ft.}^2}}{454 \frac{\text{g.}}{\text{lb.}}} \times \text{Surface Area of Coupon} - \text{in.}^2 \times \frac{1 \text{ day}}{24 \text{ hrs.}} = \text{Factor}$$

Example: Test time, 6 hours, Surface Area of Coupon, 4.0 in.², then

$$\frac{144}{454 \times 4.0 \times 6/24} = \frac{144 \times 4}{454 \times 4.0} = 0.317$$

For temperatures in excess of 200° F., tests were conducted in high temperature and pressure autoclaves that were designed and built by the Halliburton Engineering Department. The autoclaves are designed to withstand temperatures up to 600° F. and pressures up to 10,000 p.s.i. They have rotating tables that hold the beakers containing the acid. This allows the acid to be agitated throughout the test. The autoclaves are unique in design in that they have an acid discharge valve over each beaker of acid. This allows a test to be terminated immediately rather than having to wait for the temperature to cool down sufficiently so that the head can be opened. There are two temperature controls, one monitors the temperature of the oil in the autoclave and the other the temperature of the acid solution. The temperature of the acid solution is recorded on an electric motor driven chart throughout the time of the test.

The methods used in the high temperature corrosion tests were basically the same as the other tests. The only difference was in the acid volume-to coupon surface area ratio which was approximately 80 cc./in.² (excess acid) and the mechanical operations of the autoclaves.

The results of these tests are set forth hereinbelow:

TABLE I.—COMPARISON OF BLEND X AND A AT VARIOUS TEMPERATURES

Corrosion rates in lbs./ft.²/24 hrs.
Pressure—Atmospheric unless otherwise indicated

Inhibitor	Conc. in gals./1,000	Test Temp., ° F.	Test Time, hrs.	Corrodent	Metal type	Corr. Rate
X.....	4.0	200	6	15% HCl.....	N-80.....	0.007
A.....	4.0	200	6	15% HCl.....	N-80.....	0.011
X.....	4.0	200	16	15% HCl.....	J-55.....	0.006
A.....	4.0	200	16	15% HCl.....	J-55.....	0.008
X.....	2.0	150	6	15% HCl.....	J-55.....	0.006
A.....	2.0	150	6	15% HCl.....	J-55.....	0.011
X.....	3.0	150	6	15% HCl.....	J-55.....	0.004
A.....	3.0	150	6	15% HCl.....	J-55.....	0.006
X.....	2.0	130	24	20° B ₆ HCl.....	J-55.....	0.010
A.....	2.0	130	24	20° B ₆ HCl.....	J-55.....	0.198
X.....	1.0	100	24	20° B ₆ HCl.....	Mld. Stl.....	0.002
A.....	1.0	100	24	20° B ₆ HCl.....	Mld. Stl.....	(1)
X.....	2.5	100	72	20° B ₆ HCl.....	Mld. Stl.....	0.001
A.....	2.5	100	72	20° B ₆ HCl.....	Mld. Stl.....	0.017
X ²	10.0	250	6	15% HCl.....	N-80.....	0.126
A ²	10.0	250	6	15% HCl.....	N-80.....	0.148

¹ Terminated.

² Pressure—3,000 p.s.i.

NOTE.—For temperatures of 200° F. or less, the acid volume-surface area ratio was 25 cc./in.². At 250° F. excess acid (80 cc./in.²) was used.

TABLE II.—COMPARISON OF BLEND X AND A WITH VARIOUS ADDITIVES

Acid volume/surface area ratio:—25 cc./in.²
Corrosion rates in lbs./ft.²/24 hrs.
Coupon—J-55 steel

Additive	Inhibitor	Con. in gals./1,000	Test Temp., ° F.	Test Time, hrs.	Corrodent	Corr. Rate
Z.....	X	6	200	16	15% HCl.....	0.017
E.....	X	6	200	16	15% HCl.....	0.009
F.....	X	6	200	16	15% HCl.....	0.027
Z.....	A	6	200	16	15% HCl.....	0.063
E.....	A	6	200	16	15% HCl.....	0.041
F.....	A	6	200	16	15% HCl.....	0.034
Z.....	X	2.0	150	6	15% HCl.....	0.009
E.....	X	2.0	150	6	15% HCl.....	0.014
F.....	X	2.0	150	6	15% HCl.....	0.017
Z.....	A	2.0	150	6	15% HCl.....	0.026
E.....	A	2.0	150	6	15% HCl.....	0.032
F.....	A	2.0	150	6	15% HCl.....	0.022

Z—Cationic non-emulsifier
E—Amphoteric surfactant
F—Anionic non-emulsifier

Remarks

Blend X consistently outperformed Blend A especially when longer exposure times and lower concentrations of inhibitor were involved.

Breakdown tests were conducted as follows, and the results recorded in Table III hereinbelow. A J-55 coupon was placed in a glass jar containing 15% hydrochloric acid inhibited with 6 gal./1000 of the inhibitor to be evaluated. The jar containing the coupon was then placed in a 200° F. water bath and checked periodically for signs of bubbling indicating that the inhibitor had broken and hydrogen gas was being evolved. The acid volume to coupon surface area ratio used in the breakdown test was 25 cc./in.².

TABLE III.—COMPARISON OF BREAKDOWN TIMES OF BLEND X AND A

Breakdown tests

Test temp. 200° F.
Corrodent 15% HCl.
Metal type J-55 Steel.
Inhibitor concentration 6 gals./1000.
Acid volume/surface area ratio, limited
Acid 25 cc./in.².

Inhibitor

Time to failure
X Approx. 62 hrs.
A Approx. 26½ hrs.

Additional tests were conducted using the individual compounds of the preferred blend alone, and following the procedure set forth in detail hereinabove for clearly showing the synergistic effect of the preferred blended composition.

TABLE IV.—COMPARISON OF BLEND X WITH INDIVIDUAL COMPONENTS THEREOF

Acid volume/surface area ratio:—25 cc./in.²
Corrosion Rates in lbs./ft.²/24 hours
Acid—15% HCl
Coupons—N-80 Steel
Test Temperature—200° F.
Test Time—6 hours

25

30

35

40

45

50

55

60

65

70

75

Inhibitor	Concentration in gals./1,000	Corr. Rate
Alkyl Pyridines HB.....	6	0.069
Crude propargyl alcohol.....	6	0.032
Pure propargyl alcohol.....	6	0.027
Ethyl octynol.....	6	0.011
Blend X.....	6	0.006

The inhibitor or inhibitor composition of the present invention is operable when employed at temperatures as high as 300° F. in various acid concentrations. The corrosion which does occur is substantially uniform regardless of temperatures from 60° F. up to and in excess of 250° F. It provides long term protection at small concentrations of inhibitor. It is particularly effective on all types of steel and especially on that used in oil field grade pipe.

Applications in which the inhibitor of the present invention is particularly useful include oil-well acidizing solutions, metal pickling, cleaning and polishing baths, boiler cleaning compositions and the like.

Broadly, the present invention relates to a new and improved corrosion inhibitor or composition for reducing the corrosive effect of acids on ferrous metals consisting essentially of an acetylenic alcohol or alcohols, a nitrogen or ammonia base compound and an ethylene or propylene oxide derivative of a naphthenic acid in certain amounts of each, to which composition may be added a suitable diluent or solubilizer.

The corrosion inhibitor compositions of the present invention are particularly adapted for use in mineral acids, especially hydrochloric acid. It may also be employed in sulfuric, phosphoric and acetic acids and the like.

The inhibitor is preferably added to the acid in amounts by volume from about ½ gallon to 20 gallons per 1000 gallons of acid. The amount of the inhibitor required will vary with the temperatures to be encountered and the strength or concentration of the acid used. A 15% hydrochloric acid is most common for oil well acidizing operations.

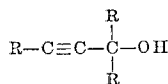
The foregoing disclosure and description of the invention is illustrative and explanatory thereof and suitable variations may be made within the scope of the appended claims without departing from the spirit of the invention.

We claim:

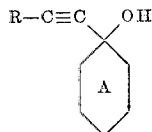
1. A metal corrosion inhibitor for use with aqueous

acids which comprises an acetylenic compound having a formula selected from the group consisting of:

(A)

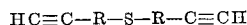


(B)

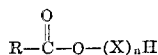


or

(C)



wherein in (A) and (B) each R represents a member selected from the group consisting of hydrogen, alkyl, phenyl, alkyl substituted phenyl and hydroxyalkyl radicals wherein each of the above mentioned alkyl and hydroxyalkyl radicals have from 1 to 4 carbon atoms, inclusive, and wherein in (C) each R represents an alkylene radical having from 1 to 4 carbon atoms inclusive; an amine selected from the group consisting of pyridine, lower alkyl pyridines, alkylamines having from 4 to 10 carbon atoms inclusive, in each alkyl substituent, and hydroxy lower alkylamines; an oxyalkylated naphthenic acid having the formula:



wherein R is a naphthenic radical

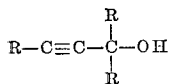
X is selected from the group consisting of ethylene oxide, propylene oxide or mixtures thereof, and n =number of moles of X ranging from about 25%–85% by weight of compound;

wherein the acetylenic compound is present in an amount by volume of 31%–85%, the amine is present in an amount by volume of 3%–9% based on the amount of the active acetylenic compound present and the oxyethylated or oxypropylated naphthenic acid is present in an amount by volume of from 12%–60%.

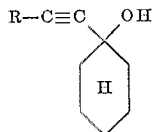
2. The corrosion inhibitor compound of claim 1, wherein a diluent is added in a concentration of from about 5%–50% of total volume.

3. A corrosion-inhibited mineral acid comprising an aqueous solution of a mineral acid and from 0.05% to 2.0% by volume of a mixture consisting essentially of from 31% to 85% by volume of an acetylenic compound having a formula selected from the group consisting of:

(A)

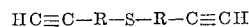


(B)

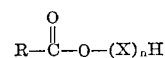


or

(C)



wherein in (A) and (B) each R represents a member selected from the group consisting of hydrogen, alkyl, phenyl, alkyl substituted phenyl and hydroxyalkyl radicals wherein each of the above mentioned alkyl and hydroxyalkyl radicals have from 1 to 4 carbon atoms, inclusive, and wherein in (C) each R represents an alkylene radical having from 1 to 4 carbon atoms inclusive; from 3% to 9% by volume of an amine compound, based on the amount of the acetylenic compound selected from the group consisting of pyridine, lower alkyl pyridines, alkylamines having from 4 to 10 carbon atoms inclusive, in each alkyl substituent, and hydroxy lower alkylamines; and from 12% to 60% by volume of an oxyalkylated naphthenic acid having the formula:



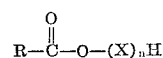
wherein R is a naphthenic radical

X is selected from the group consisting of ethylene oxide, propylene oxide or mixtures thereof, and n =number of moles of X ranging from about 25%–85% by weight of compound.

4. The composition of claim 3, wherein a diluent is added to the mixture in a concentration of from about 5%–50% of total volume of the mixture.

5. A metal corrosion inhibitor for use with aqueous acids consisting essentially of propargyl alcohol of about 4.0 parts by volume, ethyl octynol of about 1.5 parts by volume, lower alkyl pyridines of about 0.34 part by volume and an oxyethylated naphthenic acid having moles of ethylene oxide ranging from about 25%–85% by weight of compound of about 1.5 parts by volume.

6. A corrosion-inhibited mineral acid comprising an aqueous solution of mineral acid containing from 0.05% to 2.0% by volume of a mixture consisting of from 3.1 to 8.5 parts by volume of propargyl alcohol, 0.3 to 0.9 part by volume of a mixture of lower alkyl pyridines and 1.2 to 6.0 parts by volume of an oxyalkylated naphthenic acid having the formula:



wherein R is a naphthenic radical

X is selected from the group consisting of ethylene oxide, propylene oxide or mixtures thereof, and n =number of moles of X ranging from about 25%–85% by weight of compound.

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LEON D. ROSDOL, *Primary Examiner.*

H. B. GUYNN, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

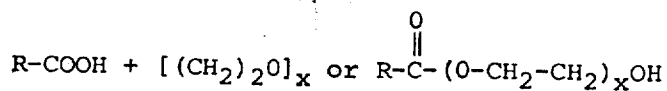
Patent No. 3,382,179

May 7, 1968

Bill R. Keeney et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 37, "tertiarylbutylamine" should read -- tertiarybutylamine --;
line 67, the formula should appear as shown below:



Column 7, line 10, in the benzene ring, "A" should read -- H --.

Signed and sealed this 10th day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents