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Description**BACKGROUND OF THE INVENTION**

U.S. Patent 3,885,914 discloses the use of zinc/polyacrylate compositions to control the corrosion of metals by oxygen bearing waters. However, such compositions are ineffective at high pH. The inventors have surprisingly discovered that the addition of a carboxylic/sulfonic acid polymer to the compositions of the '914 patent synergistically inhibits corrosion in alkaline systems.

U.S. Patent 4,640,793 discloses the use of zinc and carboxylic acid/sulfonic acid polymers to control the corrosion of steel in contact with aqueous systems.

U.S. Patent 4,663,053 discloses a method of inhibiting the corrosion of metallic parts in contact with aqueous systems using a water soluble zinc compound in combination with a water soluble sulfonated styrene/maleic anhydride copolymer and an organophosphorus acid compound or water soluble salt thereof.

The instant invention relates to the inhibition of corrosion in alkaline water systems in which oxygen bearing waters contact metallic surfaces.

More particularly, this invention relates to the use of compositions comprising a water-soluble, low molecular weight polycarboxylic acid, a water-soluble zinc salt and a water-soluble carboxylic acid/sulfonic acid polymer to inhibit the corrosion of metals in water systems which contain high pH, oxygen bearing waters.

Oxygen corrosion is a serious problem in any metal-containing water system. The corrosion of iron and steel is a primary concern because they are extensively used in water systems. Copper and its alloys, aluminum and its alloys, and galvanized steel are also used in water systems and are subject to corrosion. The inventors have discovered novel corrosion inhibiting compositions which inhibit oxygen corrosion in high pH water systems containing such metals.

SUMMARY OF THE INVENTION

The inventors have found that compositions comprising low molecular weight, water soluble polycarboxylates, water soluble zinc salts and water soluble carboxylic/sulfonic polymers are effective corrosion inhibitors at high pH. Suitable carboxylic polymers include low molecular weight acrylic acid polymers, low molecular weight methacrylic acid polymers and hydrolyzed polyacrylamides. These polymers may be homo-, co-, or ter- polymers of any of the aforementioned types and may have molecular weights ranging from about 500 to about 25,000.

Suitable water soluble zinc sources include, but are not limited to, salts such as zinc chloride, zinc acetate, zinc nitrate and zinc sulfate. Of course, the zinc ion may also be supplied by adding zinc to the system being treated.

The carboxylic/sulfonic polymer is an acrylic acid/2-acrylamido-2-methylpropyl sulfonic acid-type polymer having a molecular weight of less than about 25,000, wherein the weight ratio of the carboxylic moiety to the sulfonic moiety is from about 1:20 to about 20:1. The addition of the carboxylic/sulfonic acid polymer to the polyacrylic acid-type polymer and the zinc source enables control of carbon steel corrosion at alkaline pH's. Polyacrylate/zinc products alone are only effective to neutral pH. Thus, the addition of the carboxylic/sulfonic polymer extends the pH range to alkaline conditions while improving corrosion control. This polymer also stabilizes zinc above pH 7.5.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a method of inhibiting the corrosion of metallic surfaces in contact with an aqueous system comprising adding to said system an effective amount of a composition comprising:

(A) a water-soluble polycarboxylate, or salt thereof, having a molecular weight of less than about 25,000, preferably about 500 to about 10,000,

(B) a source of zinc ions; and

(C) a water soluble polymer having an intrinsic viscosity of 0.05 to 2.5 (dl/g) prepared from:

(i) an unsaturated carboxylic acid, or salt thereof; and

(ii) an unsaturated sulfonic acid, or salt thereof, having an (i):(ii) weight ratio of from 1:20 to 20:1, preferably 1:10 to 10:1 and most preferably 1:4 to 4:1; wherein the weight ratio of (A):(B) ranges from 1:1 to 5:1, and the weight ratio of (B):(C) ranges from 2:1 to 1:2. In more preferred compositions, the weight ratio of (A):(B):(C) is about 3.5-4.5:1:0.5-2. The most preferred compositions contain (A):(B):(C)

weight ratios of about 4:1:1.

The above described compositions are also claimed.

An effective amount of one of the instant compositions should be added to the aqueous system being treated. As used herein, the term "effective amount" is that amount of an instant composition necessary to inhibit the corrosion of metallic surfaces in contact with the alkaline aqueous system being treated. Generally, the effective amount will range from about 1 to about 1,000 ppm of the total composition, on an active basis, based on the total weight of the aqueous system being treated.

The term "aqueous system" as used herein, is meant to include any type of system containing water, including but not limited to, cooling water systems, boiler water systems, desalination systems, gas scrubber water systems, blast furnace water systems, reverse osmosis systems, evaporator water systems, paper manufacturing systems, mining systems and the like.

The essential aspect of this invention is that the instant compositions are effective at controlling corrosion in alkaline systems. Thus, the instant compositions are effective when the pH of the aqueous system being treated is greater than 7.0, preferably from about 7.0 to about 10.0, more preferably from about 7.0 to about 9.0, and most preferably about 7.0 to about 8.5.

Component (A) of the instant compositions may be any water-soluble polycarboxylate selected from the group consisting of polymers prepared from acrylic acid, methacrylic acid, vinyl acetic acid, allyl acetic acid, fumaric acid, maleic acid or anhydride, itaconic acid, α -halo acrylic acid and β -carboxyethylacrylate. Preferably, component A is selected from the group consisting of water soluble homopolymers of acrylic acid, water soluble homopolymers of methacrylic acid, water soluble copolymers of acrylic acid and methacrylic acid and water soluble hydrolyzed polyacrylamides, wherein the molecular weight is less than about 25,000, preferably about 1,000 to about 10,000, and salts of these polymers.

Any zinc ion source may be used as component B. For example, the zinc ion may be added by utilizing a water-soluble zinc salt, such as zinc chloride, zinc acetate, zinc nitrate or zinc sulfate. Also, the zinc ion may be added by supplying zinc to the aqueous system being treated.

For component C, any unsaturated carboxylic acid or salt thereof may be used as (i). Examples include, but are not limited to, acrylic acid, methacrylic acid, α -halo acrylic acid, maleic acid, itaconic acid, vinyl acetic acid, allyl acetic acid, fumaric acid, β -carboxyethyl acrylate, their salts and admixtures thereof. The most preferred carboxylic monomers are acrylic acid, methacrylic and their salts.

Any unsaturated sulfonic acid or salt thereof may be used as (ii) in component C. Examples include, but are not limited to, 2-acrylamido-2-methylpropyl sulfonic acid, 2-methacrylamido-2-methylpropyl sulfonic acid, styrene sulfonic acid, vinyl sulfonic acid, sulfo alkyl acrylate or methacrylate, allyl sulfonic acid, methallyl sulfonic acid, 3-methacrylamido-2-hydroxy propyl sulfonic acid acrylate, their salts and mixtures thereof. The most preferred sulfonic monomers are 2-acrylamido-2-methylpropylsulfonic acid, 2-methacrylamido-2-methylpropylsulfonic acid and their salts.

Mixtures of the various monomers may be used, and nonionic monomers (such as acrylamide, methacrylamide and acrylonitrile) may also be present in the polymers. However, copolymers are preferred.

These polymers are prepared using an (i):(ii) monomer weight ratio of about 1:20 to about 20:1, preferably about 1:10 to about 10:1, and most preferably about 1:4 to about 4:1.

Thus, the preferred polymers for component C are water soluble polymers having an intrinsic viscosity of 0.05 to 2.5 (dl/g), prepared from:

(i) an unsaturated carboxylic compound selected from the group consisting of acrylic acid, methacrylic acid, their salts and mixtures thereof; and

(ii) an unsaturated sulfonic compound selected from the group consisting of 2-acrylamido-2-methylpropyl sulfonic acid, 2-methacrylamido-2-methylpropylsulfonic acid, their salts and mixtures thereof.

Most preferably component C is 20 to 80%, by weight, acrylic acid or its salt and 80 to 20%, by weight, 2-acrylamido-2-methylpropylsulfonic acid, or its salt, wherein the intrinsic viscosity is 0.05 to 0.5 (dl/g).

An additional advantage of the instant compositions is that the component C polymer stabilizes the aqueous system being treated against zinc deposition, especially at pH's above 7.5.

The use of components A, B, and C is critical to the instant method in that compositions comprising these components effectively control corrosion of metallic surfaces in contact with aqueous systems having alkaline pH's.

Optionally, additional components, such as an azole compound, can be added. Preferred azole compounds are tolyltriazole and mercaptobenzotriazole.

The components of the instant invention may be added to the aqueous system being treated by any technique known in the art of water treatment. The components may be added as a mixture or separately. However, if added separately, the zinc source should be added last to prevent deposition of zinc salts in highly alkaline waters.

EP 0 311 192 B1

EXAMPLES

In the examples, an 8L cell equipped with a pH stat and heater was used to measure the corrosion of mild steel coupons. The water composition was as follows:

HCO_3^-	100 mg/l
Cl^-	18 mg/l
SO_4^{2-}	120 mg/l
Ca^{+2}	36 mg/l
Mg^{+2}	3.1 mg/l

Each test was run for one (1) week. After this time, the corrosion rate in mils per year (mpy) for a 1" X 2" mild steel coupon was determined. The results are shown in Table I.

TABLE I

Example Number	Inhibitor	Weight Ratio	Active Inhibitor Dosage (mg/L)	Mild Steel Corrosion Rates (mpy)	
				@ pH 6.5	@ pH 7.3
1*	PAA/Zn	15/3.8	23.5	5 (1.27×10^{-2} cm)	15 (3.81×10^{-2} cm)
2	PAA/Zn/AA-AMPS ¹	7.5/3/7.5	22.5	5 (1.27×10^{-2} cm)	3 (7.62×10^{-3} cm)
3	PAA/Zn/AA-AMPS	12/3/3	22.5	5 (1.27×10^{-2} cm)	2 (5.08×10^{-3} cm)
4*	None	-	-	-	89 (2.26×10^{-1} cm)

1. AMPS is a registered trademark of The Lubrizol Corporation.

* Comparison Example.

Claims

1. A method of inhibiting corrosion of metallic surfaces in contact with an aqueous system comprising adding to said system 1 to 1,000 ppm of a composition comprising:

(A) a water-soluble polycarboxylate, having a molecular weight of less than about 25,000; wherein the polycarboxylate is a homopolymer of acrylic acid, a homopolymer of methacrylic acid, a hydrolysed polyacrylamide, a copolymer of acrylic acid and methacrylic acid or a salt thereof;

(B) a source of zinc ions; and

(C) a water soluble polymer having an intrinsic viscosity of 0,05 to 2,5 (dl/g) prepared from:

(i) an unsaturated carboxylic acid which is acrylic acid, methacrylic acid or a salt, thereof; and

(ii) an unsaturated sulfonic acid selected from 2-acrylamido-2-methyl propyl sulfonic acid, 2-methylacrylamido-2-methyl propyl sulfonic acid or salts thereof, having an (i):(ii) weight ratio of from 1:20 to 20:1; wherein said aqueous system has an alkaline pH, wherein the weight ratio of

(A):(B) is from 1:1 to 5:1, and wherein the weight ratio of (B):(C) is from 2:1 to 1:2.

2. The method of Claim 1, wherein (i):(ii) is about 1:10 to about 10:1.

3. The method of Claim 1, wherein said alkaline pH is from about 7.0 to about 10.0.

4. The method of Claim 3, wherein said alkaline pH is from about 7.0 to about 9.0.

5. The method of Claim 4, wherein the weight ratio of (A):(B):(C) is about 4:1:1.

Revendications

1. Procédé d'inhibition de la corrosion des surfaces métalliques en contact avec un système aqueux, qui consiste à ajouter audit système de 1 à 1000 ppm d'une composition comprenant :

(A) un polycarboxylate hydrosoluble d'une masse moléculaire inférieure à 25.000 environ, ledit polycarboxylate étant un homopolymère d'acide acrylique, un homopolymère d'acide méthacrylique, un polyacrylamide hydrolysé, un copolymère acide acrylique/acide méthacrylique ou un sel de ceux-ci ;

(B) une source d'ion zinc ; et

(C) un polymère hydrosoluble ayant une viscosité intrinsèque de 0,05 à 2,5 dl/g, préparé à partir de:

(i) un acide carboxylique insaturé qui est l'acide acrylique, l'acide méthacrylique ou un sel de l'un de ceux-ci ; et

(ii) un acide sulfonique insaturé qui est l'acide 2-acrylamido-2-méthyl-propylsulfonique, l'acide 2-méthyl-acrylamido-2-méthylpropylsulfonique ou un sel de ceux-ci, le rapport pondéral (i):(ii) étant compris entre 1:20 et 20:1, ledit système aqueux ayant un pH alcalin, le rapport pondéral (A):(B) étant compris entre 1:1 et 5:1, et le rapport pondéral (B):(C) étant compris entre 2:1 et 1:2.

2. Procédé selon la revendication 1, dans lequel le rapport (i):(ii) est compris entre environ 1:10 et 10:1.

3. Procédé selon la revendication 1, dans lequel ledit pH alcalin est d'environ 7,0 à 10,0.

4. Procédé selon la revendication 3, dans lequel ledit pH alcalin est d'environ 7,0 à 9,0.

5. Procédé selon la revendication 4, dans lequel le rapport pondéral (A):(B):(C) est d'environ 4:1:1.

Patentansprüche

1. Verfahren zur Inhibierung der Korrosion von Metallflächen im Kontakt mit einem wässrigen System, bei dem man dem System 1 bis 1000 ppm einer Zusammensetzung zusetzt, enthaltend:

(A) ein wasserlösliches Polycarboxylat von einem Molekulargewicht von Weniger als etwa 25000; wobei das Polycarboxylat ein Homopolymer von Acrylsäure, ein Homopolymer von Methacrylsäure, ein hydrolysiertes Polyacrylamid, ein Copolymer von Acrylsäure und Methacrylsäure oder ein Salz davon ist;

(B) eine Quelle von Zinkionen; und

(C) ein wasserlösliches Polymer von einer Intrinsic-Viskosität von 0,05 bis 2,5 (dl/g) ist, hergestellt aus:

(i) einer ungestättigten Carbonsäure, die Acrylsäure, Methacrylsäure oder ein Salz davon ist; und

(ii) einer ungesättigten Sulfonsäure, hergestellt aus 2-Acrylamido-2-methylpropylsulfonsäure, 2-Methylacrylamido-2-methylpropylsulfonsäure oder Salzen davon, von einem (i):(ii)-Gewichtsver-

EP 0 311 192 B1

hältnis von 1:20 bis 2=:1; worin das wässrige System ein alkalisches pH hat und worin das Gewichtsverhältnis von (A):(B) 1:1 bis 5:1 und das Gewichtsverhältnis von (B):(C) 2:1 bis 1:2 beträgt.

- 5 **2.** Verfahren nach Anspruch 1, worin (i):(ii) etwa 1:10 bis etwa 10:1 ist.
- 3.** Verfahren nach Anspruch 1, worin das alkalische pH etwa 7,0 bis etwa 10,0 beträgt.
- 4.** Verfahren nach Anspruch 3, worin das alkalische pH etwa 7,0 bis etwa 9,0 beträgt.
- 10 **5.** Verfahren nach Anspruch 4, worin das Gewichtsverhältnis von (A):(B):(C) etwa 4:1:1 ist.

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