(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 364 030 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89202510.7

(51) Int. Cl.⁵: C23F 11/167

(22) Date of filing: 05.10.89

(30) Priority: 11.10.88 US 255287

(43) Date of publication of application: 18.04.90 Bulletin 90/16

(84) Designated Contracting States: AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: CALGON CORPORATION
Route 60-Campbell's Run Road
Robinson Township Pennsylvania 15205(US)

(72) Inventor: Boffardi, Bennett
5723 Glen Hill Drive
Bethel Park, PA 15102(US)
Inventor: Schaefers, Thomas H.
109 Delafield
Pittsburgh, PA 15215(US)

(74) Representative: Hesketh, Alan, Dr. et al
European Patent Department Merck & Co., Inc. Terlings Park Eastwick Road
Harlow Essex, CM20 2QR(GB)

(54) Synergistic compositions and method for inhibiting carbon steel corrosion in aqueous systems.

(57) This invention relates to synergistic compositions and a method for inhibiting carbon steel corrosion in aqueous systems which comprises treating said aqueous systems with compositions comprising a phosphorus containing compound and borate and optionally, a copolymer, acrylic acid/2-acrylamide-2-methyl propyl sulfonic acid (AA/AMPS).

EP 0 364 030 A1

SYNERGISTIC COMPOSITIONS AND METHOD FOR INHIBITING CARBON STEEL CORROSION IN AQUEOUS SYSTEMS

BACKGROUND OF THE INVENTION

This invention relates to synergistic compositions and a method for inhibiting carbon steel corrosion in aqueous systems due to dissolved oxygen which comprises adding to said aqueous systems an effective amount of said compositions comprising a phosphorus-containing compound and borate and optionally, a copolymer, acrylic acid/2-acrylamide-2-methyl propyl sulfonic acid (hereinafter referred to as AA/AMPS).

The action of dissolved gases such as oxygen and carbon dioxide are the main factors that lead to corrosion of aqueous systems. Therefore, in order to understand the role of dissolved gases in corrosion, one must understand the electrochemical nature of corrosion. Under most conditions, there is a tendency for iron to dissolve in water, and two electrons are released for each iron atom that dissolves.

The presence of oxygen in aqueous systems causes corrosion to occur. Other oxygen molecules combine with metal ions to form insoluble metal oxide compounds. With respect to oxygen, the severity of attack will depend on the concentration of dissolved oxygen in the water, pH and temperature. As water temperature increases, corrosion in feed lines, heat exchanges and return lines made of iron and steel increases.

The literature discloses numerous references for corrosion protection of aqueous systems such as polyphosphates, phosphates and zinc. For example:

1) U.S. Patent No. 4,640,793 discloses an admixture, and its use in inhibiting scale and corrosion in aqueous systems, comprising:

(a) a water-soluble polymer having a weight average molecular weight of less than 25,000, as determined by low angle laser light scattering, comprising an unsaturated carboxylic acid and an unsaturated sulfonic acid, or their salts, having a ratio of 1:20 to 20:1, and

(b) at least one compound selected from the group consisting of water-soluble polycarboxylates, phosphonates, phosphates, polyphosphates, metal salts and sulfonates.

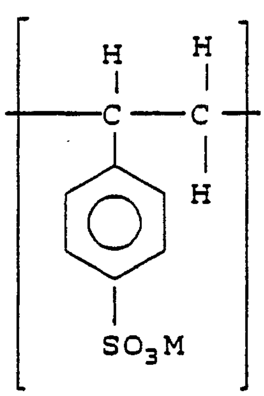
Also, this reference discloses a method of inhibiting the formation of insoluble alluvial, metal oxide and metal hydroxide deposits in an aqueous system, comprising adding to the system at least 0.1 mg/l of a water-soluble polymer having a weight average molecular weight of less than 25,000, as determined by low angle laser light scattering, comprising an unsaturated carboxylic acid and an unsaturated sulfonic acid, or their salts, having a ratio of 1:20 to 20:1 and a phosphonate.

2) U.S. Patent No. 4,401,587 discloses a method of inhibiting corrosion of low carbon steel in an aqueous system comprising treating said system with 1.0 to 300 parts per million by weight of the total aqueous content of said system, of a composition comprising aminomethylphosphonic acid compounds and polymaleic anhydride or amine adducts thereof in a weight ratio of from 10:1 to 1:10.

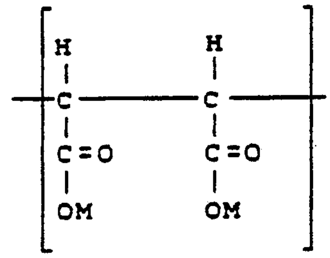
3) U.S. Patent No. 4,663,053 discloses a method of treating cooling water systems of the type prone to scale formation on, and corrosion of, metallic parts in contact with said cooling water system, said method comprising the steps of adding to said cooling water system

(1) from about 0.1 to about 15 parts per million of a water soluble zinc compound adapted to liberate Zn^{2+} ions in solution;

(2) from about 0.5 to about 50 parts per million of a water soluble sulfonated styrene/maleic anhydride copolymer, said copolymer comprising sulfonated styrene moieties of the formula



and moieties derived from maleic anhydride of the formula



wherein M is H or a water soluble cation, and

(3) from about 0.2 to about 50 parts per million of an organophosphorus acid compound or water soluble salt thereof, all (1) (2) and (3) being based on 1 million parts of said cooling water system.

SUMMARY OF THE INVENTION

This invention relates to synergistic compositions and method of inhibiting carbon steel corrosion of aqueous systems wherein said compositions comprise a phosphorus-containing compound and borate and optionally, a copolymer, AA/AMPS. Therefore, in accordance with this invention, it is found that when the compositions described herein are added to aqueous systems, the components of said compositions are effective in inhibiting carbon steel corrosion of said aqueous systems.

A further object of the invention to describe a process wherein components of the compositions described herein produce a synergistic product that effectively inhibits corrosion of in aqueous systems.

A still further object of the invention is to describe concentration levels wherein the phosphorus containing compound of the composition is substantially reduced such that the potential for calcium phosphate precipitation is minimized.

Another object of the invention is to describe synergistic compositions that substantially subdue the pitting propensity of AA/AMPS.

Further objects will become apparent from the description which follows.

DESCRIPTION OF THE INVENTION

The synergistic compositions of the present invention are effective in inhibiting corrosion of carbon steel surfaces of aqueous system when added to said aqueous systems in amounts sufficient to maintain a concentration level ranging between 0.1 to 300 parts per million (PPM) by weight of the total aqueous content of said aqueous system. Preferably, the concentration level ranges from 1.0 to 50 ppm.

Also, the compositions disclosed herein are improved in their corrosion inhibiting activity by the addition of zinc (calculated as Zn^{++}), which acts as an synergist in aqueous systems. The ratio of the combined phosphorus-containing compound and borate and optionally, AA/AMPS are 1:1 to 10:1 and optionally 1:1:1 to 10:1:1, respectively.

The zinc ion component of the corrosion inhibiting compositions of the present invention is provided by employing zinc in any convenient water soluble form, such as chloride or the sulfate salt.

The present invention contemplates inclusion with the corrosion inhibiting compositions thereof other known additives for the treatment of aqueous systems. For example, a copper corrosion inhibitor selected from the group consisting of 1,2,3-triazoles, thiols of thiazoles, oxazoles, and imidazoles as described in U.S. Pat. Nos. 2,941,953 and 2,742,369, respectively, may be employed in an amount of up to about 10% by weight.

The compositions of the present invention will actively inhibit corrosion so long as they are effectively present in the aqueous system being treated. This effective presence is dependent on the lack of any degradation or decomposition of the inhibitor compositions occassioned by pH, temperature, pressure, or other conditions. Thus, it is anticipated that the inhibitor compositions of the invention will be effective generally in a pH range of from about 7 to 9, preferably at pH 8.

The corrosion inhibiting compositions of the present invention are synergistic in their activity, i.e., they possess a degree of corrosion inhibiting activity which is greater than the corrosion inhibiting activity of either component alone.

The synergistic compositons disclosed herein are prepared via conventional methods. The manner in which the components of said compositions are added is not critical, i.e., either of the two components or optionally three compounds can be added first and formulated via conventional procedure.

Some studies that further emphasize the concepts of the invention disclosed herein are shown below:

Corrosion rate data is shown in Table II on Page 9.

The coupon immersion test consisted of a cylindrical battery jar with a capacity of 8 liters. A Haake constant temperature immersion circulator (Model E-52) was used to control the solution temperature and agitate the controlled bath. The unit contained a 1000 watt fully adjustable stainless steel heater which permitted temperature control to ±0.01 °C., and a 10 liter per minute pump with a built in pressure nozzle aGitator that ensured high temperature uniformity in the bath. A mercury contact thermoregulator was used as the temperature sensing element.

The pH of the solution was controlled with Kruger and Eckels Model 440 pH Controller. This unit was capable of turning power on and off to a Dias minipump whenever the pH of the corrosive liquid environment fell below the set point. The peristaltic Dias pump, with a pumping capacity of 20 ml. per hour, maintained the solution pH with the addition of sulfuric acid. Standard glass and sensing elements. The oath was continuously aerated saturated calomel electrodes were used as the through a medium porosity plastic gas dispersion tube to ensure air saturation.

Two SAE-1010 steel coupons, each having a surface area of 4.2 square inches, were suspended by a glass hook. The solution volume to metal surface area ratio for the test was approximately 1000:1.

The composition of the synthetic water used in the test is shown in TABLE 1 below indicating content per liter of distilled water:

TABLE I

Ion:	Ca^{++}	Mg^{++}	HCO_3^-	Cl^-	SO_4^-
Mg./l.:	88	24	40	70	328

The inhibitory properties of B_2O_3/PO_4 pair was investigated both in the presence and absence of AA/AMPS. At pH 7, in water with chemical composition as represented by Table II below, at 50 °C, there is approximately a 50 percent reduction in corrosion. However, at pH 8, an 88 percent reduction is achieved. The B_2O_3/PO_4 pair is synergistic at this pH. Corrosion rate data is shown in Table II below.

TABLE II

EXPLORATORY			
System	Concentration mg/l	pH	Corrosion Rate (mpy)
Control	--	7.0	52
B_2O_3	10	7.0	35
B_2O_3/PO_4	5/5	7.0	23
B_2O_3/PO_4/AA-AMPS	5/5/5	7.0	21

The inhibitory properties of B_2O_3/PO_4 pair was investigated in the same water as Table 1 at 50 °C and pH 8 in the presence of AA/AMPS and zinc. The B_2O_3/PO_4 pair is synergistic at this pH. The presence of AA/AMPS improves the corrosion rate while zinc acts as an antagonist. The data is shown in Table III below.

TABLE III

System	Concentration, mg/L	PH	Corrosion Rate, mpy
Control	---	8.0	45
B_2O_3	10	8.0	50
B_2O_3/PO_4	5/5	8.0	4
B_2O_3/PO_4/AA-AMPS	5/5/5	8.0	2
B_2O_3/PO_4/AA-AMPS	5/5/5/5	8.0	13

Any phosphorus containing compound may be used in this invention. Examples include polyphosphates, phosphonates, and phosphates.

Examples of water-soluble phosphonates include 2-phosphono-1,2,4-tricarboxybutane, aminotri-(methylene phosphonic acid), hydroxyethylidene diphosphonic acid, phosphonosuccinic acid, benzenephosphonic acid, 2-aminoethyl-phosphonic acid, polyaminophosphonates and the like. Additional phosphonates are identified in U.S. Patent 3,837,803, and are hereby incorporated herein by reference. The preferred phosphonates are aminotri(methylene phosphonic acid) and hydroxyethylidene diphosphonic acid.

Any water-soluble phosphate may be used. Examples include orthophosphate; condensed phosphates, such as sodium hexametaphosphate; phosphate ester; organophosphate esters, such as the loweralkyl mono-, di- and trialkyl phosphates. The alkyl group is selected from C_1-C_4 and may be branched or unbranched. The alkyl group may be substituted with hydroxy, amino, halide, sulfate or sulfonate, alone or in combination; and molecularly dehydrated phospahates. The most preferred phosphorous-containing compound is orthophosphate.

Any water-soluble borate compound may be used in the present invention. Examples include tetraborate pentaboate metaborate, boric acid and the like.

Optionally, Zinc may be added to the composition at ratios ranging from 10:1 to 1:10, thereby enhancing corrosion Inhibitant Values.

The synergistic compositions disclosed are used at a minumum dosage of 0.1 ppm in inhibiting corrosion, preferably in a dosage of 1 to 500 ppm, and most preferably 1 to 200 ppm.

Claims

1. A synergistic composition for inhibiting carbon steel corrosion in an aqueous system comprising an effective corrosion inhibiting amount of a phosphorus-containing compound and borate compound.

2. The composition of Claim 1, wherein the concentration of the corrosion inhibiting compounds is from 0.1 to 500 ppm by weight of said aqueous system. said phosphorus-containing compound is selected from the group consisting of polyphosphates, phosphonates and phosphates and said borate compound is selected from the group consisting of borate, boric acid, metaborate, tetraborate and pentaborate combined at ratios ranging from 1:1 to 10:1, respectively.

3. The composition of Claim 2, wherein said concentration is from 1.0 to 50 ppm, said phosphorus-containing compound is a phosphate selected from the group consisting of orthophosphate and sodium hexametaphosphate and said borate compound is borate, boric acid or tetraborate combined at a 1:1 ratio.

4. The composition of Claim 2, wherein said compounds are combined at a 10:1 ratio.

5. The composition of Claim Z, further comprising acrylic acid/2-acrylamide-2-methylpropyl sulfonic acid.

6. The composition of Claim 5, further comprising zinc.

7. The composition of Claim 5, wherein said phosphorus-containing compound is selected from the group polyphosphates, phosphonates and phosphates and said borate compound is selected from the group consisting of borate, boric acid, metaborate tetraborate and pentaborate combined at ratios ranging form 1:1:1 to 10:1:1, respectively.

8. The compositon of Claim 7, wherein said phosphorus containing compound is a phosphate selected from the group consisting of orthophosphate and sodium hexametaphosphate and said borate compound is borate, boric acid or tetraborate combined at a 1:1:1 ratio.

9. The compostion of Claim 8, wherein said phosphorus-containing compound is orthophosphate and said borate compound is borate.

10. A method of inhibiting carbon steel corrosion in aqueous systems which comprises adding to said aqueous systems a synergistic composition comprising a phosphorus-containing compound and a borate compound.

11. The method of Claim 10, wherein the concentration of the corrosion inhibiting compounds of said composition is from 0.1 to 500 ppm by weight

12. The method of Claim 11, further comprising a copolymers.

13. The method of Claim 12, wherein said copolymer is acrylic acid/2-acrylamide-2-methylpropyl sulfonic acid combined of ratios ranging from 1:1:1 to 10:1:1, respectively.

14. The method of Claim 13, wherein said phosphate-containing compound is orthophosphate and said borate compound is borate combined at a 1:1:1 ratio.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 89202510.7

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	WO - A1 - 82/00 665 (HENKEL KOMMANDITGESELL-SCHAFT AUF AKTIEN) * Page 2, lines 6-13; claims 10,18 *	1,10	C 23 F 11/167
A		2	
X	GB - A - 1 386 718 (BETZ LABORATORIES, INC.) * Claims 1,22; page 8, line 38 - page 9, line 3 *	1,10	
P,X	EP - A1 - 0 307 309 (ETAT-FRANCAIS) * Abstract *	1,2,10	
A	US - A - 4 717 542 (MITCHELL) * Claims 1-9 *	1,2,4, 5,10-13	
A	EP - A1 - 0 225 051 (W.R.GRACE & CO.) * Abstract; page 2, lines 23-37; page 3, lines 10-35 *	1,2,5, 6	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 23 F C 02 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	03-01-1990	HAUSWIRTH

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO Form 1503 03.82