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CORROSION INHIBITOR COMPOSITION

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This invention relates to water-soluble corrosion-inhibiting compositions and is more particularly concerned with inhibitors for use primarily in water circulating systems such as automobile radiators, certain industrial heat exchangers, cooling towers and the like.

The requirements of a good water-soluble corrosion inhibitor can be summarized as follows:

(*a*) It shall protect steel or iron from the normally corrosive action of hard or soft water containing normal amounts of dissolved oxygen or air.

(*b*) It shall not attack or corrode other metal normally used in circulating systems, such as copper, brass, aluminum, lead or sloder.

(*c*) It shall be completely water-soluble.

(*d*) It is desirable, also, that it be soluble in alcohols (methanol, ethanol) and ethylene glycols in the required concentrations.

(*e*) It is desirable that the inhibitor provide some residual protection of the metal after it is removed from contact with the inhibited water. Thus, if some water evaporates from a cooling bath or system; the exposed metal should be protected for a short time. Uninhibited water will cause corrosion while in contact with the steel and will accelerate further corrosion as it evaporates.

It has been found that a corrosion inhibiting composition having outstanding properties may be prepared by blending about equal parts of para tertiary butyl benzoic acid, hereinafter referred to as "ptBBA," with relatively high molecular weight aliphatic carboxylic acids derived from a petroleum fraction, e. g., from a normally liquid petroleum fraction such, for instance, as 36–40° distillate, by liquid-phase, controlled partial oxidation of the same according to the process disclosed in U. S. Patents Nos. 1,690,768 and 1,690,769 to Arthur W. Burwell, and completely neutralizing the free acids present in the resulting mixture by treating the latter, at an elevated temperature not substantially higher than 100° C., with a suitable organic amine such for example as diethanolamine,, triethanolamine, mixtures of these amines, morpholine, and the like.

As disclosed in the aforesaid Patents Nos. 1,690,768 and 1,690,769, the acids content of the oxidate is removed from the latter by saponification and subsequent acidification. Said acids are, in major portion, aliphatic carboxylic acids ranging in carbon chain length from C_7 to C_{18}, with a mean length of C_{14}. The acids content may, and usually does, include in minor proportion straight and branched chain aliphatic hydroxy carboxylic acids having substantially the same carbon chain length.

The neutralization reaction, being exothermic, must be so conducted that the temperature of the reaction mixture does not rise more than a few—e. g., two or three—degrees above 100° C. Control of the rate at which the organic amine is added to the hot mixture affords a suitable mode of control of temperature rise. Also, the presence in the mixture, to which the organic amine is being added, of a substantial but minor proportion of water aids

in maintaining the temperature at approximately 100° C. during the neutralization. The presence of water effects the further advantage that the reaction mixture—which, in the absence of water, is or may be viscous and which may tend to crystallize on standing at room temperature—thereby is given a desirable fluidity for ease of handling.

The resulting completely neutralized reaction mixture is soluble in water in practically all proportions, and is soluble also in methanol, ethanol, ethylene glycols and other commonly employed alcoholic anti-freeze agents. It can be added directly to the water of the system to be protected; or it may be dissolved in an alcoholic anti-freeze agent and added to the water circulating systems in the dissolved form. In industrial water circulating systems the additive of the present invention—whether added directly or as a solution in anti-freeze—normally is used in an amount to yield a concentration of from 0.1 to 1.0% by weight of the system to be protected.

SPECIFIC EXAMPLE

A typical preparation illustrative of the present invention is prepared as follows, all percentages being by weight:

a. Blend: 37.5% oxidized petroleum acids "Alox 425"=375 g.
37.5% ptBBA=375 g.
25.0% water=250 g.

b. Heat above mixture to 100° C. Slowly add, with stirring 348.0 g. diethanolamine at a rate such that the temperature does not exceed 103° C.

c. Stir until cool (not essential)

The final composition is, then, a reaction mixture of:

27.1% "Alox 425"
27.1% ptBBA
27.7% diethanolamine
18.1% water

By the expression "oxidized petroleum acids 'Alox 425'" as used above applicant means the mixture of aliphatic carboxylic acids, ranging in carbon chain length between C_7 and C_{18} and having a mean carbon chain length of C_{14}, derivable from an oxidate of 36–40° petroleum distillate.

The product, prepared as above described, is completely soluble in water and in commonly employed alcoholic anti-freeze agents. When dissolved in water in an amount to give a concentration of 0.1 to 0.1% (a 0.2% concentration being usual, it protects steel, or iron, from the normally corrosive action of water containing a normal amount of dissolved oxygen or air; moreover, it provides residual protection of the metal after the latter has been removed from contact with the inhibited water. It has no significantly detrimental effect on copper, brass, aluminum, lead or solder. It is effective at from room temperature to at least 160° F., and in water having a pH of from 6 to 10.

VARIABLES IN PREPARATION OF INHIBITOR

1. *Effect of components*

Inhibitors having limited performance characteristics may be prepared by neutralizing, with the organic amine, e. g., diethanolamine, either the ptBBA alone or the oxidized petroleum acids alone: however, neither of these products is as advantageous as that described in the above specific example. Thus, the amine-neutralized oxidized petroleum acids per se have only a limited solubility in glycols; and, the amine-neutralized ptBBA per se is a less effective corrosion inhibitor at elevated tempera-

tures, besides being expensive. The amine-neutralized, approximately 50–50, mixture of ptBBA and oxidized petroleum acids combines the advantages of full range of solubilities, performance at elevated as well as low temperatures, limited attack on lead, copper and brass, and desirably low cost. Where alcohol solubility is not required, the proportion of ptBBA to petroleum acids may be lowered, e. g., to 20–80 or to a ratio intermediate these extremes.

In lieu of the oxidized petroleum acids referred to above "red oil" (oleic acid) has been found to be an operable although not preferred component. A 50–50 blend of red oil and ptBBA when 100% neutralized with diethanolamine was found to be effective, in water, at concentrations above 0.5%. This suggests that other relatively high molecular weight organic acids may have at least limited effectiveness.

It does not appear that the ptBBA can be replaced with worthwhile results. Thus, benzoic acid substituted for the ptBBA yielded a greatly inferior product.

As was suggested above, either triethanolamine or morpholine can be substituted for diethanolamine with fair effectiveness.

2. *Effects of temperature*

The neutralization of the mixture of ptBBA and oxidized petroleum acids may be carried out at any temperature between about 25° and 100° C. If the temperature is permitted to rise appreciably above 100° C., amides rather than amine complexes or salts tend to be produced, which amides are insoluble or only poorly soluble in water. As to the observance of temperatures substantially below 100° C., it is to be noted that effective inhibitors have been prepared at 25° C., 30° C., 50° C., and 80° C. However, because the temperature rise, due to the exothermicity of the reaction, is difficultly controllable when the reaction is started, at lower temperature, it seems preferable to control the temperature during neutralization at about 100° C.

3. *Effect of degree of neutralization*

The degree of neutralization of the acids is critical in terms of meeting all of the requirements set forth for a good inhibitor.

The amount of amine to use for complete neutralization (called 100%) is as follows:

The ASTM acid number of the blend of oxidized petroleum acids, e. g., "Alox 425," and ptBBA is calculated as follows:

Acid No. ptBBA=315 (calculated from molecular weight or determined)

Acid No. "Alox 425"=150–180 (determined)

Therefore, a 50–50 blend has an acid number of

50% of 315=157.5
50% of 180= 90.0
Combined acid No.=247.5

When 1000 g. of this is neutralized directly, the calculation for diethanolamine is:

$$\frac{247.5}{56.1}=\frac{x}{105.1}$$

Mol. wt. KOH= 56.1
Mol. wt. DEA=105.1
x=464 g. DEA per 1000 g. mixed acids

Under (*b*) of the specific example, 348 g. diethanolamine is added. This is so because of the 1000 g. mixture only 750 g. were mixed acids, the remainder being water. Thus only 75% of the 464 g. calculated above is used, when water is added before the neutralization. The amine is calculated on the total weight of acids present.

The same general calculations hold for acid numbers calculated from any other combination of ptBBA and "Alox 425."

Tests have been performed in which as much as 13% excess of diethanolamine has been added. The resulting product is hazy and tends to separate a slight clear layer. The product containing an excess of amine is essentially as effective a corrosion inhibitor as the normal product, but is wasteful of amine and yields a physically unstable product.

Products have also been prepared in which only 75% of the theoretical amount of amine has been used. Such products are effective protective agents, but show mild corrosion of lead, copper and brass.

Thus, the optimum range of neutralization is 95–103%. Complete, or 100% neutralization is preferred. To repeat, a wide range of degress of neutralization is possible to yield products which protect steel. However, increased attack of non-ferrous metals occurs at less than 100% neutralization, and a loss of clarity of product occurs when an excess of amine is used.

TEST PROCEDURES AND RESULTS

1. *Immersion test.—Corrosion of steel*

This is a static test in which a 2" x 4" cold rolled steel panel, with a sand-blasted surface, is immersed in the test solution. The panel is examined daily for evidence of rusting, staining or other visible signs of corrosion.

The steel panels are tested in solutions of the inhibitor in tap water. In addition panels are tested at a range of solution pH values. Thus, to the solution of inhibitor in tap water, HCl is added to adjust the pH (4 or 6 in the tests). Other solutions are adjusted with concentrated NH_4OH to pH values of 8 and 10.

In addition to static tests at pH 4, 6, 7.6 (pH of inhibitor in tap water), 8, 10 at temperature (77° F.), a similar series is run, at 160° F. Thus protection tests were run at varying pH and at two temperatures.

2. *Rotating metals test*

This test was designed to determine the effect of moving water over various metals. It is hoped that this test will simulate actual conditions in a circulating system.

One inch squares of metal with holes drilled through their centers are weighed and then suspended on a brass rod. Each metal square is separated from the others by a ⅛" thick brass washer. The test metals are copper, brass, brass with a ½" diameter solder spot, lead, magnesium, steel and cast iron.

The brass rod and test metals are immersed in the test solution at 160° F. and rotated at 500 R. P. M. for two weeks. At the end of that period each metal is cleaned, examined for staining, etc., and then re-weighed. The weight loss per square centimeter of surface is calculated.

3. *Residual protection test*

This test is designed to determine whether steel will be protected after removal from contact with inhibited water.

A sand-blasted panel is immersed in the test solution, removed and allowed to drain for one hour. It is then stored in a static humidity cabinet which is essentially a desiccator body containing water in the bottom well. The static humidity cabinet is then stored in the laboratory so that the panels are exposed to ambient temperatures from 70–80° F. and 100% relative humidity. This is an accelerated test over exposure to the atmosphere in the laboratory.

In this cabinet, a blank, untreated panel will show definite signs of rust in 24 hours.

4. *Test results*

Selected test data are summarized in the following tables, in which Table I compares corrosion protection versus degree of neutralization, and Table II compares temperatures at which the product was prepared.

TABLE I

[Corrosion protection versus degree of neutralization.]

Code Designation	Composition			React Temp., ° C.	Percent of theory Neutralized	Percent additive in Water	Std. pH,* R. T.	Corrosion tests (Days to fail)					Residual Protection (Days)
	Percent ptBBA	Percent 425	Percent Water					Std. pH,* 160° F.	pH 4 @160° F.	pH 6, 160° F.	pH 8, 160° F.	pH 10, 160° F.	
OP-1-112	37.5	37.5	25.0	100	13 X'S	0.05	1						
						0.10	1	1	1	1	1	1	
						0.20	60+	14	1	1	26+	33+	
						0.30		30+					
						0.50							5
OP-1-117	37.5	37.5	25.0	100	100	0.05	1						
						0.10	1	1	1	1	1	1	
						0.20	60+	17	1	1	24+	30+	
						0.30		30+					
						0.5							8
						1.0							16
OP-1-111	37.5	37.5	25.0	100	75	0.05	1						
						0.10	60+	1	1	1	1	1	
						0.20	60+	2	1	3	24+	26+	
						0.3		17					
						0.5		31+					4

*Standard pH refers to the pH resulting from dissolving the inhibitor in tap water without addition of HCl or NH_4OH. The pH of such solutions is approximately 7.6.

TABLE II

[Preparation temperature versus corrosion protection.]

Code Designation	Percent of theory Neutralized	React Temp., ° C.	Percent in Water	Std. pH, R. T.	Corrosion tests (Days to Fail)				
					Std. pH, 160° F.	pH 4, 160° F.	pH 6, 160° F.	pH 8, 160° F.	pH 10, 160° F.
OP-1-117	100	100	0.05	1					
			0.10	1	1	1	1	1	1
			0.20	60+	17	1	1	24+	30+
			0.30	60+	30+				
OP-1-119A	100	80	0.05	1	2				
			0.10	60+	4				
			0.20	60+	35				
OP-1-119B	100	50	0.05	1					
			0.10	60+	4				
			0.20	60+	30+				

I claim:

1. A water-soluble corrosion inhibiting composition for use in aqueous liquid systems, in contact with ferrous and non-ferrous metals, consisting essentially of substantially completely neutral diethanolamine salts of about equal parts by weight of para tertiary butyl benzoic acid and a high molecular weight aliphatic carboxylic acids mixture derived from an oxidized petroleum fraction, said aliphatic carboxylic acids having carbon chain lengths between C_7 and C_{18} and a mean carbon chain length of C_{14}.

2. A liquid coolant composition for use in contact with ferrous and non-ferrous metals, characterized in that the same is a solution in aqueous medium of from about 0.1% to about 1.0% by weight of a water-soluble corrosion inhibiting composition consisting essentially of substantially completely neutral diethanolamine salts of about equal parts by weight of para tertiary butyl benzoic acid and a high molecular weight aliphatic carboxylic acids mixture derived from an oxidized petroleum fraction, said aliphatic carboxylic acids having carbon chain lengths between C_7 and C_{18} and a mean carbon chain length of C_{14}.

3. The composition defined in claim 1, in which the oxidized petroleum fraction is an oxidized 36–40° distillate of petroleum origin.

4. The coolant composition defined in claim 2 in which said medium is a solution of alcohol in water.

References Cited in the file of this patent

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