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CORROSION INHIBITING COMPOSITION

Ralph I. Gottshall, Willow Grove, Pa., and John G. Peters, Audubon, N. J., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

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This invention relates to an improved corrosion inhibiting composition, useful for inhibiting the corrosion of metals coming into contact with aqueous fluids.

Corrosion inhibitors are conventionally added to various aqueous systems, such as the cooling systems of internal combustion engines, water heating systems, refrigeration systems and hydraulic systems. Furthermore, when water is injected along with the fuel in internal combustion engines for increasing the horsepower of the engine, it is essential to add a corrosion inhibitor to the water in order to prevent rusting and corrosion of the metals contacted by the water.

We have found that alkali metal salts of diisoamyl orthophosphoric acid, particularly the sodium salt, are excellent water-soluble corrosion inhibitors for various aqueous systems. However, such salts have the disadvantage of not maintaining their corrosion inhibiting efficacy over extended periods of time. We have discovered that the loss in corrosion inhibiting potency of the alkali metal diisoamyl orthophosphates results from their reaction with the water-hardening ions and other heavy metal ions present in water to form insoluble precipitates. As is well known, water contains varying amounts of calcium and magnesium ions, measured in terms of hardness of the water, unless the water is softened by zeolitic or equivalent ion exchange treatment or is distilled. Furthermore, water may contain other heavy metal ions which may be initially present or which may form in the system, for example, in the cooling system of an internal combustion engine. All of these ions react unfavorably with the alkali metal diisoamyl orthophosphates to form insoluble precipitates, thereby destroying the activity of the corrosion inhibitor. The formation of precipitates is also disadvantageous because such precipitates tend to cause clogging of the passages of the various aqueous systems, particularly the water injection systems for internal combustion engines where the water is introduced into the engine through relatively small openings as a fine spray or mist.

In accordance with our invention, we have found that the difficulties inherent in the precipitation of alkali metal salts of diisoamyl orthophosphoric acid by the above described polyvalent metal ions can be obviated and the efficacy of such salts as corrosion inhibitors maintained over extended periods of time by employing with the alkali metal diisoamyl orthophosphates, ethylenediaminetetraacetic acid or a metal salt thereof. Aqueous systems containing the above mixture of compounds are maintained in a non-corrosive condition for substantial periods of time and the formation of precipitates is either completely prevented or substantially retarded.

Although we prefer to use the tetrasodium salt of ethylenediaminetetraacetic acid in our new composition, the free acid itself or any other metal salt of the acid can be used. For example, in place of the tetrasodium salt of ethylenediaminetetraacetic acid, the acid itself, the disodium calcium, disodium magnesium, monosodium ferric, dihydrogen ferrous, disodium copper, disodium

cobalt, disodium nickel, disodium zinc and disodium manganese salts can be employed. Obviously, the other alkali metals, e. g., potassium and lithium, can be substituted for the sodium in the above compounds. Similarly, instead of the sodium salt of diisoamyl orthophosphoric acid, the other alkali metal salts can be employed as the corrosion inhibitors.

The akali metal salt of diisoamyl orthophosphoric acid is employed in an amount sufficient to inhibit corrosion, and the ethylenediaminetetraacetic acid compound is employed in an amount sufficient to prevent the precipitation of water insoluble salts of the diisoamyl orthophosphoric acid. In general, satisfactory corrosion inhibition in aqueous systems is obtained without undue loss of the corrosion inhibitor by precipitation when the weight ratio of the alkali metal salt of diisoamyl orthophosphoric acid to the ethylenediaminetetraacetic acid compound is between about 4:1 and 24:1. In a preferred embodiment of our invention, we have employed the sodium salt of diisoamyl orthophosphoric acid and the tetrasodium salt of ethylenediaminetetraacetic acid in a weight ratio of 9:1. As will be understood by those skilled in the art, larger amounts of the ethylenediaminetetraacetic acid compound may be required when the water of the aqueous system is especially hard or where large amounts of other heavy metal ions may exist or may be formed during service.

We have found that the incorporation in water of from about 0.01 percent to about 1 percent total weight of the alkali metal diisoamyl orthophosphate and ethylenediaminetetraacetic acid compound imparts satisfactory corrosion inhibiting properties for most purposes. More can be added, if desired, without harmful effect. When our corrosion inhibiting composition is added to the water used for injection into internal combustion engines where corrosion conditions are more severe, it is desirable that not less than about 0.125 percent by weight of the combination of the two ingredients be used; 0.25 percent by weight is preferred. Excellent results have been obtained using 0.225 percent by weight of the sodium salt of diisoamyl orthophosphoric acid and 0.025 percent by weight of the tetrasodium salt of ethylenediaminetetraacetic acid.

For convenience in adding our corrosion inhibiting composition to various aqueous systems, we prefer first to dissolve the alkali metal diisoamyl orthophosphate and the ethylenediaminetetraacetic acid compound in water to form a concentrated solution. The concentrate is then added to the aqueous system to be protected in such amount as to give the desired concentration of the ingredients. We have used with good results a concentrate containing 25 percent total weight of the sodium salt of diisoamyl orthophosphoric acid and the tetrasodium salt of ethylenediaminetetraacetic acid in a weight ratio to each other of 9:1.

It will be understood that other materials can be added to aqueous systems in addition to the essential ingredients disclosed herein without departing from the spirit of the invention. Such materials include, for example, dyes, anti-leak agents, freezing point depressants, etc. The corrosion inhibiting composition of our invention is used with excellent results in aqueous systems containing freezing point depressant amounts of water-soluble alcohols, such as methanol, ethanol, propanol, ethylene glycol, propylene glycol, diethylene glycol and glycerol. For example, an excellent water injection liquid for use in aircraft engines contains, in addition to water and the corrosion inhibiting composition of our invention, a freezing point depressing amount of a lower alkanol of not more than two carbon atoms, i. e., methanol or ethanol.

We have demonstrated the efficacy of our corrosion inhibiting compositions as shown in the following il-

lustrative examples. The compositions were tested according to the provisions of Wright Field test ML TN-WCRT 52-161 for water for injection into aircraft engines. In accordance therewith, the activity of the corrosion inhibitor was tested in tap water and in tap water containing an equal weight of methanol as a 25 percent by weight of active ingredients of which 22.5 percent was the sodium salt of diisoamyl orthophosphoric acid and 2.5 percent was the tetrasodium salt of ethylenediaminetetraacetic acid.

The results of the tests are shown in the following tables.

TABLE I

Example No.	1	2	3	4
Make-up, percent by Wt.:				
Tap Water	100	99.75	99.50	99.00.
Corrosion Inhibitor (25% concentrate)		0.25	0.50	1.00.
Inspection:				
Appearance, 24 Hrs.	clear	clear	clear	clear.
Appearance, 30 Days	precipitate	precipitate	trace precipitate	Do.
Rust Test, ASTM D 665-52T—				
Procedure A: Steel Rod, Appearance	100% rust	5% rust	bright-passes	bright-passes.
Corrosion Test, ML TN-WCRT 52-161—				
Appearance:				
Low Carbon Steel After—				
1 Day	do	trace rust	bright	bright.
10 Days	do	10% rust	trace rust	Do.
20 Days	do	do	5% rust	Do.
30 Days	do	25% rust	10% rust	Do.
Copper [1] After—				
1 Day	dark stain	bright	bright	Do.
10 Days	do	do	do	Do.
20 Days	do	do	do	Do.
30 Days	do	light stain	do	Do.
Aluminum [1] After—				
1 Day	bright	bright	do	Do.
10 Days	medium stain	trace corrosion	do	Do.
20 Days	stain and pitting	5% corrosion	trace corrosion	Do.
30 Days	do	do	5% corrosion	Do.

[1] Each aluminum and copper panel was coupled with a stainless steel panel. The stainless steel panels were all bright at the end of 30 days.

TABLE II

Example No.	5	6	7	8
Make-up, Percent by Wt.:				
Methanol	50	49.875	49.75	49.50.
Tap Water	50	49.875	49.75	49.50.
Corrosion Inhibitor (25% concentrate)		0.250	0.50	1.00.
Inspection:				
Appearance, 24 Hrs.	clear	clear	clear	clear.
Appearance, 30 Days	precipitate	do	do	Do.
Rust Test, ASTM D 665-52T—				
Procedure A: Steel Rod, Appearance.	100% rust	bright-passes	bright-passes	bright-passes.
Corrosion Test, ML TN-WCRT 52-161—				
Appearance:				
Low Carbon Steel After—				
1 Day	50% rust	bright	bright	bright.
10 Days	100% rust	do	do	Do.
20 Days	do	do	do	Do.
30 Days	do	do	do	Do.
Copper [1] After—				
1 Day	bright	do	do	Do.
10 Days	do	do	do	Do.
20 Days	do	do	do	Do.
30 Days	do	do	do	Do.
Aluminum [1] After—				
1 Day	do	do	do	Do.
10 Days	5% corrosion	do	do	Do.
20 Days	10% corrosion	trace corrosion	trace corrosion	Do.
30 Days	50% corrosion	5% corrosion	5% corrosion	Do.

[1] Each aluminum and copper panel was coupled with a stainless steel panel. The stainless steel panels were all bright at the end of 30 days.

freezing point depressant. The test was run by placing into glass containers an amount of the particular liquid tested sufficient to cover two-thirds of a 1" x 5" metal test panel, and then sealing the container. The metal test panel was observed periodically for corrosion. The metals tested were 1020 low-carbon steel and couples of 18-8 stainless steel with copper and with 24 ST aluminum. To pass the test, no corrosion should appear after thirty days at room temperature on any portion of the panels immersed in the liquid.

In addition to the foregoing test the compositions were also tested for corrosion and rust inhibiting properties according to ASTM D 665-52 T, modified in that no oil was present. Furthermore, the appearance of the test liquids was observed after 24 hours and after 30 days for signs of precipitation.

The inhibitor composition tested was added to the water and the water-methanol solution in the form of a concentrate of a tap water solution containing a total of

As is apparent from the above examples, the corrosion-inhibiting compositions of our invention materially retarded or completely prevented (1) the harmful precipitation of the sodium diisoamyl orthophosphate and (2) the corrosion of a wide variety of metals.

The corrosion-inhibiting compositions of our invention are thus useful in any instance where metals are corroded by aqueous fluids. They are added with good effect to aqueous heating and cooling systems, hydraulic systems and to the aqueous layer which may be present in metal tanks used for the storage of petroleum products. They are particularly effective as additives to aqueous liquids used for injection into internal combustion engines.

We claim:

1. A composition of matter useful as a corrosion inhibitor in aqueous systems consisting essentially of an alkali metal salt of diisoamyl orthophosphoric acid and a compound selected from the class consisting of ethylenediaminetetraacetic acid and the alkali metal salts thereof

in a weight ratio in the range of about 4:1 to about 24:1.

2. A composition of matter useful as a corrosion inhibitor in aqueous systems consisting essentially of the sodium salt of diisoamyl orthophosphoric acid and the tetrasodium salt of ethylenediaminetetraacetic acid in a weight ratio of 9:1.

3. A composition of matter consisting essentially of an aqueous solution containing from about 0.01 to about 1 percent total weight of an alkali metal salt of diisoamyl orthophosphoric acid and a compound selected from the class consisting of ethylenediaminetetraacetic acid and the alkali metal salts thereof in a weight ratio in the range of about 4:1 to about 24:1, the water of said aqueous solution containing calcium and magnesium ions tending to form a precipitate with said alkali metal salt of diisoamyl orthophosphoric acid in the absence of said ethylenediaminetetraacetic acid compound.

4. The composition of claim 3, containing a water soluble alcohol in an amount sufficient to depress the freezing point.

5. The composition of claim 4, wherein the water soluble alcohol is a lower alkanol containing not more than two carbon atoms and the total weight of the alkali metal salt of diisoamyl orthophosphoric acid and the alkali metal salt of ethylenediaminetetraacetic acid is at least about 0.125 percent.

6. The composition of claim 5, wherein the lower alkanol is methanol and which contains 0.225 percent by weight of the sodium salt of diisoamyl orthophosphoric acid and 0.025 percent by weight of the tetrasodium salt of ethylenediaminetetraacetic acid.

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