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CORROSION INHIBITION OF MONOBASIC ACIDS

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This invention relates to the corrosion inhibition of various monobasic acids as regards stainless steels, and particularly to a method of inhibiting the corrosiveness in aqueous solution of one or more of the group comprising formic, acetic, glycolic and sulfamic acids by the incorporation of ferric ion.

Formic, acetic, glycolic and sulfamic acids are appre-

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Generally, the objects of this invention are obtained by incorporating in the acid solution a minor amount of ferric ion by addition to the acid of a ferric salt, preferably a salt of substantial solubility, after which the solution is employed in its customary manner without regard to the fact that the inhibitor is present. The inhibited solution may also contain wetting and dispersing agents to facilitate cleaning, where this is the objective, or may contain oxalic acid or sodium bisulfate either singly or in mixture, the inhibitory effect of ferric ion as regards oxalic acid being taught in my application S. N. 423,504 and as regards sodium bisulfate in my application S. N. 423,506, both filed on the same date as the instant application.

The following table is a compilation of data covering a number of tests which demonstrate the efficacy of the method of this invention as regards boiling aqueous solutions of individual members of the group of acids, the ferric salt utilized in each particular series of tests being indicated parenthetically under the acid involved and the column headings being self-explanatory:

Solution	Acid Concentration in Wt. Percent	Steel, AISI Designation Unless Otherwise Indicated	Uninhibited Corrosion Rate, g./sq. dm./hr.	Min. Amt. of Fe Giving Complete Inhibition, Unless Otherwise Indicated, in g./liter
Sulfamic Acid (ferric ion added as oxalate and sulfate individually).	10	304	0.452	0.13.
	30	304	3.469	0.11.
	10	16% Cr-17% Mn-1% Ni	13.757	0.21.
	10	430	33.359	0.77 (not determined as minimum).
Acetic Acid (ferric ion added as nitrate and oxalate individually).	10	446	34.633	0.17.
	10	304	0.027	0.0023.
	10	446	0.000	-----
	10	430	0.344	1 0.206.
	50	304	0.048	0.110.
	99.7	304	0.013	0.018.
Formic Acid (ferric ion added as nitrate and oxalate individually).	99.7	16% Cr-17% Mn-1% Ni	0.017	0.012.
	10	304	0.251	0.068.
	10	446	2.292	0.023.
	10	430	3.79	0.182.
	45	304	0.404	0.110.
	90	304	0.244	0.017.
Glycolic Acid (ferric ion added as oxalate and nitrate individually).	90	16% Cr-17% Mn-1% Ni	0.069	0.069.
	10	304	0.0844	0.076.
	10	446	0.153	0.023.
	10	430	0.691	0.23.
	70	16% Cr-17% Mn-1% Ni	0.0068	0.230.
		304	0.200	0.076.

¹ No corrosion, but specimen had brown coloration.

ciably corrosive to the stainless steels, and this characteristic causes adulteration of the acids from corrosion products as well as injury to the manufacturing and processing equipment. Recently, aqueous solutions of glycolic acid and sulfamic acid have been employed with good results for the cleaning of stainless steel dairy equipment, since the calcium salts of these acids are water-soluble and are thus readily rinsed away. One objection to the use of sulfamic acid, particularly, in this application, is the development over a period of continued use of an adherent black coating, which interferes with visual inspection for cleanliness.

It is an object of this invention to provide a method of inhibiting the corrosiveness of formic, acetic, glycolic and sulfamic acids alone or in mixture in aqueous solution for stainless steels. Another object of this invention is to provide a method of inhibiting the corrosiveness of these acids in aqueous solution while preventing objectionable contamination of the solutions, and while retaining the original bright surface of the stainless steel intact. Yet another object of this invention is to provide a method of inhibiting the corrosiveness of one or more of these acids in aqueous solution, with or without oxalic acid or sodium bisulfate added, as herein-after described, for stainless steels which is cheap and not dangerous to using personnel.

The tests reported in the table were conducted over periods of 7 hours using boiling acids in the concentrations reported, the concentration level being maintained constant throughout the tests by the use of condensers which returned all material boiled off to the metal sample-containing flask during the course of the tests. Additional tests, not reported in the table, confirmed the corrosion inhibitory action of ferric ion for much greater periods of time, up to and beyond 60 hours and, independently, for exposures of the steels at lower temperatures. In all cases, except for A. I. S. I. 430 steel exposed to 10% acetic acid, the original bright finish of the steel was preserved intact upon exposure to the corrosion-inhibited acids. In contrast, uninhibited acids affect the finish deleteriously to varying degrees depending upon the particular acid, temperature and concentration involved. Yet other tests disclosed that the inhibition data reported for A. I. S. I. 304 steel is applicable within $\pm 20\%$ to the A. I. S. I. 300 series steels generally.

As will be apparent from the parenthetical notes adjacent each of the acids identified in the left-hand column of the table, a variety of ferric salts were employed in conducting the tests reported. These salts were employed individually, as distinguished from mixtures of one with another, and the preference, based on order of solubility in the acid solution inhibited, is in the order of recita-

tion. The only requirement for operability according to this invention is that the ferric salt utilized be appreciably soluble in the acid solution to be inhibited, so that ferric ion is contributed readily to the solution. Halogen salts, such as the chloride, fluoride or bromide, are not favored for inhibition service, not only because corrosive halide residues might remain on the metal surfaces if not removed by thorough rinsing, but also because I have found that halogen ions exert an inhibition-counteracting effect on the ferric ions above certain limiting total salt concentration levels. In all cases investigated, the salt concentration at which the inhibition-counteracting effect occurred was found to be considerably in excess of the ferric ion concentration which it was necessary to maintain for complete corrosion inhibition, and therefore ferric halides are effective for the purposes of this invention with the limitations mentioned.

In this connection, the following data were obtained in testing samples of 304 stainless steel over periods of one hour in boiling 10% sulfamic acid containing the tabulated amounts of ferric ion added as the chloride:

Amount of iron added as ferric chloride, g./l. sol'n.	Corrosion rate in g./sq. dm.
0.0448.....	0.825
0.448.....	0.0000
2.24.....	0.348
3.45.....	1.261

From these data it will be apparent that, while only 0.13 g./l. of iron is required for complete inhibition of type 304 steel under exposure to 10% sulfamic acid solution (refer previous table), complete inhibition persisted for more than three times this minimum, namely, 0.448 g./l., even when the ferric ion was incorporated via the chloride.

All of the data hereinbefore set out is convertible to the basis of penetration in inches per month by simply multiplying by the factor 0.36.

The mechanism responsible for the corrosion inhibition of the acids reported toward stainless steels by the ferric ion, while keeping the surface bright, is not understood; however, the effect appears to result from a specific property of the ion itself.

From the foregoing it will be understood that my invention comprises an effective method of inhibiting the corrosion of the acids reported with respect to the stainless steels, within which term it is intended to comprehend both the conventional stainless steels and the so-called "substitute stainless steels," the 16% Cr-17% Mn-1% Ni composition being a typical member of the latter class, and that the limiting concentrations which are employed depend upon the particular acid solution, the specific analysis of the stainless steel involved and the salt through which the ferric ion is introduced, all of which are subject to relatively wide modification, for which reasons it is intended to be limited only by the following claims.

What is claimed is:

1. The method of substantially inhibiting the corrosiveness in aqueous solution of at least one of the group consisting of formic, acetic, sulfamic and glycolic acids toward stainless steels comprising incorporating in said solution a minor quantity of a ferric ion-contributing salt other than an iron halide, but not less than an amount yielding from about 0.02 to about 0.23 gram/liter of ferric iron, depending upon the specific solution and steel involved, and thereafter contacting said stainless steels with said solution.

2. The method according to claim 1 in which said ferric ion-contributing salt consists of ferric oxalate.

3. The method of substantially inhibiting the corrosiveness in aqueous solution of at least one of the group consisting of formic, acetic, sulfamic and glycolic acids toward A. I. S. I. series 300 stainless steels comprising incorporating in said solution a quantity of a ferric ion-contributing salt other than an iron halide furnishing from about 0.02 to 0.13 gram of iron/liter of said solution depending upon the specific solution and the steel involved, and thereafter contacting said stainless steels with said solution.

4. The method of substantially inhibiting the corrosiveness in aqueous solution of at least one of the group consisting of formic, acetic, sulfamic and glycolic acids toward A. I. S. I. series 400 stainless steels comprising incorporating in said solution a quantity of a ferric ion-contributing salt other than an iron halide furnishing from about 0.02 to 0.77 gram of iron/liter of said solution depending upon the specific solution and the steel involved, and thereafter contacting said stainless steels with said solution.

5. The method of substantially inhibiting the corrosiveness in aqueous solution of at least one of the group consisting of formic, acetic, sulfamic and glycolic acids toward Cr-Mn-Ni stainless steels comprising incorporating in said solution a quantity of a ferric ion-contributing salt other than an iron halide furnishing from about 0.02 to 0.23 gram of iron/liter of said solution depending upon the specific solution and the steel involved, and thereafter contacting said stainless steels with said solution.

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