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3,585,136
CORROSION INHIBITION OF AQUEOUS SOLUTIONS OF INORGANIC MINERAL ACIDS
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No Drawing. Filed Mar. 4, 1968, Ser. No. 709,918
Int. Cl. C11d 7/08
U.S. Cl. 252—8.55

7 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous solutions of inorganic mineral acids are inhibited against their corrosive tendencies by the addition thereto of from 0.001 to 2% by volume of a composition comprising:

- (A) A Mannich reaction condensation product formed by reacting one mole of hydroabietyl amine with two moles of formaldehyde and two moles of an aldehyde containing from two to six carbon atoms and at least one hydrogen atom on the carbon atom adjacent to the aldehydic carbonyl carbon atom, and
- (B) An acetylenic alcohol which contains three to twelve carbon atoms with the ratio of A:B being within the range of from 5:1 to 1:5.

INTRODUCTION

The present invention is directed to providing inhibited acid solutions whereby their aggressiveness toward ferrous metals is substantially reduced.

Mineral acid solutions are used in numerous industrial applications. They are used in cleaning of metals and in processes wherein they contact a variety of ferrous metals.

A particularly corrosive use of mineral acids is the employment of 15% solutions and, in some instances, even more concentrated solutions of hydrochloric acid in oil well acidizing applications. Due to the excessive temperatures encountered in the lower levels of many oil wells the acid solutions are elevated to excessive temperatures, thereby greatly increasing their corrosiveness to ferrous metals. In such acidizing treatments it is not uncommon for the temperatures of the acid solutions to be raised to between 150–300° F.

In recent years the art has developed a number of inhibitors in an attempt to reduce the corrosive tendencies of acids such as hydrochloric towards ferrous metals. A common type of inhibitor used either alone or in combination with other chemicals are the acetylenic alcohols such as propargyl alcohol and 4-ethyl-1-octyn-3-ol. The use of this latter alcohol is described in U.S. 3,249,548.

While the acetylenic alcohols have proven to be of some value in reducing the corrosive tendencies of hydrochloric acid solutions at elevated temperatures, their use is not entirely satisfactory. At effective levels their cost is prohibitive. Also they are not completely effective when the temperature of the acid solutions is in excess of 150° F.

If it were possible to improve the effectiveness of acetylenic alcohols whereby they could be used in small amounts and yet at the same time provide improved corrosion inhibition, a major advance would be afforded to the art.

OBJECTS OF THE INVENTION

It therefore becomes an object of the invention to provide improved acetylenic alcohol containing compositions for use in rendering aqueous solutions of inorganic mineral acids noncorrosive.

Another object of the invention is to provide corrosion inhibitors for hydrochloric acid which are effective in

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preventing corrosion of ferrous metals in contact with such solutions whose temperature has been elevated to 150° F. and above.

Other objects will appear hereinafter.

THE INVENTION

In accordance with the invention it has been found that aqueous solutions of inorganic mineral acids particularly hydrochloric acid solutions may be inhibited against their corrosive tendencies toward ferrous metals by adding thereto novel compositions of the invention whereby inhibited mineral acid aqueous solutions are provided.

In its simplest embodiment the invention comprises using in combination the Mannich reaction products of a hydroabietyl amine, formaldehyde, and certain aliphatic aldehydes in combination with an acetylenic alcohol which contains from 3 to 12 carbon atoms.

The Mannich reaction products are combined with the acetylenic alcohols to provide a weight ratio within the range from 5:1 to 1:5. In a preferable embodiment of the invention the weight ratio of Mannich reaction products to acetylenic alcohols is within the range of 3:1 to 1:3 and, most preferably, 1:1 to 1:3.

The compositions of the type described above are added to aqueous solutions of mineral acids to provide on a volume basis from .001 to 2% by volume although, in most instances, dosages between 0.005 to 1% by volume give adequate results. This dosage is based on the volume of the total solution. The invention further contemplates finished corrosion inhibiting compositions utilizing the Mannich reaction products and acetylenic alcohols as described above in combination with oil soluble dispersants having nonionic or anionic characteristics. Such blends are further utilized in combination with an organic solvent—most preferably, a petroleum derived organic solvent such as a highly aromatic petroleum fraction.

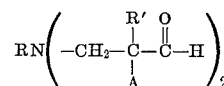
When such corrosion inhibiting compositions are employed, they may be combined to provide finished products having the following general compositions as set forth below in General Formula I.

General Formula I

Ingredients:	Percent by weight
Mannich reaction products and acetylenic alcohol (wt. ratio—5:1 to 1:5)	10–30
Oil soluble dispersant	5–40
Organic solvent	Balance

MANNICH REACTION PRODUCTS

The Mannich reaction products are formed by reacting hydroabietyl amines with at least 2 moles of formaldehyde and at least 2 moles of an aldehyde containing 2–6 carbon atoms. Illustrative of the starting aldehydes are acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde and isobutyraldehyde. Of the above aldehydes, the monoaldehydes, particularly acetaldehyde is preferred. Compositions of the type prepared from reacting these compounds have the following structural formula:



where in the above formula R is a hydroabietyl radical; R' and A are radicals from the group consisting of hydrogen and lower aliphatic hydrocarbon groups with the total number of carbon atoms in A+R' being not greater than 4.

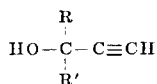
In order to be capable of entering into the Mannich reaction, the aldehyde must contain at least 1 hydrogen atom on the carbon atom adjacent to the aldehydic carbonyl carbon atom. The Mannich reaction is described in

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greater detail in "Introduction to Organic Chemistry," Condon & Meislich, Holt, Rinehart & Winston, Inc., New York (1961).

ACETYLENIC ALCOHOLS

The acetylenic alcohols include those alcohols containing the acetylenic grouping and contain from 3-12 carbon atoms. The preferred alcohols used in the practices of this invention are propargyl alcohol and, most preferably, 4-ethyl-1-octyn-3-ol. Other alcohols suitable for use in preparing the compositions of the invention come within the following structural formula:



wherein R is —H, alkyl or phenyl and R' is —H or lower alkyl.

Alcohols of the above type are set forth in U.S. 3,049,496, the disclosure of which is incorporated herein by reference.

THE OIL SOLUBLE DISPERSANTS

The oil soluble dispersants used in preparing finished inhibitor products are most preferably oil soluble or at least oil dispersible. They are either anionic or non-ionic at use levels. The non-ionic products are prepared by reacting fatty acids, alcohols, alkyl phenols and the like with between 5-50 moles of either ethylene or propylene oxide.

Preferred chemicals of this type are the alkyl phenols or fatty acids which have been reacted with from between 5-25 moles of ethylene oxide.

Fatty acids per se, e.g. C12-C22 fatty acids, may be used as well as the polymerized diethanoid fatty acids which form dimers and trimers and mixtures thereof upon polymerization. See particularly U.S. 2,482,761 and 2,763,612. When the fatty acids are used alone it is desirable that they be used as the free acid rather than as their soaps or salts.

The oil soluble dispersants of the types described above when used in preparing corrosion inhibiting compositions tend to improve the operability of the Mannich reaction products in combination with the acetylenic alcohol. They allow the alcohol, particularly the higher alcohols, to be dissolved or dispersed into the mineral acid. They perform a similar function with respect to Mannich reaction products. They are also important in that they provide a better wetting of the inhibitor on the metal surfaces sought to be protected.

THE ORGANIC SOLVENTS

Many of the well-known organic solvents can be used to dissolve the above-described ingredients. Preferably these solvents are petroleum base solvents and contain at least 20% by weight of aromatic constituents. Thus, such well-known fractions as aromatic oils, Stoddard solvents, naphthas and the like may be utilized. Generally those aromatic solvents having a boiling point above that of gasoline but below that of lubricating oils are satisfactory.

Other well-known organic solvents that may be used are for instance, benzene, toluene, xylene, dimethylformamide, dimethylsulfoxide and the like.

THE EVALUATION OF THE INVENTION

Listed below are typical compositions of the invention; Compositions I through III and IX and X are Mannich reaction products.

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EXAMPLE I

Composition 1

	Gms.
5 Rosin amine D ¹ -----	90
Muriatic acid (30% HCl) -----	30
Isopropanol (99%) -----	100
Formalin (37%) -----	80
Acetaldehyde -----	88

10 ¹ Hydroabietyl amine.

The above were added to a three necked flask and heated between 60° and 70° C. for 4 hours to yield the finished product.

EXAMPLE II

Composition 2

	Gms.
15 Rosin amine D ¹ -----	17
Muriatic acid -----	6
20 Isopropanol (99%) -----	50
Formalin (37%) -----	8
Acetaldehyde -----	9

¹ Hydroabietyl amine.

25 The above were added together to a Fisher Pressure bottle in the order listed, sealed and mounted on a revolving wheel at 160° F. for 16 hours.

EXAMPLE III

Composition 3

	Gms.
30 Rosin amine D ¹ -----	9
Muriatic acid -----	3
35 Isopropanol -----	50
Formalin (37%) -----	8
Acetaldehyde -----	9

¹ Hydroabietyl amine.

40 The above were added together to a Fisher Pressure bottle and mounted on the wheel for 24 hours at 160° F.

Composition 4

	Gms.
45 Composition 2 -----	20
Nonyl phenol+12 moles ethylene oxide -----	30
Crude tall oil -----	20
Propargyl alcohol -----	10

Composition 5

	Gms.
50 Composition 3 -----	40
Nonyl phenol+12 moles ethylene oxide -----	20
Crude tall oil -----	30
Propargyl alcohol -----	10

Composition 6

	Gms.
55 Composition 2 -----	20
Nonyl phenol+12 moles ethylene oxide -----	15
Tall oil+15 moles ethylene oxide -----	15
60 Crude tall oil -----	40
Propargyl alcohol -----	10

Composition 7

	Gms.
65 Composition 2 -----	30
Nonyl phenol+12 moles ethylene oxide -----	15
Tall oil+15 moles ethylene oxide -----	15
Crude tall oil -----	30
Propargyl alcohol -----	10

Composition 8

	Gms.
70 Composition 2 -----	12
Nonyl phenol+12 moles ethylene oxide -----	7
Tall oil+15 moles ethylene oxide -----	8
Crude tall oil -----	20
75 Propargyl alcohol -----	2

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EXAMPLE IV

Composition 9

	Gms.
Rosin amine D ¹	51
Muriatic acid	18
Isopropanol (99%)	25
Formalin (37%)	24
Acetaldehyde	27

¹ Hydroabietyl amine.

The above was added to a Fisher Pressure bottle and mounted on a revolving wheel at 160° F. for 72 hours.

EXAMPLE V

Composition 10

	Gms.
Rosin amine D ¹	34
Muriatic acid	12
Isopropanol (99%)	25
Formalin (37%)	40
Acetaldehyde	40

¹ Hydroabietyl amine.

The above were added to a Fisher Pressure bottle and mounted on the wheel for 72 hours.

Composition 11

	Gms.
Composition 9	67
Isopropanol (99%)	62

Composition 12

	Gms.
Composition 11	30
Aromatic solvent	50
Octynol ²	10
Nonyl phenol+12 moles ethylene oxide	10

² 4-ethyl-1-octyn-3-ol.

Composition 13

	Gms.
Composition 11	20
Tall oil+15 moles ethylene oxide	15
Nonyl phenol+12 moles ethylene oxide	15
Crude tall oil	20
Aromatic solvent	20
Octynol ²	10

² 4-ethyl-1-octyn-3-ol.

Composition 14

	Gms.
Composition 13	80
Polyamine bottoms	20

Composition 15

	Gms.
Composition 13	80
Dimer and trimer fatty acids-still bottoms	20

Composition 16

	Gms.
Composition 13	80
Sulfurized tall oil	20

Composition 17

	Gms.
Composition 13	80
KI	4
Water	16

Composition 18

	Gms.
Composition 13	80
Dimer and trimer fatty acids-still bottoms	20

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Composition 19

	Gms.
Composition 11	20
Nonyl phenol+12 moles ethylene oxide	15
Tall oil+15 moles ethylene oxide	15
Aromatic solvent	40
Octynol ²	5
Aromatic solvent	15

² 4-ethyl-1-octyn-3-ol.

Composition 20

	Gms.
Composition 11	30
Aromatic solvent	50
Octynol ²	10
Nonyl phenol+12 moles ethylene oxide	10

² 4-ethyl-1-octyn-3-ol.

Composition 21

	Gms.
Composition 9	20
Nonyl phenol+12 moles ethylene oxide	15
Tall oil+15 moles ethylene oxide	15
Crude tall oil	20
Aromatic solvent	20
Octynol ²	10

² 4-ethyl-1-octyn-3-ol.

Composition 22

	Gms.
Composition 9	10
Tall oil+15 moles ethylene oxides	25
Nonyl phenol+12 moles ethylene oxide	15
Crude tall oil	20
Aromatic solvent	20
Octynol ²	10

² 4-ethyl-1-octyn-3-ol.

Composition 23

	Gms.
Composition 13	90
KI	5
Water	5

Composition 24

	Gms.
Composition 13	80
KI	10
Water	10

Composition 27

	Gms.
Composition 13	45
Hydroabietyl amines+5 moles ethylene oxide+15% hydroabietyl amine	5

CORROSION TESTS

In the small scale laboratory tests which follow, three different types of ferrous metal specimens were used:

Specimens

(1) High pressure steel tubing—American Petroleum Institute designation N-80.

(2) Mild steel coupons SAE 1020 cold rolled steel.

(3) High carbon steel drill rod.

All tests used 15% HCl solutions as the test media.

No blank results are indicated since under the test conditions at temperatures in excess of 150° the test specimens were completely destroyed.

In a series of tests corresponding to those hereinafter described the Mannich reaction products were evaluated and were found to be no better than the blank test results.

4-ethyl-1-octyn-3-ol was evaluated under the test conditions shown and the concentrations used in the test and in all instances gave 50% poorer results than the compositions of the invention.

Results of testing the various compositions of the invention are set forth below in Table I.

TABLE I

Test No.	Comp. No.	Time, hrs.	Temp., ° F.	Specimen type	Conc., gal. 1,000	Wt. loss, g.
1.....	4	6	200	1	4	3.0062
2.....	5	6	200	1	4	2.9763
3.....	4	6	200	1	2	4.5123
4.....	4	6	200	1	2	5.2470
5.....	6	6	200	1	4	0.5123
6.....	7	5½	200	1	2	2.8084
7.....	7	5½	200	1	4	0.5458
8.....	8	5½	200	1	2	1.4868
9.....	8	5½	200	1	4	1.2646
10.....	6	24	200	1	2	20.7465
11.....	6	24	200	1	4	1.5616
12.....	14	6	200	3	4	148.9
13.....	16	6	200	3	4	147.9
14.....	17	6	200	3	4	160.5
15.....	18	6	200	3	4	176.6
16.....	13	6	200	3	4	160.4
17.....	19	6	200	3	4	161.4
18.....	20	6	200	3	4	167.7
19.....	21	8	200	3	4	176.4
20.....	22	8	200	3	4	144.9
21.....	13	8	200	3	4	137.5
22.....	13	18	200	3	2	175.4
23.....	23	18	200	3	1	179.0
24.....	23	18	200	3	2	113.9
25.....	24	18	200	3	1	162.1
26.....	24	18	200	3	2	111.5
27.....	28	5	200	3	4	135.9
28.....	7	24	72	2	1	10.2047
29.....	7	24	72	2	2	10.1672

¹ In milligrams.

CONCLUSION

While the tests have shown the compositions to be effective in inhibiting 15% hydrochloric acid, they are also effective in inhibiting the various strength hydrochloric acid solutions up to its saturation solubility. They are similarly effective in inhibiting solutions of phosphoric, sulfuric and nitric acids.

What is claimed is:

1. An aqueous solution substantially non-corrosive to ferrous metals which consists essentially of a major proportion of an inorganic mineral acid from the group consisting of hydrochloric, phosphoric, sulfuric, and nitric acid and from 0.001 to 2% by volume of a composition consisting essentially of:

(A) the Mannich reaction condensation product of one mole of a hydroabietyl amine with at least two moles of formaldehyde and at least two moles of an aldehyde containing from 2 to 6 carbon atoms and having at least one hydrogen atom on the carbon atom adjacent to the aldehydic carbonyl carbon atom, and

(B) a monohydroxy acetylenic alcohol which contains from 3 to 12 carbon atoms:

with the ratio of A to B being within the range of from 5:1 to 1:5.

2. The aqueous solution of an inorganic mineral acid as set forth in claim 1 where the mineral acid is hydrochloric.

3. The aqueous solution of an inorganic mineral acid as set forth in claim 1 wherein R' and A are hydrogen and the acetylenic alcohol is 4-ethyl-1-octyn-3-ol.

4. The aqueous solution of an inorganic mineral acid as set forth in claim 3 wherein the ratio of A to B is within the range of from 3:1 to 1:3.

5. The aqueous solution of an inorganic mineral acid as set forth in claim 4 wherein the ratio of A to B is within the range of 1:1 to 1:3.

6. A composition useful in inhibiting the corrosive tendencies of aqueous solutions of inorganic mineral acids from the group consisting of hydrochloric, phosphoric, sulfuric, and nitric acid, which consists essentially of from 10% to 30% by weight of a composition consisting essentially of:

(A) the Mannich reaction condensation product of one mole of hydroabietyl amine with at least two moles of formaldehyde and at least two moles of an aldehyde containing from 2 to 6 carbon atoms and having at least one hydrogen atom on the carbon atom adjacent to the aldehydic carbonyl carbon atom, and

(B) a monohydroxy acetylenic alcohol which contains from 3 to 12 carbon atoms;

with the ratio of A to B being within the range of from 5:1 to 1:5, 5-40% by weight of an oil soluble dispersant formed by reacting higher fatty acids and higher alkyl phenols with 5-50 moles of an alkoxide from the group consisting of ethylene oxide and propylene oxide; the balance being a hydrocarbon solvent for the above ingredients having a boiling point above 75° C.

7. The composition of claim 6 wherein R' and A are hydrogen and the acetylenic alcohol is 4-ethyl-1-octyn-3-ol; and wherein the oil soluble dispersant is an ethoxylated nonyl substituted phenol which contains from 5-50 moles of reacted ethylene oxide.

References Cited

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MAYER WEINBLATT, Primary Examiner

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U.S. Cl. X.R.

252—146, 148, 392; 260—584

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,585,136

Dated June 15, 1971

Inventor(s) James R. Stanford 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 5, Composition 12 should read as follows:

	Gms.
Composition 11 -----	20
Nonyl phenol+12 moles ethylene oxide-----	15
Tall oil+15 moles ethylene oxide -----	15
Aromatic solvent -----	40
Octynol ² -----	5
Aromatic solvent -----	15

²4-ethyl-1-octyn-3-ol.

Column 6, Composition 19 should read as follows:

	Gms.
Composition 11 -----	30
Aromatic solvent -----	50
Octynol ² -----	10
Nonyl phenol+12 moles ethylene oxide -----	10

²4-ethyl-1-octyn-3-ol.

Signed and sealed this 11th day of January 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents