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⑫ # EUROPEAN PATENT APPLICATION

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(54) **Method and compositions for controlling corrosion in low and high hardness water.**

(57) A method for inhibiting corrosion in aqueous systems comprising adding to the system being treated an effective amount of a composition comprising a molybdate ion source, a carboxylic acid/sulfonic acid polymer or salt thereof and polyphosphoric acid or an ester of polyphosphoric acid.

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METHOD AND COMPOSITION FOR CONTROLLING CORROSION IN LOW AND HIGH HARDNESS WATERS

BACKGROUND OF THE INVENTION

The instant invention relates to a method for inhibiting the corrosion of metallic surfaces in contact with aqueous systems and to compositions for use in such a method, particularly where the water of the aqueous system is oxygen-bearing. More particularly, the present invention relates to the use of compositions comprising a molybdate ion source, a water soluble polymer containing a sulphonic acid and a carboxylic acid moiety or salt thereof and a polyphosphoric acid or ester of polyphosphoric acid, to inhibit the corrosion of metallic surfaces of water-carrying systems.

The term "aqueous system" as used herein, is intended to describe any system which contains water in any physical state, including water which contains one or more dissolved or dispersed substances such as inorganic salts.

The term "metallic" as used herein, is intended to include ferrous and ferrous-containing materials.

The corrosion of a metallic surface in an aqueous system consists of the destruction of the ferrous metal by chemical or electrochemical reaction of the metal with its immediate environment.

Where the corrosion is electrochemical in nature, a transfer or exchange of electrons is necessary for the corrosion reaction to proceed. When corrosion of the metal takes place, at least two electrochemical processes occur, and must occur, simultaneously. There is an anodic oxidation reaction in which metal ions go into solution, leaving behind electrons; and at least one cathodic reduction reaction in which species in solution are reduced by consuming the electrons produced by the anodic reaction. With respect to ferrous or ferrous containing materials, when the water contains oxygen and is at a neutral pH or above, these processes may be illustrated by the following equations:

Anodic oxidation:

$Fe \rightarrow Fe^{+2} + 2e^-$

Cathodic reaction:

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

The two ionic reaction products, ferrous ion and hydroxyl ion, combine to form ferrous hydroxide, $Fe(OH)_2$, which is then oxidized to form ferric hydroxide, $Fe(OH)_3$ (rust). For ferrous or ferrous-containing materials as well as other metals in aqueous systems, the principle factors influencing the corrosion process are the characteristics of the water in the system, including but not limited to the rate of water flow, the temperature of the system and contact between dissimilar metals in the system. Variable characteristics of the water which impact upon its corrosiveness are its dissolved oxygen concentration, carbon dioxide content, pH, hardness and total dissolved ion concentration. Critical dissolved ions include, but are not limited to, chloride and sulfate ions.

The presence of dissolved oxygen in the water of an aqueous system is primarily the result of contact between the water and the atmosphere. The oxygen solubility in water is primarily temperature dependent, with increases in temperature lowering oxygen solubility.

Corrosion produced by the presence of oxygen in the water of an aqueous system can take place in the form of small pits or depressions and/or in the form of general metal loss. As a corrosive process continues, pits or depressions generally increase in depth. The corrosive attack is more severe when it causes pits or depressions, since the deeper penetration of the metal causes more rapid failure at these points.

Description of the Prior Art

A variety of compositions have been employed in the art for the purpose of inhibiting corrosion of surfaces in water-carrying systems where the cause of corrosion is dissolved oxygen. Polyphosphates such as sodium tripolyphosphate are widely used in the treatment of once-thru systems. See U.S. Patent No. 2,742,369. Silicates, for example sodium silicate, have also found acceptance.

U.S. Patent No. 3,483,133 discloses a corrosion inhibiting composition comprising amino-tris(methylene phosphonic) acid compounds in combination with water soluble zinc salts. U.S. Patent No. 3,762,873 discloses a corrosion inhibiting method using substituted succinimides. Canadian Patent No. 854,151 discloses a composition and method for inhibiting corrosion and/or the formation of calcium and magnesium containing scales wherein a combination of organophosphonic acid compounds and water soluble polymers having carboxyl or amide groups is employed.

U.S. Patent No. 3,810,834 discloses a method of treating the water of an aqueous system with hydrolyzed polymaleic anhydride having a molecular weight of 300 to 5,000 for the purpose of inhibiting scale formation, and U.S. Patent Nos. 3,897,209; 3,963,636; and 4,089,796 disclose the use of the same hydrolyzed polymaleic anhydride material in combination with a zinc salt for the purpose of inhibiting both corrosion and scale formation.

U.S. Patent 3,965,027 discloses certain amine adducts of polymaleic anhydride for use as scale and corrosion inhibitors.

U.S. Patent 4,176,059 discloses the use of compositions comprising molybdates, organic cationic or non-ionic surfactants, a water-soluble polyphosphate and a triazole for corrosion inhibition. U.S. Patent 4,217,216 discloses a corrosion inhibiting composition comprising a azole, a molybdate and at least one aminomethylene phosphonic or derivative thereof. U.S. Patent 4,246,030 discloses corrosion inhibiting compositions comprising a water-soluble carboxylic polymer and/or salt thereof and amino alkylene phosphonic acid or a derivative thereof, a water-soluble polymeric dispersing agent and other inhibitors such as molybdates, azoles, and various inorganic metal compounds.

U.S. Patent 4,675,158 discloses mercaptobenzothiazole/tolyltriazole corrosion inhibiting compositions, and U.S. Patent 4,668,474 discloses the use of mercaptobenzothiazole in combination with a ferrous ion source as corrosion control compositions.

U.S. Patent 4,640,793 discloses synergistic scale and corrosion inhibiting admixtures containing carboxylic acid/sulphonic acid polymers and molybdates. U.S. Patent 4,618,448 discloses the use of carboxylic/sulphonic/polyalkylene oxide polymers for use as scale and corrosion inhibitors.

However, none of the prior art references described above in any way suggest the unexpected results obtained with the novel compositions of the instant invention.

SUMMARY OF THE INVENTION

The method of the instant invention for inhibiting corrosion in an aqueous system comprises the step of treating an aqueous system with an effective amount of a composition comprising a molybdate ion source, a water-soluble polymer containing sulphonic acid and carboxylic acid moieties, or a salt thereof, and polyphosphoric acid or an ester of polyphosphoric acid.

The corrosion inhibiting compositions of this invention may optionally contain other known corrosion inhibitors, such as triazoles. The addition of a triazole, such as tolyltriazole, makes the instant compositions excellent copper and copper alloy corrosion inhibitors.

The instant invention also concerns the novel compositions used in the method of the present invention for inhibiting corrosion.

The instant compositions are especially effective over a pH range of from about 6.5 to about 8.2, preferably about 7.0 to about 8.0, and these compositions are effective in waters of various hardness. At pH's above about 8.2, use of the instant compositions generally becomes unfeasible due to calcium carbonate and/or calcium phosphate scaling.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a method for inhibiting corrosion in an aqueous system comprising adding to said system an effective amount of a corrosion inhibiting composition comprising:

(A) from about 1.0% to about 20%, as active MoO_4^{-2} , of a molybdate ion source;

(B) from about 2.0% to about 25%, as active polymer, of a water soluble polymer containing a carboxylic acid moiety and a sulphonic acid moiety, or a water soluble salt thereof;

(C) from about 5% to about 40%, on an active basis, of a component selected from the group consisting of polyphosphoric acid, esters of polyphosphoric acid and combinations thereof.

Any source of molybdate ions can be used. The preferred sources are water soluble molybdate salts, and the most preferred molybdate salts are magnesium molybdate, ammonium molybdate and alkali metal molybdates such as lithium molybdate, sodium molybdate and potassium molybdate.

The carboxylic/sulfonic polymer of the instant invention may be any water soluble polymer having a weight average molecular weight of less than 25,000, as determined by low angle light scattering, comprising:

(a) about 25 to about 95%, by weight, of an unsaturated mono-carboxylic compound selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof; and

(b) about 5 to 75%, by weight, of an unsaturated sulfonic compound selected from the group consisting of 2-acrylamido-2-methylpropylsulfonic acid, 2-methacrylamido-2-methylpropylsulfonic acid and combinations thereof.

Water soluble salts of these polymers may also be used. Examples of these polymers include TRC-233, available from Calgon Corporation, and Acrysol QR-1086, available from Rohm and Haas.

Also, other monomers may be used. For example, non-ionic monomers such as acrylamide, methacrylamide and acrylonitrile may be present in the polymers.

The preferred carboxylic/sulfonic polymers of the instant invention are prepared by polymerizing 50-95%, by weight, of the unsaturated mono-carboxylic acid and 5-50%, by weight, of the unsaturated sulfonic acid. The most preferred carboxylic acid is acrylic acid and the most preferred sulfonic acid is 2-acrylamido-2-methylpropylsulfonic acid.

These polymers may be prepared by mixing the monomers in the presence of a free radical initiator, as described in U.S. Pat. Nos. 3,928,196 and 4,640,793, which are hereby incorporated into this specification by reference. Theoretically, any free radical initiator may be used. Examples of preferred initiators include peroxides, azo initiators and redox systems. The polymerization may also be initiated photochemically. The preferred catalysts are sodium persulfate and sodium metabisulfite.

The preferred polyphosphoric acid of the instant invention is an equilibrium mixture of orthophosphoric acid, pyrophosphoric acid and higher linear polyphosphoric acid which is commercially available from FMC Corporation. Polyphosphoric acid esters may also be used as component (c). The preferred esters are esters of polyhydroxy alcohols, such as glycol esters and esters of pentaerythritol. Such esters are available from Calgon Corporation as Conductor 5712.

The instant compositions comprise about 1 to about 20%, on an active weight basis, of (A), about 2 to about 25% of (B) and about 5% to about 40% (C), with the balance being water. Preferably, (A) is about 3 to about 12%, (B) is about 8 to about 15% and (C) is about 8% to about 20% of the composition, all on an active weight basis.

An effective amount of the instant compositions should be used. As used herein, the term "effective amount" refers to that amount which inhibits or prevents the corrosion of metallic surfaces in contact with the aqueous system being treated. Preferably, the instant compositions should be added at a dosage of from about 0.1 to about 200 ppm, on an active weight basis, based on the total weight of the water in the aqueous system being treated. Components (A), (B) and (C) can be added separately or in combination, which ever is most convenient.

The instant compositions are effective in preventing mild steel corrosion, and also inhibit aluminum corrosion. These compositions are especially effective where excessive phosphate levels or zinc are undesirable.

The instant method is effective at pH's ranging from about 6.5 to about 8.2, preferably from about 7.0 to about 8.0. Also, the instant method is effective at various levels of hardness. For example, effective corrosion inhibition was maintained systems containing from about 50 to about 500 mg/L of total hardness, measured as $CaCO_3$. It is desirable to maintain at least about 2-5 mg/L, preferably 10 mg/L, calcium so that an effective inhibitor film is established.

Other known corrosion inhibitors, such as an azole, or an orthophosphate source, may be used in conjunction with the instant compositions.

EXAMPLES

The following examples further illustrate this invention. However, they are not intended to limit the scope of this invention in any way.

Corrosion studies were initiated by precleaning 1"x2" carbon steel coupons with xylene, Calclean, (an alkaline silicate phosphate cleaner available from Calgon Corporation), water and acetone, respectively in an ultrasonic bath, then drying them with house air. The coupons were weighed and then hung in eight liter test solutions which were adjusted to and maintained at pH 7.0 or 8.0, heated to and maintained at 50° C, circulated and aerated. Three test solutions of varying hardness were used.

Soft water was prepared by adding 1.40L of 4X Pittsburgh water to 6.60L of deionized water. 4X Pittsburgh water is a solution of 50.2 mg/L $MgCl_2$ $6H_2O$, 43.2 mg/L Na_2SO_4, 13.8 mg/L $NaHCO_3$ and 379.5 mg/L $CaSO_4$ $2H_2O$. Moderately hard water was prepared by adding 7.30L of 4X Pittsburgh water to 0.70 L of deionized water. Hard water was prepared by adding 43.26 grams of 50.0 g/L $CaCL_2$ $2H_2O$ to 8.0 L of 4X Pittsburgh water. The ions in the waters tested are summarized below.

ION	WATER QUALITIES (mg/L)		
	Soft	Moderate	Hard
CA^{2+}	15	80	160
Mg^{2+}	4	22	24
Na^+	13	67	73
HCO_3-	7	37	40
Cl	12	64	197
SO_4^{2-}	57	299	328
TH as $CaCO_3$	55	290	498

Inhibitor stock solutions were made up at an active concentration of 8.0 g/L and were added individually to the various test solutions before coupon immersion. The MoO_4^{-2} source in all tests was Na_2MoO_4 $2H_2O$. For tests at pH 8.0, 15 mLs of an 8.0 g/L active solution of an acrylic acid/acrylamidosulfonic acid/polyalkylene oxide inhibitor was added to each test solution, in addition to the inhibitor stock solution, to prevent Ca^{+2}/MoO_4^{-2} and/or Ca^{+2}/PO_4^{-3} precipitation. Various inhibitors were tested, including:

Calgon (Sodium hexametaphosphate);

HEDP (hydroxyethylidene diphosphonic acid);

Ortho-phosphate;

Conductor 5712 (3% pentaerythritol ester of polyphosphoric acid, 15% active polyphosphoric acid and 3% active orthophosphate (weight basis), commercially available from Calgon Corporation);

AA-AMPSA (a 60/40 acrylic acid/2-acrylamido-2-methylpropyl sulfonic acid copolymer, MW approximately 8200, commercially available from Calgon Corporation); and

AA-AMPSA/CONDUCTOR 5712/MoO_4^{-2} (a composition comprising 10% AA/AMPSA, 5% MoO_4^{-2} and 43% Conductor 5712, on an active weight basis.)

After seven days, coupons were removed and cleaned with inhibited acid, water and acetone, respectively in an ultrasonic bath. Inhibited acid contains 50.0 g $SnCl_2$ and 20.0 g Sb_2O_3 per liter of 1:1 HCl. Coupons were then dried using house air and reweighed. From the coupon weight losses, the corrosion rates in mpy were calculated.

The results are shown in Table 1.

TABLE 1

Component(s) Tested	Active Concentration (mg/L)	Mild Steel Corrosion Rates, mpy (as a function of pH and hardness)					
		pH 7.0			pH 8.0		
		Soft	Moderate	Hard	Soft	Moderate	Hard
Control*	---	76	70	89	77	56	55
MoO_4^{-2}*	15	70	66	74	68	73	37
MoO_4/HEDP*	15/15	5	29	32	3	7	23
MoO_4/Calgon*	15/15	5	21	12	2	1	1
MoO_4/Orthophosphate*	15/15	6	7	6	1	1	1
MoO_4/Calgon/AA-AMPSA*	5/15/10	5	3	2	0.4	0.3	0.5
MoO_4/Conductor 5712*	15/15	2	0.7	4	0.3	2	1
AA-AMPSA/Conductor 5712/MoO_4	10/9/5	3	0.8	0.7	0.3	0.2	0.4

*Comparison Example

Claims

1. A method for inhibiting corrosion in an aqueous system comprising adding to said system an effective amount of a corrosion inhibiting composition comprising:

(a) about 1% to about 20%, on an active MoO_4^{-2} weight basis, of a molydbate ion source;

(b) about 2.0% to about 25%, on an active weight basis; of a water soluble polymer having a molecular weight of less than about 25,000 containing about 25 to about 95% of a carboxylic acid moiety and about 5 to about 75% of a sulfonic acid moiety, on a weight basis, wherein said carboxylic acid moiety is selected from the group consisting of acrylic acid and methacrylic acid and wherein said sulfonic acid moiety is selected from the group consisting of 2-acrylamido-2-methylpropyl sulfonic acid and 2-methacrylamido-2-methylpropyl sulfonic, or a salt of such a polymer; and

(c) about 5% to about 40%, on an active basis, of a component selected from the group consisting of polyphosphoric acid, an ester of polyphosphoric acid and combinations thereof.

2. A composition comprising:

(a) about 1% to about 20%, on an active MoO_4^{-2} weight basis, of a molybdate ion source;

(b) about 2.0% to about 25%, on an active weight basis, of a water soluble polymer having a molecular weight of less than about 25,000 containing about 25 to about 95% of a carboxylic acid moiety and about 5 to about 75% of a sulfonic acid moiety, on a weight basis, wherein said carboxylic acid moiety is selected from the group consisting of acrylic acid and methacrylic acid and wherein said sulfonic acid is selected from the group consisting of 2-acrylamido-2-methylpropyl sulfonic acid and 2-methacrylamido-2-methylpropyl sulfonic, or a salt of such a polymer; and

(c) about 5% to about 40%, on an active basis, of a component selected from the group consisting of polyphosphoric acid, an ester of polyphosphoric acid, and combinations thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 20 0969

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,Y	US-A-4 176 059 (F. SUZUKI) * Claim 1; column 7, table 1 *	1,2	C 23 F 11/08
D,Y	EP-A-0 122 013 (CALGON CORP.) *Claims 1,4,7,8; page 24, table V; examples 93,94,98 * & US-A-4 640 793	1,2	
A	EP-A-0 210 590 (CALGON CORP.)		
A	US-A-4 512 552 (S. KATAYAMA)		
A	US-A-4 409 121 (E.J. LATOS)		
A	US-A-4 717 495 (R.D. HERCAMP)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 23 F 11/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31-07-1989	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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