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CORROSION INHIBITION

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3 Claims. (Cl. 252—151)

The present invention relates to the inhibition of metal corrosion and more particularly relates to a new and useful composition which prevents the corrosion of metals when they are in contact with acids.

Most known corrosion inhibitors decompose in the presence of oxidizing acids, such as dilute nitric acid and the like. Further, many of the useful inhibitors have very narrow limits of operation necessitating the use of customer-tailored acid compositions.

It is therefore an object of the present invention to provide an acid-system metal corrosion inhibitor composition which is operative over a wide range of concentrations of both oxidizing acids and non-oxidizing acids. Another object of the present invention is to provide a corrosion inhibitor composition which will not decompose under oxidizing conditions. These and other objects will become apparent to those skilled in the art from the following specification and claims.

It has now been found that acid corrosion of metals, particularly that caused by the oxidizing acids, can be inhibited by mixing with the acid system a composition containing propargyl sulfide and one or more of the thio compounds of the class alkanedithiols, mercaptoalkanols, mercaptoalkanoic acids, thiolalkanoic acids, alkyl sulfides, or inorganic sulfides. Good results are obtained when the inhibitor composition is employed in an amount of from 0.0625 to 1.00 percent by volume of ultimate composition.

In accordance with the present invention, when the composition of the present invention is mixed with an acid, i.e., a mineral acid such as nitric, hydrochloric, sulfuric, phosphoric or perchloric acid or the lower organic acids such as acetic and the like in an amount of from 0.0625 percent to 1.0 percent and preferably from 0.125 percent to about 0.5 percent by volume of the ultimate composition, the corrosion of metal surfaces in contact therewith is substantially inhibited.

Various combinations of sulfur-containing compounds may be employed to prepare the inhibitor compositions of the present invention. Thus, propargyl sulfide can be admixed with one or more of the following sulfur-containing compounds, i.e., ethanedithiol, thiolacetic acid, mercaptoacetic acid, ethyl sulfide, hydrogen sulfide, ferrous sulfide, and the like. The ratios of sulfur-containing compound to propargyl sulfide which are within the scope of the present invention are from 0.25 to 1.0 part by volume of sulfur compound per volume of propargyl sulfide.

The following examples are illustrative of the present invention but are not to be construed as limiting.

Examples 1–20

Corrosion rate data on various mixtures of propargyl

sulfide and sulfur compound as the active inhibitor in 10 percent nitric acid.

Volume acid—150 ml. (10 percent nitric acid).
Metal—AISI 1010 mild steel coupon (2.75" x 1.0" x 0.12") duration of test 6 hours.

Example No.	Inhibitor Concentration in percent by volume	Temperature (° F.)	Corrosion Rate (lbs/ft.²/day)
1	0.4 percent propargyl sulfide	80	0.172
2	0.5 percent ethanedithiol	80	0.001
3	0.25 percent propargyl sulfide + 0.25 percent ethanedithiol.	80	0.0001
4	do	150	0.0023
5	0.5 percent mercaptoethanol	80	0.006
6	0.25 percent propargyl sulfide + 0.25 percent mercaptoethanol.	80	0.0008
7	do	150	0.005
8	0.5 percent thiolacetic acid	80	0.097
9	0.25 percent propargyl sulfide + 0.25 percent thiolacetic acid.	80	0.0007
10	do	150	0.0025
11	0.5 percent mercaptoacetic acid	80	0.122
12	0.25 percent propargyl sulfide + 0.25 percent mercaptoacetic acid.	80	0.0001
13	do	150	0.0031
14	0.5 percent ethyl sulfide	80	>1.0
15	0.25 percent propargyl sulfide + 0.25 percent ethyl sulfide.	80	0.004
16	do	150	0.007
17	0.5 percent hydrogen sulfide	80	>1.0
18	0.25 percent propargyl sulfide saturated with hydrogen sulfide.	80	0.0003
19	0.5 percent ferrous sulfide	80	0.205
20	0.4 percent propargyl sulfide + 0.5 percent ferrous sulfide.	80	0.0004

Examples 21–26

Results of tests made to determine the concentration of inhibitor composition required for adequate protection are shown below. The composition contained equal parts by weight of propargyl sulfide and 1,2-ethanedithiol.

Volume acid—150 ml. 10 percent nitric acid.
Metal—AISI 1010 mild steel coupons (2.75" x 1.0" x 0.12").
Length of test—6 hours.
Temperature—80° F.

Example No.	Concentration Inhibitor (percent by volume)	Corrosion Rate (lbs./ft.²/day)
21	None	too high to measure.
22	.0625	0.110.
23	.125	0.0042.
24	.25	0.0003.
25	.5	0.0001.
26	1.0	0.00008.

Examples 27–37

Tests were run with various ratios of propargyl sulfide to other sulfur-containing compound to determine the limits of the mixtures which give corrosion protection.

Volume acid—150 ml. 10 percent nitric acid.
Metal—AISI 1010 mild steel coupons.
Length of tests—6 hours.
Temperature—80° F.

Test No.	Conc. Propargyl Sulfide (percent by vol.)	Conc. other Sulfur Containing Compound (percent by vol.)	Corrosion Rate (lbs./ft.²/day)
27	0.5	None	0.172.
28	0.4	0.10 ethanedithiol	0.028.
29	0.30	0.20 ethanedithiol	0.0032.
30	0.25	0.25 ethanedithiol	0.0001.
31	0.125	0.375 ethanedithiol	0.0007.
32	None	0.5 ethanedithiol	0.001.
33	0.4	0.1 mercaptoacetic acid	0.068.
34	0.3	0.2 mercaptoacetic acid	0.0009.
35	0.25	0.25 mercaptoacetic acid	0.0001.
36	0.125	0.375 mercaptoacetic acid	0.014.
37	None	0.5 mercaptoacetic acid	0.122.

Examples 38–48

Additional tests were run, varying the acid concentration and temperature to show the effectiveness of the inhibitor.

Volume aicd—150 ml., nitric acid.
Inhibitor—0.5 percent (by volume) of a mixture of 1 part by volume propargyl sulfide plus 1 part 1,2-ethanedithiol.
Metal—AISI 1010 mild steel coupons (2.75" x 1.0" x 0.125").
Length of test—6 hours.

Test No.	Conc., Nitric Acid, percent	Temperature (° F.)	Corrosion Rate (lbs./ft.²/day)
38	10	80	0.0001.
39	10	150	0.0023.
40	15	80	0.0006.
41	15	150	0.0081.
42	20	80	0.0084.
43	20	150	0.014.
44	25	80	0.0091.
45	25	150	too high to meas.
46	30	80	0.023.
47	30	150	too high to meas.
48	50	80	Do.

Examples 49–58

Various metals were exposed to other acids of industrial importance using an inhibitor composition of the instant invention. The results indicated below show the inhibitor is effective in these other acids.

Inhibitor: one part by volume propargyl sulfide to 1 part 1,2 ethanedithiol.
Volume acid—150 ml.
Metal—AISI 1020 mild steel coupons (2.75+1.0" x 0.125").
Conditions of test—16 hours exposure at 150° F.

Test No.	Acid Medium	Concentration Inhibitor (Percent by volume)	Corrosion Rate (lbs./ft.²/day)
49	10 percent Hydrochloric	None	>1.0
50	do	0.5	0.0010
51	10 percent Acetic	None	0.140
52	do	0.5	0.0002
53	5 percent Sulfuric	None	0.185
54	do	0.5	0.0087
55	5 percent Phosphoric	None	0.086
56	do	0.5	0.00091
57	10 percent Perchloric	None	0.15
58	do	0.5	0.0003

Examples 59–68

A series of metals was exposed to dilute nitric acid inhibited with one of the inhibitor compositions of this invention. The inhibitor was a 50–50 mixture of propargyl sulfide and 1,2-ethanedthiol.

Volume Acid—150 ml.
Length of Test—6 hours.
Temperature 80° F.

Test No.	Metal Coupon	Conc. Inhibitor, (percent by volume)	Corrosion Rate (lbs./ft.²/day)
59	AISI 347	None	0.0018.
60	do	0.5	0.0007.
61	Cast Iron	None	too high to meas.
62	do	0.5	0.092.
63	Copper	None	0.0040.
64	do	0.5	0.00029.
65	Admiralty	None	0.020.
66	do	0.5	0.0019.
67	3003H14 Aluminum	None	0.0039.
68	do	0.5	0.0028.

I claim:

1. A metal corrosion inhibiting composition comprising one part by volume of propargyl sulfide and from 0.25 to 1.0 part by volume of a sulfur-containing compound selected from the group consisting of ethanedithiol, thiolacetic acid, mercaptoacetic acid, ethyl sulfide, hydrogen sulfide, and ferrous sulfide.

2. An aqueous acid solution comprising, as a metal corrosion inhibitor therefor, about 0.0625 to 1.0 percent by volume of the composition defined in claim 1.

3. An aqueous acid solution comprising as a metal corrosion inhibitor therefor, about 0.125 to 0.5 percent by volume of the composition defined in claim 1.

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