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CORROSION PREVENTIVE COMPOSITION

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The invention relates to an improved corrosion preventive composition for use in non-oxidizing acid solutions to decrease the corrosion of metal in contact with said solutions.

It is known that propargyl alcohol is an excelent corrosion inhibitor for acid solutions. It is also known that a synergistic corrosion inhibitor can be obtained by employing as the inhibitor a mixture of propargyl alcohol and an amine such as pyridine, tributylamine, etc. The activity of the amine and propargyl alcohol is effectively synergized when the amine is employed in amounts of from 10% to 90% by volume of the inhibitor composition.

It is the principal object of the present invention to provide a corrosion preventive composition which inhibits the corrosion of various metals in contact with corrosive acids.

A further object is to provide a process for inhibiting the corrosion of various metals, such as iron, steel, nickel and ferrous alloys when in contact with corrosive acids.

Other objects and advantages will become manifest from the following description.

We have found that a synergistic corrosion inhibiting composition is obtained by employing as the inhibitor a mixture of 95% by volume of propargyl alcohol and 5% by volume of dipropargyl formal. The inhibitor mixture is used at a level ranging from 0.001–1.% by volume based on the volume of the aqueous acid solution in which the acid concentration ranges from 1 to 15% by weight.

Various acids, especially the mineral acids, are effectively inhibited against metal corrosion by employing the inhibitor mixture. The acids include acetic, hydrochloric, phosphoric, sulfuric, and other non-oxidizing acids.

The dipropargyl formal in the inhibitor mixture has the following formula:

$$H_2C(OCH_2C{\equiv}CH)_2$$

and is prepared by the following procedure:

Propargyl alcohol (450 grams, 8 moles), s-trioxymethylene (90 grams, 1 mole), benzene (150 grams) and Dowex 50 (H^+ form) are refluxed in a 1-liter flask equipped with a Barrett water trap. When the ternary azeotrope breaks, the lower layer containing propargyl alcohol and water is removed and the water content measured periodically. After the theoretical amount of water has been removed, the reaction mixture is subjected to fractional distillation. The portion boiling at 110–111° C./100 mm. Hg is isolated. The yield of pure dipropargyl formal (B.P. 172.5° C./760 mm. n_D^{25} 1.4440, Sp. $Gr._{27}$ −0.987) is 260 grams or about 70% of theoretical.

The dipropargyl formal per se is insoluble in water, but when present in an amount up to 5% by volume in propargyl alcohol, the mixture is soluble in water at a 1% concentration and also soluble at the same concentration in the foregoing acids and aqueous solutions thereof. The inhibitor mixture is soluble in various concentractions of non-oxidizing acids, even commercial hydrochloric acid of about 37% strength. Aqueous solutions of such acids usually contain from 1 to 15% by weight of acid to which the inhibitor mixture is added in the

aforestated amounts to yield the corrosion preventive composition.

The corrosion preventive composition of the present invention will inhibit the corrosion of various metals such as iron, steel, nickel and ferrous alloys when in contact with said composition. The corrosion preventive composition is ideal for use in metal-pickling, metal cleaning and polishing baths, boiler cleaning and as corrosion inhibitor of oil-well casing and tubing.

The inhibitor mixture of the present invention is effective at a temperature ranging from room to 212° F. The limit of the latter temperature is dependent on the concentration of the acid used in practical application or in the test, the more dilute the acid, i.e., at about 5% concentration, the higher the temperature limit of the inhibitor mixture.

In order to demonstrate the effectiveness of our inhibitor mixture, a series of tests was run in which 0.4% by volume of the inhibitor mixture was put into a 15% by weight of aqueous solution of hydrochloric acid held at 200° F. and a N–80 steel coupon, previously pickled, cleaned, dried and weighed was suspended in the acid for 16 hours. As controls, 0.4% by volume of each of propargyl alcohol and a dipropargyl formal were placed separately in the same acid and the procedure repeated. The coupons were then washed, dried and reweighed to determine the appearance and the amount of metal dissolved by the acid. This was calculated as milligrams of weight loss. Results of these tests are shown in Table 1.

TABLE 1

Inhibitor	Milligram Weight Loss	Appearance of Coupon
Propargyl alcohol	108.8	Slight pitting.
Dipropargyl formal	82.2	Clean.
Inhibitor mixture (95% by volume of propargyl alcohol and 5% by volume of dipropargyl formal)	70	Clean.

From the foregoing results, it is clearly evident that inhibitor mixture is far superior to propargyl alcohol. In view of this finding, we prepared the acetal and the acetaldehyde of propargyl alcohol and found that results paralleling those for dipropargyl formal shown in Table 1 were obtained under the same test. Improved results were obtained when the dipropargyl formal was dispersed in the aqueous acid by means of an ionic or non-ionic surface active agent that is stable in aqueous non-oxidizing acid. The ratio of formal should be 3 parts to 1 part of surfactant, our preference being non-ionic surfactants obtained by the condensation of 1 mole of diisobutyl phenol with 6 to 10 moles of ethylene oxide.

Improved results are also obtained when the inhibitor mixture is blended with a quaternized N-heterocyclic base and the preferred surfactant in the ratio of 5:4:1 parts by weight, respectively. Representative of such bases are those disclosed in U.S. Patents 2,037,762; 2,080,553; 2,403,153; 2,606,873; and 2,814,593. In lieu of such bases, various amines or mixtures thereof, such as primary, secondary or tertiary aliphatic amines, i.e., butylamine, dibutylamine, tributylamine, amylamine, diamylamine, triamylamine, etc., heterocyclic amines, i.e., alkylpyridines, preferably those known as alkylpyridines HB, a commercially available mixture of alkylated pyridines having an average molecular weight of 170, may be used to yield improved results.

We claim:

1. An aqueous solution consisting essentially of an aqueous solution of a non-oxidizing acid, having an acid concentration of from 1 to 15% by weight and from

0.001 to 1.0% by volume based on the volume of said aqueous acid of a corrosion inhibiting mixture consisting of 95% by volume of propargyl alcohol and 5% by volume of dipropargyl formal.

2. A corrosion inhibited mineral acid consisting essentially of an aqueous solution of mineral acid in a concentration of from 1 to 15% by weight and containing from 0.001 to 1.0% by volume based on the volume of said aqueous acid of a corrosion inhibiting mixture consisting of 95% by volume of propargyl alcohol and 5% by volume of dipropargyl formal.

3. A corrosion inhibited aqueous hydrochloric acid solution consisting of from 1 to 15% by weight of hydrochloric acid inhibited against corrosion by the addition thereto of from 0.001 to 1.0% by volume of a composition consisting of 95% by volume of propargyl alcohol and 5% by volume of dipropargyl formal.

4. A process for inhibiting the corrosion of a metal of the group consisting of iron, steel, nickel and ferrous alloys by aqueous mineral acid in a concentration of from 1 to 15% by weight in contact therewith, which consists of maintaining in said acid from 0.001 to 1.0% by volume based on the volume of said aqueous acid of a corrosion inhibiting mixture consisting of 95% by volume of propargyl alcohol and 5% by volume of dipropargyl formal.

5. A process according to claim 4 wherein the mineral acid is hydrochloric.

6. A process according to claim 4 wherein the concentration of the corrosion inhibiting mixture is about 0.01 to 1% by volume.

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