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INHIBITION OF METAL CORROSION

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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 ferrous 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 either oxidizing acids or non-oxidizing acids. Another object of the present invention is to provide a corrosion inhibitor composition which will not decompose under the oxidizing conditions. It is still a further object of the present invention to provide an inhibitor which will permit the storage of nitric acid in metal containers. 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 oxidation effect of nitric acid, can be inhibited by mixing with the acid system a beta-activated mercaptan and/or a gamma-activated sulfur compound such as, for example, one or more of the sulfur compounds of the class alkanedithiols, mercaptoalkanols, dimercaptoalkanols, mercaptoalkanoic acids, or thioalkanoic acids, furfurylthiol and the like. Good results are obtained when the sulfur-containing inhibitor is employed in an amount of from 0.06 to 1.0 percent by volume of ultimate composition.

In accordance with the present invention, when the sulfur compound or compounds of the present invention are mixed with acid i.e., a mineral acid such a nitric, hydrochloric, sulfuric, phosphoric or perchloric acid or the lower organic acids such as acetic and the like in an amount of from 0.06 percent to 1.0 percent and preferably from 0.25 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, one or more of the following sulfur-containing compounds, i.e., ethanedithiol, 1,2- or 1,3-propanedithiol, butanedithiol, pentanedithiol, hexanedithiol, thiolacetic acid, 2,3-dimercapto-1-propanol, 1,3-dimercapto-2-propanol, furfurylmercaptan or the like may be employed.

The inhibitor of the present invention can be added to the aqueous oxidizing acid or the acid can be added to an aqueous dispersion of the inhibitor. The latter method is more often preferred since the mixing of the acid can take place in ferrous containers whereas the first method requires non-corrodible equipment prior to complete dispersion of the inhibitor in the acid solution.

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

Examples 1–6

Corrosion rate tests employing various concentrations of 1,2-ethanedithiol as the active inhibitor in 10 percent nitric acid were made to determine the concentration of

inhibitor composition required for adequate protection the results of which are shown below:

Volume acid—150 ml.
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)
1	none	too high to measure.
2	.0625	Do.
3	.125	0.061.
4	.25	0.0017.
5	.5	0.0010.
6	1.0	0.0009.

Examples 7–14

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

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

Example No.	Conc., Nitric Acid, percent	Temperature (° F.)	Corrosion Rate, (lbs./ft.²/day)
7	10	80	0.0010.
8	10	150	0.0030.
9	15	80	0.0026.
10	15	150	broke down in 2.5 hours.
11	20	80	0.0036.
12	20	150	broke down in 2 hours.
13	25	80	0.0059.
14	30	80	broke down in 3.5 hours.

Examples 15–26

AISI 1010 mild steel was exposed to other acids of industrial importance using various inhibitors of the instant invention. The results indicated below show the inhibitors are effective in those other acids.

Volume acid—150 ml.
Metal—AISI 1010 mild steel (2.75" x 1.0" x 0.125")
Conditions of test—16 hours' exposure at 150° F.

Ex. No.	Acid Medium	Concentration Inhibitor (percent by volume)	Corrosion Rate (lbs./ft.²/day)
15	10 percent Hydrochloric	None	0.612
16	do	0.5 2-furylmethanethiol	0.0021
17	do	0.5 1,2-ethanedithiol	0.0013
18	do	0.5 1,3-propanedithiol	0.0009
19	5 percent Acetic	None	0.140
20	do	0.5 1,2-ethanedithiol	0.00063
21	do	0.5 1,3-propanedithiol	0.00087
22	do	0.5 furfurylthiol	0.0009
23	5 percent Sulfuric	None	0.185
24	do	0.5 1,2-ethanedithiol	0.0082
25	5 percent Phosphoric	None	0.086
26	do	0.5 1,2-ethanedithiol	0.00072

Examples 27–36

A series of metals was exposed to 10 percent nitric acid with and without inhibitor to determine the effectiveness of the inhibitor in preventing corrosion of these

various metals. 0.5 percent by volume of 1,2-ethanedithiol was employed.

Volume acid—150 ml.
Length of test—6 hours
Temperature—80° F.

Ex. No.	Metal Coupon	Conc. Inhibitor, (percent by volume)	Corrosion Rate (lbs./ft.²/day)
27	AISI 347	None	0.0018
28	AISI 347	0.5	0.0009
29	Cast Iron	None	0.828
30	do	0.5	0.079
31	Copper	None	0.0040
32	do	0.5	0.0004
33	Admiralty	None	0.020
34	do	0.5	0.0023
35	do	None	0.0039
36	3003H14 Aluminum	0.5	0.0029

Examples 38–41

Tests were run with various sulfur-containing compounds to determine the length of time the mixtures 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.

Ex. No.	Conc. of Sulfur-containing Compound (percent by vol.)	Corrosion Rate (lbs./ft.²/day)	
		1 Mo.	3 Mo.
37	None	Immediate and rapid attack too high to measure	
38	0.5 ethanedithiol	0.00016	0.00018.
39	0.5 propanedithiol	0.00014	0.00015.
40	0.5 furfurylthiol	0.00011	0.00012.
41	0.5 2,3-dimercaptopropanol	0.00011	rapid corrosion began after 2 mos.

I claim:

1. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and, as a corrosion inhibitor therefor, about 0.125 to 1.0 percent by volume of a sulfur-containing compound selected from the group consisting of lower alkanedithiols, furfurylthiol, lower mercaptoalkanols, lower dimercaptoalkanols, and lower thiolalkanoic acid.

2. An aqueous acid solution as set forth in claim 1 wherein said corrosion inhibitor is employed in a concentration of from 0.25 to 0.5 percent by volume.

3. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of 1,2-ethanedithiol.

4. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of 1,3-propanedithiol.

5. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of furfurylthiol.

6. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of 1,4-butanedithiol.

7. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of 1,5-pentanedithiol.

8. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of 1,6-hexanedithiol.

9. A corrosion-inhibited aqueous nitric acid solution comprising nitric acid and from 0.125 to 1.0 percent by volume of 2,3-dimercaptopropanol.

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CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, in the first table, column 2, line 9 thereof, for "do" read -- 3003H14 Aluminum --.

Signed and sealed this 10th day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

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