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McDougall et al.

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[45] **Dec. 18, 1973**

[54] **INHIBITION OF CORROSION**

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[21] Appl. No.: **161,994**

[52] **U.S. Cl.** ..... **252/149,** 252/8.55 E, 252/146, 252/148, 252/151, 252/390, 252/391, 252/392

[51] **Int. Cl.** **C11d 7/48,** C23f 11/16

[58] **Field of Search** .....252/146–149, 142, 252/8.55 E, 388, 390, 392

[56] **References Cited**

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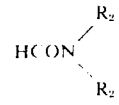
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[57] **ABSTRACT**

Corrosion of ferrous metals by corrosive acids at elevated temperatures is inhibited by adding to the corrosive acid a composition comprising effective amounts of at least one acetylenic alcohol, a quaternary ammonium compound and/or an amine, a surfactant, an organic solvent, and a formic acid compound selected from the group consisting of formate esters of the structure:

HCOOR

where R is a mono-aryl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH,—OH,=C=O, —COOH, —SH, and NH_2 and formamides of the structure:



Where R_2 is hydrogen, mono-aryl groups, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2.

The composition suitably contains a surfactant and an organic solvent.

15 Claims, No Drawings

INHIBITION OF CORROSION

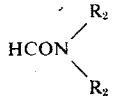
BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to inhibition of corrosive acids. More particularly, the invention is concerned with inhibition of corrosive acid in contact with ferrous metals. In its more specific aspects, the invention is concerned with a method and composition for inhibiting corrosion of ferrous metals by corrosive acids in which the composition comprises one or more acetylenic alcohols, a quaternary ammonium compound and/or an amine and a formic acid compound having the structural formula:

HCOOR

where R is a phenyl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl group having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2 and formamides of the structure:



where R_2 is hydrogen, phenyl groups, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2.

2. Description of the Prior Art

It is known to use formic acid and its compounds as corrosion inhibitors. It is also known to use one or more acetylenic alcohols as corrosion inhibitors. The use of amines and various nitrogen compounds as corrosion inhibitors is also old in the art. Most corrosion inhibitors have been largely ineffective in combatting the corrosive effects of corrosive acids such as mineral acids, particularly at elevated temperatures.

The use of aziridinyl ester of formic acid as corrosion inhibitors to prevent reaction of aluminum with degreasing solvents has been taught. However, the combination of a particular formic acid compound, one or more acetylenic alcohols and quaternary ammonium compounds such that the combination is more effective as a corrosion inhibitor than any of its components has not been taught as a corrosion inhibitor for corrosive acids in contact with ferrous metals.

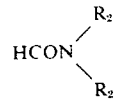
Prior art considered with respect to this invention includes the following listed U.S. Pat. Nos.: 2,258,578; 2,415,161; 2,423,343; 2,449,585; 2,493,462; 2,799,659; 3,072,460; 3,249,548; 3,338,885; 3,382,179; 3,391,085; 3,404,094; 3,472,666;

SUMMARY OF THE INVENTION

The present invention may be briefly described and summarized as involving a corrosion inhibitor composition comprising effective amounts of one or more acetylenic alcohols, a quaternary ammonium compound and/or an amine, and a formic acid compound selected from the group consisting of formate esters of the structure:

HCOOR

where R is a phenyl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2 and formamides of the structure:

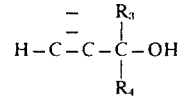


where R_2 is hydrogen, a phenyl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2.

The invention also may be summarized as a method of inhibiting the corrosivity of corrosive acids in contact with ferrous metals, such as steel, by adding to the corrosive acid an effective amount of the aforementiond composition.

VARIABLES OF THE INVENTION

The acetylenic alcohols employed in the present invention may suitably include ethyl octynol, propargyl alcohol, hexynol and other acetylenic alcohols having the structural formula:



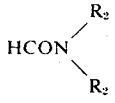
where R_3 is selected from the group consisting of CH_3 and H and R_4 is selected from the group consisting of hydrogen, alkyl groups having 1 to 18 carbon atoms, naphthalyl, phenyl, and alkyl substituted phenyls having 1 to 10 carbon atoms in the alkyl substituent. Examples of such alcohols include: methyl butynol, methyl pentynol, hexynol, ethyl octynol, propargyl alcohol, benzyl butynol, naphthalyl butynol, and the like. Acetylenic alcohols which have 3 to 10 carbon atoms are preferred.

The quaternary ammonium compounds may be illustrated by C-alkyl pyridine-N-methyl chloride quaternary, C-alkyl pyridine-N-benzyl chloride quaternary, quinoline-N-benzyl chloride quaternary, isoquinoline-N-benzyl chloride quaternary, thioalkyl pyridine quaternaries, thioquinoline quaternaries, benzoquinoline quaternaries, thiobenzoquinoline quaternaries, imidazole quaternaries, pyrimidine quaternaries, carbazole quaternaries, the corresponding ammonium compounds, pyridines and quinolines may also be used alone or in combination with the quaternary compounds. Thus a pyridine plus quinoline quaternary, a quinoline plus quinoline quaternary, or quinoline or amine alone or in combination may be used.

The formic acid compound may be selected from the esters and amides of formic acid. The formic acid compound may be from the group consisting of formate esters of the structure:

HCOOR

where R is a monoaryl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2 and formamides of the structure:



where R_2 is hydrogen, a phenyl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which may contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2. Examples of the formic acid compound are: methyl formate, ethyl formate, benzyl formate, other alkyl and aryl formates, and the like. Other examples include formamide, dimethyl formamide, formanilide, and the like. Mixtures of the esters and mixtures of the amides may be used.

An alkanol may also be employed in the composition as a solvent as illustrated by methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, heptyl, octyl and the higher liquid members of these aliphatic alcohols.

Also, a non-ionic surfactant may be used such as as ethoxylated oleate such as ethoxylated sorbitol hexaoleate and ethoxylated polyol oleate. Other ethoxylated oleates, tall oils, and other fatty acids may be used as surfactants. The 8–12 ethylene oxide adduct of tridecyl phenol, nonyl phenol, and octyl phenol are preferred surfactants.

Typical amounts of the various components of the composition are shown below:

	Wt. %
1st acetylenic alcohol	about 3 to about 25
2nd acetylenic alcohol	0 to about 10
quaternary ammonium compound and/or amine	about 5 to about 35
formic acid compound	about 40.0 to about 90.0
alkanol	about 0 to about 40.0 (0.1 to about 2.0)
surfactant	about 0.25 to about 2.0

The essential components of the present invention are at least one acetylenic alcohol which may have 3 to 10 carbon atoms, the quaternary ammonium compound and the formic acid compound all of which cooperate to reduce the corrositivity of corrosive acids. The alkanols perform the function of a solvent. The ethoxylated compounds function as a surfactant.

DESCRIPTION OF THE PREFERRED EMBODIMENTS AND MODES

Formulations including those of the present invention were made up as follows:

TABLE I

1. 12 percent ethyl octynol
   8 percent hexynol
   15 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated polyol oleate
   14 percent isopropyl alcohol
   50 percent formamide
2. 20 percent hexynol
   15 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated polyol oleate
   14 percent isopropyl alcohol
   50 percent formamide
3. 5 percent hexynol
   5 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated octyl phenol (8–10 moles)
   89 percent formamide
4. 5 percent hexynol
   5 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated octyl phenol (8–10 moles)
   89 percent dimethyl formamide
5. 5 percent hexynol
   5 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated octyol phenol (8–10 moles)
   89 percent methyl formate
6. 50 percent standard acid corrosion inhibitor
   10 percent propargyl alcohol
   20 percent ethyl octynol
   27 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated poyol oleate
   0.4 percent perfluorated imidazoline
   19 percent isopropyl alcohol
   10 percent pine oil
   10 percent oleic acid
   2.6 percent ethyl alcohol
   50 percent formamide
7. 100 percent formamide
8. commercially available inhibitor with no formic acid derivative which is soluble in organic solvents. It does however contain acetylenic alcohol(s), amine, surfactant, and organic solvents.
9. 10 percent hexynol
   10 percent quinoline-N-benzyl chloride quaternary
   1 percent ethoxylated octyl phenol (8–10 moles)
   79 percent formamide

Any of the acetylenic alcohols may be used in the above formulation but propargyl alcohol and ethyl octynol and optionally hexynol are preferred alone or in admixture. Likewise the surfactant is preferably the 8–10 mole ethoxylated nonyl phenol.

In the oil industry a maximum allowable corrosion rate of about 0.05 pounds per square foot of metal exposure is employed for the ferrous metal (steel) equipment exposed, particularly when acidizing a well where HCL is introduced into the wall and thence into the formation to remove alkaline deposits or to open channels into the formation. Table I shows the compositions while the following Tables II and III show the effect of the compositions on various ferrous metal coupons:

TABLE II

Conditions: Pressure: 2000–4000 psig
Acid volume/surface ratio: 45 ml./in.²
Stirring: 40 rpm

Temperature (°F.)	Exposure time (hours)	HCl (%)	Inhibitor	Inhibitor conc. (ml./1000 ml. acid)	Coupon	Corrosion rate (lbs./ft.²)
200	24	30	(1)	3	P–105	0.015
				3	J–55	.011
200	24	30	(2)	3	P–105	.019
				3	N–80	.012
300	2	15	(1)	4	J–55	.042
300	2	15	(2)	4	J–55	.043
300	2	15	(3)	5	N–80	.017
				5	J–55	.008
300	6	15	(3)	5	P–105	.029
				5	N–80	.055
				6	P–105	.025
				6	N–80	.028
300	1	15	(3)	5	P–105	.009
				5	N–80	.010
300	1	15	(4)	8	P–105	.009
				8	N–80	.010
300	2	15	(5)	7	P–105	.036
					N–80	.033
300	2	15	(6)	4	J–55	.043
300	2	15	(7)	4	P–105	1.57
300	2	28	(3)	5	N–80	.040
				5	J–55	.029
300	2	28	(8)	2.5	N–80	.345
				2.5	J–55	2.56
300	6	28	(8)	5	P–105	1.98
				5	N–80	2.72
300	6	28	(9)	5	P–105	.045
				5	N–80	.071

The amount of the inhibitor composition of the present invention may vary from about 0.1 percent to about 10 percent by weight based on one acid or acidic medium. A preferred amount is within the range from about 0.5 to about 5 percent by weight.

It will be clear that inhibitor compositions 1, 2, 3, 4, 5, 6, and 9 mitigate the corrosion of metals in HCL of varying strengths much below the acceptable level. It is also clear that inhibitor compositions 7 and 8 are over the accepted figure while the inhibitor compositions of the present invention practically inhibit all corrosive effects of the acid.

TABLE III

Conditions: Pressure: atmospheric
Exposure time: 24 hours
Acid volume/surface ratio: 29 ml./in.²
Stirring: none

Temperature (°F.)	HCl (%)	Inhibitor	Inhibitor conc. (ml./100 ml. acid)	Coupon	Corrosion rate (lbs./ft.²)
150	30	(1)	0.5	P–105	0.0006
				N–80	.0007
				J–55	.0009
150	15	(1)	.5	P–105	.0006
				N–80	.0006
				J–55	.0006
150	30	(2)	.5	P–105	.0008
				N–80	.0010
				J–55	.0016
150	15	(2)	.5	P–105	.0004
				N–80	.0005
				J–55	.0017

The invention has been described and illustrated by reference to metals as J-55, P-105, and N-80. These are ASTM designations for well known steels.

The data show that the particular compositions of the present invention are unobviously better than the components thereof and, therefore, the invention may be quite valuable in combatting corrosion of corrosive acids such as sulfuric, nitric, hydrochloric, carbonic acid, acetic acid, other organic acids, and the like against ferrous metals.

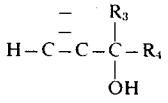
The invention may be used in oil and gas fields and well environments since acid is used in acidizing and preventing scale formation by injection into wells. It may also be used in other acid environments such as in acids used in cleaning ferrous metal equipment such as oil refinery and other equipment as illustrated by heat exchangers of deposited scale, acid soluble salts, and the like.

The nature and objects of the present invention having been fully described and illustrated and the best modes and embodiments contemplated set forth.

What we wish to claim as new and useful and secure by Letters Patent is:

1. A ferrous metal corrosion inhibiting composition consisting essentially of corrosion inhibiting effective amounts of:

a. about 3 to about 25 weight percent of at least 1 acetylenic alcohol having the structural formula:



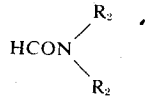
where R_3 is selected from the group consisting of CH_3 and H and R_4 is selected from the group consisting of hydrogen, alkyl groups having 1 to 18 carbon atoms, naphthyl, phenyl, and alkyl substituted phenyls having 1 to 10 carbon atoms in the alkyl substituent;

b. about 5 to about 35 weight percent of an ammonium compound selected from the group consisting of quaternary and unquaternized ammonium compounds selected from the group consisting of: C-alkyl pyridine-N-methyl chloride quaternary, C-alkyl pyridine-N-benzyl chloride quaternary, quinoline-N-benzyl chloride quaternary, isoquinoline-N-benzyl chloride quaternary, thioalkyl pyridine quaternaries, thioquinoline quaternaries, benzoquinoline quaternaries, thiobenzoquinoline quaternaries, imidazole quaternaries, pyrimidine quaternaries, carbazole quaternaries, pyridines and quinolines, and mixtures thereof; and

c. about 40 to about 90 weight percent of a formic acid compound selected from the group consisting of formate esters of the structure:

HCOOR

where R is a phenyl group, alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which are unsubstituted or contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2; and formamides of the structure:



where R_2 is hydrogen, a phenyl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which are unsubstituted or contain functional groupings selected from —C—OH, =C=O, —COOH, —SH, and NH_2.

2. A composition in accordance with claim **1** in which the ammonium compound is a quaternary compound.

3. A composition in accordance with claim **1** in which the ammonium compound is an amine.

4. A composition in accordance with claim **1** in which the acetylenic alcohol has 3 to 10 carbon atoms.

5. A composition in accordance with claim **1** containing a solvent effective amount up to 40 weight percent of a liquid alkanol.

6. A composition in accordance with claim **5** in which the alkanol is isopropyl alcohol.

7. A composition in accordance with claim **1** containing a non-ionic surfactant in an amount from about 0.25 to 2.0 weight percent.

8. A composition in accordance with claim **7** in which the surfactant is an 8 to 12 mole polyoxyethylene adduct of nonyl phenol.

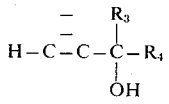
9. A composition in accordance with claim **7** in which the surfactant is an 8 to 12 mole ethylene oxide adduct of an alkyl phenol having 8 to 20 carbon atoms in the alkyl group.

10. A composition in accordance with claim **9** in which the acetylenic alcohol has 3 to 10 carbon atoms.

11. A composition in accordance with claim **1** in which the acetylenic alcohol is a mixture of ethyl octynol, propargyl alcohol and hexynol.

12. A method for inhibiting the corrosivity of a corrosive acid in contact with a ferrous metal at elevated temperatures which comprises adding to said corrosive acid an inhibiting amount of a ferrous metal corrosion inhibiting composition consisting essentially of corrosion inhibiting effective amounts of:

a. about 3 to about 25 weight percent of at least 1 acetylenic alcohol having the structural formula:



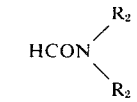
where R_3 is selected from the group consisting of CH_3 and H and R_4 is selected from the group consisting of hydrogen, alkyl groups having 1 to 18 carbon atoms, naphthalyl, phenyl, and alkyl substituted phenyls having 1 to 10 carbon atoms in the alkyl substituent;

b. about 5 to about 35 weight percent of an ammonium compound selected from the group consisting of quaternary and unquaternized ammonium compounds selected from the group consisting of: C-alkyl pyridine-N-methyl chloride quaternary, C-alkyl pyridine-N-benzyl chloride quaternary, quinoline-N-benzyl chloride quaternary, isoquinoline-N-benzyl chloride quaternary, thioalkyl pyridine quaternaries, thioquinoline quaternaries, benzoquinoline quaternaries, thiobenzoquinoline quaternaries, imidazole quaternaries, pyrimidine quaternaries, carbazole quaternaries, pyridines and quinolines, and mixtures thereof; and

c. about 40 to about 90 weight percent of a formic acid compound selected from the group consisting of formate esters of the structure:

HCOOR

where R is a phenyl group, alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which are unsubstituted or contain functional groupings selected from —C—OH, —OH, =C=O, —COOH, —SH, and NH_2; and formamides of the structure:



where R_2 is hydrogen, a phenyl group, an alkyl group having 1 to 6 carbon atoms, cyclo-alkyl residues having 5 to 6 carbon atoms, alkenyl and alkynyl groups having 2 to 6 carbon atoms which are unsubstituted or contain

functional groupings selected from —C—OH, =C=O, —COOH, —SH, and NH_2.

13. A method in accordance with claim **12** in which the corrosive acid is hydrochloric acid.

14. A method in accordance with claim **12** in which the inhibiting amount is within the range from about 0.25 percent to about 10.0 percent by volume based on the corrosive acid.

15. A method in accordance with claim **12** in which the ferrous metal is steel.

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