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(54) Corrosion inhibition of metals in water systems using organic phosphorous derivatives containing carboxyl groups.

(57) The inhibition of metal corrosion in water systems by an organic phosphonocarboxylic and/or phosphinocarboxylic acid compound is improved by using in combination therewith a manganese compound capable of providing a manganese ion. The manganese may be in the chelated form with the phosphono-or phosphinocarboxylic compound.

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CORROSION INHIBITION OF METALS IN WATER SYSTEMS USING ORGANIC PHOSPHOROUS DERIVATIVES CONTAINING CARBOXYL GROUPS

One of the main problems which occurs in hydraulic engineering is the corrosion of metals in both treated and untreated cooling water systems. The corrosion of metals such as steel, aluminum, brass and copper which are commonly found in water systems, is primarily due to dissolved oxygen and carbon dioxide. Materials which remove oxygen such as sodium sulfite or hydrazine are not economical and are technically inadequate. Hence Zn^{++}, chromates, molybdates, polyphosphates, orthophosphate, and organophosphonates are added to cooling water to form protective films on metal surfaces. Chromates are very efficient corrosion inhibitors. However, they are often environmentally undesirable due to the well known toxic effects. Zn^{++} has similar environmental problems and it also has low solubility products with ortho phosphates, hydroxides and carbonates which can form sludge and deposits responsible for promoting corrosion.

Polyphosphates are not as efficient as chromates and they are unstable in a cooling water environment, decomposing by hydrolysis to ortho and pyrophosphates, often causing sludge and deposits. Orthophosphates are not as efficient as chromates and if they are not controlled properly they can also form sludge and deposits. Although organophosphonates provide some corrosion protection, they are not nearly as efficient as chromates.

Organic phosphonocarboxylic acids or phosphinocarboxylic acids have been disclosed as useful to prevent calcium and other scale deposits and to prevent corrosion of iron in circulating water systems. Such compounds are disclosed in U.S. patents 3,933,427, 4,042,324 and 4,159,946. Examples of compounds disclosed in U.S. 3,933,427 are phosphonosuccinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid; in U.S. 4,042,324 are disclosed carboxymethane-phosphonic acid and 1-carboxypropane-2-phosphonic acid; in U.S. 4,052,160 are disclosed compounds such as 2-phosphonoacetic, 2-phosphonopropionic, 2,3-diphosphonopropionic, 2,4-diphosphonobutyric and 2-phosphonomethylacrylic acids; and in U.S. 4,159,946 are disclosed the telomeric products of the reaction of acrylic acid and hypophosphorous acid and the products of acrylic acid and butyl hypophosphite; and in U.S. 4,606,890 are disclosed 2-hydroxyphosphonoacetic acid employed in combination with certain metal ions, e.g. zinc, cadmium, manganous, ferrous and chromium which are said to be synergistic in preventing corrosion. The compounds disclosed in U.S. 3,933,427 are said to provide improved corrosion inhibition when zinc salts, e.g. zinc sulfate or phosphate, are added to the aqueous system containing the phosphonocarboxylic or phosphinocarboxylic compound.

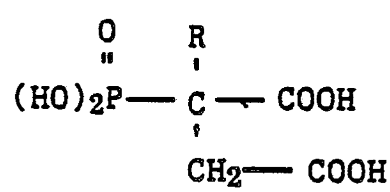
U.S. patent 4,640,818 discloses the combination of a manganese compound with an aminophosphonic acid derivative as an inhibitor of metal corrosion in water systems.

It has now been found that the combination of manganese compounds with such phosphonocarboxylic or phosphinocarboxylic compounds, will provide improved corrosion protection of metals in aqueous systems.

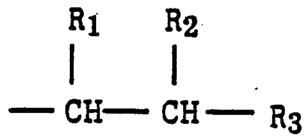
The invention is an improved process for inhibiting corrosion of metals in water conducting systems. It comprises employing a composition useful for inhibiting metal corrosion in water conducting systems which comprises;

(A) a phosphorous-containing carboxylic acid compound, or a salt thereof, wherein said compound corresponds to at least one of

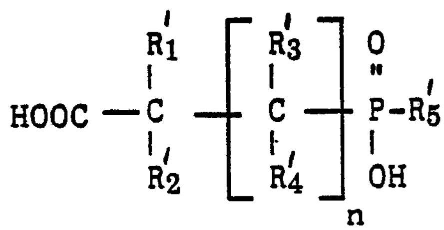
(1)



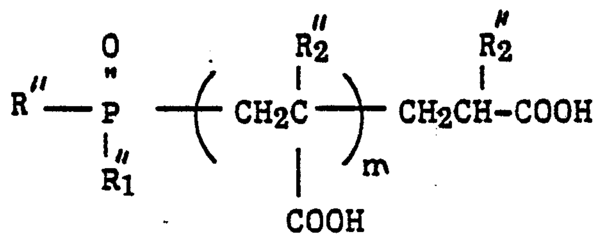
wherein R is a hydrogen atom, an alkyl having 1 to 4 carbon atoms, alkenyl or alkynyl group, each having 2 to 4 carbon atoms, an aryl, cycloalkyl or aralkyl group or the group



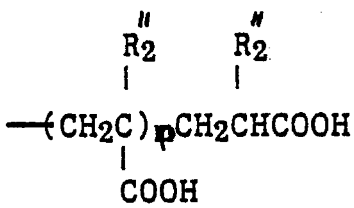
in which R_1 is hydrogen, an alkyl group having 1 to 4 carbon atoms or a carboxyl group; R_2 is hydrogen or methyl; and R_3 is a carboxyl group; or

(2) 

wherein each of the substituents R_1', R_2', R_3' and R_4' is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; R_5' is hydrogen, an OH-group or an alkyl group having from 1 to 3 carbon atoms; and n is 0 or 1; or

(3) 

wherein R_2'' is hydrogen or a methyl or ethyl group; R'' is hydrogen, a straight or branched alkyl group having from 1 to 18 carbon atoms, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group, an aralkyl group, a moiety having the formula



wherein R_2'' has its previous significance, and the sum m + p is a positive integer of no more than 100, or a residue -OX wherein X is hydrogen or an alkyl group having from 1 to 4 carbon atoms; and R_1'' is a residue -OX wherein X has its previous significance;

(b) together with a manganese compound capable of providing a manganese ion.

Surprisingly, it has now been found that synergistic combinations, comprising manganese compounds together with organic phosphonocarboxylic or phosphinocarboxylic acid derivatives or their salts, provide metal corrosion protection comparable to chromates. The various organic phosphonocarboxylic or phosphinocarboxylic acid derivatives tested alone in water do not provide this level of protection. The corrosion protection of metals provided by an organic phosphonocarboxylic or phosphinocarboxylic acid compound, however, is enhanced by the addition of a manganese compound which provides a source of manganese ion.

The organic phosphonocarboxylic or phosphinocarboxylic acid derivatives useful in the practice of the present invention as shown by the above formulae are known compounds.

As used herein the terms "alkenyl" and "alkynyl" refer to both straight and branched-chain hydrocarbon moieties having either their respective double or triple bond(s) and from 2 to 4 carbon atoms.

The term "alkyl" refers to both straight and branched-chain hydrocarbon having from 1 to 18 carbon atoms.

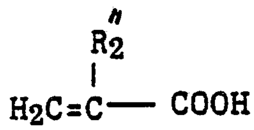
The term "cycloalkyl" refers to a saturated hydrocarbon having a cyclic structure and from to 5 to 12 carbon atoms.

The term "aryl" refers to an aromatic hydrocarbon having from 6 to 12 carbon atoms. The term "aralkyl" is an C_1-C_4 alkyl substituted aryl.

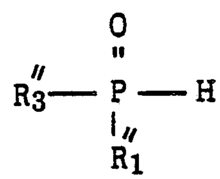
Representative compounds of formula (1) are: α-methylphosphonosuccinic acid; phosphonosuccinic acid; 1-phosphonopropane-2,3-dicarboxylic acid; and 2-phosphonobutanetricarboxylic acid(1,2,4). The preparation of such phosphonocarboxylic acids has been described, e.g. in German Offenlegungsschrift No. 2,015,068.

Representative of formula (2) are compounds such as carboxymethanephosphonic acid; 1-carboxyethan-1-phosphonic acid; 1-carboxyethane-2-phosphonic acid; 2-carboxypropane-3-phosphonic acid; 1-carboxypropane-2-phosphonic acid and methyl(carboxyethyl)phosphonic acid. These compounds are prepared by methods known in the art, e.g. U.S. Patent 4,052,160.

Representative telomers of formula (3) are provided by reacting an unsaturated acid of the formula



or a salt thereof, wherein R_2'' is defined as before, with a compound of the formula



wherein R_1'' is defined as before, and R_3'' is hydrogen, a straight or branched chain alkyl group having from 1 to 18 carbon atoms, a cycloalkyl residue of 5 to 12 carbon atoms, a phenyl or benzyl moiety, or OX wherein X is defined as before.

Representative of suitable manganese compounds which may be employed as a source of manganese ion are, for example, MnO, MnO_2, $MnCl_2 4H_2O$, $KMnO_4$, $Mn(CH_3COO)_2 4H_2O$ and the like. The manganese compound can be added simultaneously with the phosphorous-containing carboxylic acid derivative or may be added separately to the water. Alternatively, the manganese can be complexed by the phosphorous-containing carboxylic acid compound prior to adding to the water. Preferred is a composition in which the weight ratio of phosphorous-containing carboxylic acid derivative to manganese is at least about 2 to 1.

For the purpose of the present invention, effective organic phosphonocarboxylic or phosphinocarboxylic acid derivatives described herein and salts thereof are considered equivalent. The salts referred to are the acid addition salts of those bases which will form a salt with at least one acid group of the subject derivatives. Suitable bases include, for example, ammonia, the alkali metal and alkaline earth metal hydroxides, carbonates, and bicarbonates such as sodium hydroxide, potassium hydroxide, calcium hydroxide, potassium carbonate, sodium bicarbonate, magnesium carbonate and the like. These salts may be prepared by treating the organic phosphonocarboxylic or phosphinocarboxylic acid derivative having at least one acid group with an appropriate base.

The preferred quantity of the organic phosphonocarboxylic or phosphinocarboxylic acid derivatives to inhibit corrosion of either copper or iron containing metal alloys in water conducting systems is from 1 to 150 ppm acid or equivalent. The operable amounts are from 0.5 to 200 ppm. The addition of manganese compounds to these phosphorous containing carboxylic acid derivatives in such water conducting systems has an unexpected enhancement on corrosion inhibition. The present invention is the use of this composition to inhibit corrosion. The manganese compound usually is employed in an amount to provide from 0.5 to 30 ppm manganese by weight in the aqueous solution. Preferred amounts provide from 0.1 to 10 ppm.

The following examples are representative of the present invention.

EXAMPLE 1

This example demonstrates the enhanced corrosion inhibition of 1018 carbon steel provided by manganese with 2-phosphonobutanetricarboxylic acid. Tanks of 8-liter capacity were filled with tap water having the following characteristics:

WATER CHARACTERISTICS	
Conductivity (µmhos/cm)	750.0
Alkalinity (ppm as $CaCO_3$)	120.0
Total Hardness (ppm as $CaCO_3$)	178.0
Ca Hardness (ppm as $CaCO_3$)	136.0
Fe (ppm)	0.28
$SO_4^=$ (ppm)	85.0
Cl^- (ppm)	126.0
pH	7.4

Air was sparged at 10 standard cubic feet ($0.3m^3$) per hour (SCFH) through a glass tube which was situated at one end of the tank and extended to the bottom of the tank. The air sparge was used to recirculate the water, oxygenate the water, and aid in evaporation. Water level in the tank was automatically controlled by a gravity feed system and heat was added to the water by electric immersion heaters. The water temperature was measured by a platinum RTD (resistance thermal device) and controlled at 125°F (51.7°C) by an "on/off" controller which provided power to the immersion heaters. The pH of the water was adjusted to pH 8.0 by addition of caustic (50%) and was automatically maintained at 8.0 by a controller which feeds HCl (1% aq. solution) to the tank in response to an increase in pH.

The 2-phosphonobutanetricarboxylic acid was introduced to two separate tanks to a concentration of 150 ppm. Manganese as $MnCl_2 \cdot 4H_2O$ was added to one of these tanks to a concentration of 7.5 ppm Mn. The pH of each tank was controlled at 8.0, using dilute HCl. Carbon steel electrodes (1018) which were cleaned with 1:1 HCl and sanded with 320 grade sandpaper to remove all surface oxides were attached to the electrode corrosion probes and immersed in the tanks. The instantaneous corrosion rates were monitored using a potentiostatic corrosion rate instrument. The experiments were conducted for a period of five days, at which time, the concentration of salts in the baths were approximately four times those of the feed water. At the end of this time, the final average corrosion rates were found to be 1.0 mpy (0.025 mm/y) (mils per year) in the tank with manganese and 2.5 mpy (0.061 mm/y) in the tank without manganese.

In two other tanks under the same conditions a test was run using manganese (same source) alone in one tank and no additives in the other. Each tank at the end of a five day-period gave an average instantaneous corrosion rate of 10.0 mpy (0.025 mm/y).

EXAMPLES 2 AND 3

Two phosphinocarboxylic acid polymers, commercially available compounds, were tested in combination with manganese against carbon steel as in Example 1. The source of manganese was the same. The final average instantaneous corrosion rates (after 5 days) are shown in tabular form following:

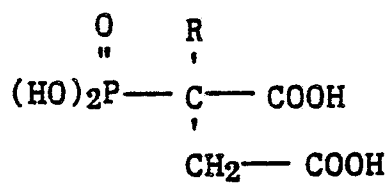
Example No.	Commercial Product* (Concn. ppm)	Mn++ (ppm)	Corrosion Rate (mpy)	
			(mpy)	(mm/y)
2 (a)	Belsperse 161 (100)	none	16.0	0.41
2 (b)	Belsperse 161 (100)	5	4.1	0.10
3 (a)	Belclene 500 (100)	none	16.0	0.41
3 (b)	Belclene 500 (100)	5	7.6	0.19

*Belsperse 161 is a phosphinocarboxylic acid polymer sold by Ciba-Geigy containing phosphonate and acrylate functionality. Belclene 500 is a phosphinocarboxylic acid polymer sold by Ciba Geigy.

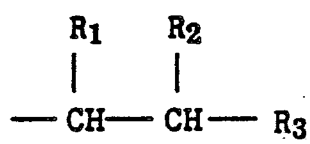
Claims

1. A composition useful for inhibiting metal corrosion in water conducting systems which comprises

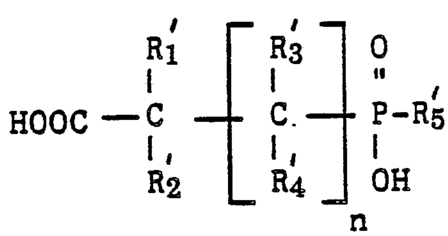
(a) a phosphorous-containing carboxylic acid compound, or a salt therof, wherein said compound corresponds to at least one of

(1) 

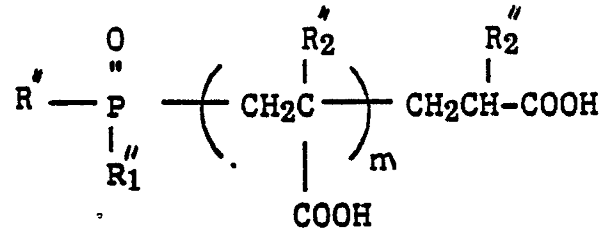
wherein R is a hydrogen atom, an alkyl having 1 to 4 carbon atoms, alkenyl or alkynyl group, each having 2 to 4 carbon atoms, an aryl, cycloalkyl or aralkyl group or the group



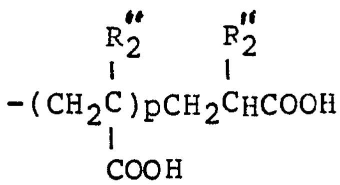
in which R_1 is hydrogen, an alkyl group having 1 to 4 carbon atoms or a carboxyl group; R_2 is hydrogen or methyl; and R_3 is a carboxyl group; or

(2) 

wherein each of the substituents R1, R2', R3'and R4'is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; R5'is hydrogen, an OH-group or analkyl group having from 1 to 3 carbon atoms; and n is 0 or 1; or

(3) 

wherein R_2'' is hydrogen or a methyl or ethyl group; R'' is hydrogen, a straight or branched alkyl group having from 1 to 18 carbon atoms, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group, an aralkyl group, a moiety having the formula



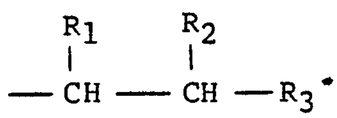
wherein R''_2 has its previous significance, and the sum m + p is a positive integer of no more than 100, or a residue -OX wherein X is hydrogen or an alkyl group having from 1 to 4 carbon atoms; and R_1 is a residue -OX wherein X has its previous significance;

(b) together with a manganese compound capable of providing a manganese ion.

2. A composition as claimed in Claim 1, wherein the phosphorous-containing carboxylic acid compound corresponds to formula (1).

3. A composition as claimed in Claim 2, wherein R is hydrogen.

4. A composition as claimed in Claim 2, wherein R in the formula is:



and R_3 is a carboxyl group.

5. A composition as claimed in Claim 4, wherein each of R_1 and R_2 is hydrogen.

6. A composition as claimed in Claim 1, wherein the phosphorous-containing carboxylic acid compound corresponds to formula (2).

7. A composition as claimed in Claim 1, wherein the phosphorous-containing carboxylic acid compound corresponds to formula (3).

8. A composition as claimed in any one of the preceding claims, wherein the manganese is chelated by the phosphorous-containing carboxylic acid compound.

9. A composition as claimed in any one of the preceding claims, wherein the weight ratio of phosphorous-containing carboxylic acid compound to manganese is at least 2:1.

10. A composition as claimed in any one of the preceding claims, wherein the manganese compound is selected from MnO, MnO_2, $MnCl_2\,4H_2O$, $KMnO_4$ and $Mn(CH_3COO)_2\,4H_2O$.

11. A process for inhibiting the corrosion of metals in water conducting systems which comprises providing in said water a phosphorous-containing carboxylic acid compound as defined in any one of claims and an amount of a manganese compound capable of providing an amount of manganese ion sufficient to enhance the corrosion-inhibiting effect of said phosphorous-containing carboxylic acid compound.

12. A process as claimed in Claim 11, wherein said phosphorous-containing carboxylic acid compound is present in an amount of 1 to 150 ppm acid or equivalent and said manganese compound is present in an amount providing 0.5 to 30 ppm manganese.

13. A process as claimed in Claim 12, wherein said manganese compound is present in an amount providing 0.1 to 10 ppm manganese.

14. A process as claimed in any one of Claims 11 to 13, wherein said manganese compound is added simultaneously with the said phosphorous-containing carboxylic acid compound.