

[54] **ORGANIC PHOSPHONIC ACID COMPOUND
CORROSION PROTECTION IN AQUEOUS
SYSTEMS**

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abandoned. Continuation-in-part of Ser. No.
581,151, Sept. 22, 1966, Pat. No. 3,431,217.

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252/389 R, 106/14

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252/86, 8.55 E; 21/2.7 A, 2.7 R, 2.5 A, 2.5 R;
106/14; 260/502.4

[56]

References Cited

UNITED STATES PATENTS

3,483,133	12/1969	Hutch et al.	252/389 A
3,532,639	10/1970	Hutch et al.	252/389 A

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[57]

ABSTRACT

The invention disclosed relates to organo-phosphonic acid compounds in combination with zinc salts for use to inhibit metal corrosion in aqueous systems. The organophosphonic acid compounds include alkylene polyphosphonic acids, and the water-soluble salts and esters thereof.

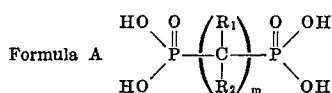
6 Claims, No Drawings

ORGANIC PHOSPHONIC ACID COMPOUND CORROSION PROTECTION IN AQUEOUS SYSTEMS

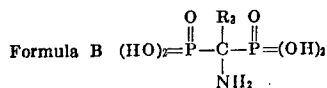
This application for United States Letters patent is a continuation of U.S. Pat. application Ser. No. 645,600 and now abandoned, filed June 13, 1967, which in turn is a continuation-in-part of U.S. Pat. application Ser. No. 581,151, filed Sept. 22, 1966, and now U.S. Pat. No. 3,431,217.

This invention relates to a method and composition for preventing corrosion of metal surfaces in contact with aqueous systems.

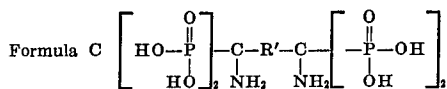
In summary the corrosion inhibiting composition of this invention consists essentially of from 1 to 80 weight percent of an alkylene polyphosphonic acid having one of the following formulae A, B or C:



or



or



wherein m is an integer from 1 to 10, R_1 is hydrogen, or an alkyl group having from 1 to 4 carbons and R_2 is hydroxyl, hydrogen, or an alkyl group having from 1 to 4 carbons, R_3 is an alkyl group having 1 to 10 carbons, benzyl or phenyl, R' is an aliphatic radical having from 1 to 10 carbons, and the water-soluble salts and esters thereof; or mixtures thereof, and from 1 to 95 weight percent of a water-soluble zinc salt. Aqueous solutions of 1 to 70 weight percent of this composition are also encompassed within this invention.

In summary, the method of this invention for preventing corrosion of metals in contact with an aqueous liquid comprises maintaining in the aqueous liquid from 1 to 10,000 ppm. of the alkylene polyphosphonic acid, salts or esters thereof, and from 1 to 10,000 ppm. of a water-soluble zinc salt.

Water-soluble inorganic chromates are widely used to treat industrial water systems to prevent corrosion of metal parts in contact therewith. When these chromates are employed alone, they are used in concentrations as low as 200 ppm. and as high as 10,000 ppm., depending upon the protection needed and the permissible cost. When these chromates are used in combinations with molecularly dehydrated inorganic phosphates such as disclosed in U.S. Pat. No. 2,711,391, chromate concentrations as low as 20 ppm. have been found adequate in mild corrosive systems. Therefore, combinations of chromates and molecularly dehydrated phosphates are widely used.

Although chromates are highly effective corrosion inhibitors, their use is subject to several difficulties. Chromates cause serious skin and eye irritations, and chromates cannot be used in aqueous systems such as cooling towers or air-wash units where the resulting spray will contact people. Chromate solutions, because they are toxic, often require chemical treatment before being discharged to waste systems. Furthermore, chromates degrade organic compounds mixed therewith, limiting the types or organic compounds which can be mixed with the chromates in dry mixtures and aqueous solutions.

The use of molecularly dehydrated inorganic phosphates in aqueous systems causes serious problems because the polyphosphates hydrolyze to form alkaline earth metal orthophosphates, causing scaling and fouling of the aqueous systems treated. Because of this hydrolysis, excess quantities of the polyphosphates must be employed.

It is an object of this invention to provide a non-toxic composition for treating aqueous systems to prevent corrosion of metal surfaces in contact therewith which does not introduce orthophosphates to the aqueous systems. The composition contains an organic phosphonic acid compound in combination with a water-soluble zinc salt.

The compositions of this invention are useful for treating a variety of aqueous systems, that is, any aqueous system corrosive to metal surfaces in contact therewith. Suitable systems which can be treated according to this invention include water treatment systems, cooling towers, water circulating systems, and the like wherein fresh water, brines, sea water, sewage effluents, industrial waste waters, and the like are circulated in contact with metal surfaces. These compounds are useful in acid pickling baths, radiator coolers, hydraulic liquids, antifreezes, heat transfer mediums, and petroleum well treatments. The process of this invention is suitable for reducing the corrosion of iron, copper, aluminum, zinc and alloys containing these metals such as steel and other ferrous alloys, brass, and the like which are in contact with corrosive aqueous systems.

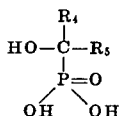
All concentrations are given herein as weight percents unless otherwise specified.

The compositions of this invention contain from 1 to 80 percent of an organo-phosphonic acid compound. The preferred organo-phosphonic acid compound for use in the composition of this invention is an alkylene diphosphonic acid having the foregoing Formula A, such as those disclosed in U.S. Pat. Nos. 3,214,454 and 3,297,578, the entire disclosures of which are incorporated herein by reference. Also suitable is an alkylene diphosphonic acid having the foregoing Formula B or Formula C such as those disclosed in U.S. Pat. No. 3,303,139, the entire disclosure of which is incorporated herein by reference. Suitable acids of this type include methylenediphosphonic acid; ethylenediphosphonic acid; isopropylidenediphosphonic acid; 1-hydroxy, ethylenediphosphonic acid; hexamethylenediphosphonic acid; trimethylenediphosphonic acid; decamethylenediphosphonic acid; 1-hydroxy, propylenediphosphonic acid; 1,6-dihydroxy, 1,6-dimethyl, hexamethylenediphosphonic acid; 1,4-dihydroxy, 1,4-diethyl, tetramethylenediphosphonic acid; 1,3-dihydroxy, 1,3-dipropyl, trimethylenediphosphonic acid; 1,4-dibutyl, tetramethylenediphosphonic acid; dihydroxy, diethyl, ethylenediphosphonic acid;

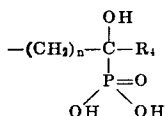
4-hydroxy, 6-ethyl, hexamethylenediphosphonic acid; 1-hydroxy, butylidenediphosphonic acid; butylidenediphosphonic acid; 1-aminoethane-1,1-diphosphonic acid; 1-aminopropane-1, 1-diphosphonic acid; 1-aminobenzyl-1,1-diphosphonic acid; 1,6-diaminohexane-1,1,6,6-tetraphosphonic acid; 1-aminoethane-1,1-diphosphonic acid monoethyl ester, and 1-amino-2-phenylethane-1,1-diphosphonic acid. The water-soluble salts of these acids such as the alkali metal, alkaline earth metal, zinc, cobalt, chromium, lead, tin, nickel, ammonium, or amine and lower alkanol amine salts can be used. Also, esters of these acids with an aliphatic alcohol having from 1 to 4 carbons, or mixtures of the above acids, salts or esters can be used. Use of mixtures of any of the general types of organo-phosphonic acid compounds described above is also contemplated within the scope of this invention.

It will be seen from the foregoing listing of acid compounds within the scope of Formula A and a number of the examples which follows, as well as the like compounds disclosed in U.S. Pat. No. 3,214,454 and 3,297,578, that a number of these can be described as methanol phosphonic acid derivatives having the following Formula D:

Formula D



where R_4 is independently selected from the group consisting of an alkyl group up to four carbon atoms and phosphonate groups, and R_5 is selected from the group consisting of alkyl groups having up to four carbon atoms, when R_4 is a phosphonate group and



where n is 0 to 6, when R_4 is an alkyl group; and water-soluble salts thereof.

Specific methanol phosphonic acid compounds thus disclosed include, for example, 1-hydroxy ethylidene diphosphonic acid (i.e., ethanol, or methyl methanol, 1,1-diphosphonic acid); 1-hydroxy, propylidene diphosphonic acid (i.e., ethyl methanol diphosphonic acid); 1,6-dihydroxy-1,6-dimethyl, hexamethylene diphosphonic acid (i.e., tetramethylene bis(methyl methanol phosphonic acid)) and its sodium salt (Examples 44 and 100); 1,4-dihydroxy-1,4-diethyl, tetramethylene diphosphonic acid (i.e., dimethylene bis(ethylmethanol phosphonic acid)); 1,3-dihydroxy-1,3-dipropyl trimethylene diphosphonic acid (i.e., methylene bis(propylmethanol phosphonic acid)) and its sodium salt (Examples 46 and 112); dihydroxy, diethyl, ethylene diphosphonic acid (i.e., bis(ethylmethanol phosphonic acid)) and its sodium salt (Examples 52 and 118); and 1-hydroxy butylidene diphosphonic acid (i.e., propyl methanol diphosphonic acid).

The compositions of this invention also contain from 1 to 95 and preferably from 25 to 45 percent of a

water-soluble zinc salt. It will be seen that the use of the more common water-soluble zinc salts such as zinc nitrate ($Zn(NO_3)_2$, molecular weight 189) zinc chloride ($ZnCl_2$, molecular weight 136.29) and zinc sulfate ($ZnSO_4$ or $ZnSO_4 \cdot H_2O$, molecular weight 161.44 and 179.44, respectively) in the aforesaid concentrations will provide zinc ion (Zn^{+2}) concentrations from as little as 0.345 weight percent (as 1 percent $Zn(NO_3)_2$) to as high as 45.5 weight percent (equivalent to 95 percent $ZnCl_2$). Thus the weight ratio of zinc (in the form of one of said water-soluble salts) to phosphonic acid compound may range from about 0.345:80 to about 45.5:1 or, in other words, from about 1:232 to about 1:0.022. At the preferred concentrations of zinc salt the weight ratio of zinc ion may range from about 8.64:80 (Zn^{+2} equivalent in 25 weight percent of $Zn(NO_3)_2$) to about 21.5:1 (Zn^{+2} equivalent in 45 weight percent of $ZnCl_2$); or in other words, from about 1:9.27 to about 1:0.0465. As seen in the following specific Example 4, a typical zinc to phosphonic acid compound weight ratio is 1:1.

The zinc salts which can be employed in the composition of this invention include any water-soluble zinc salt such as zinc sulfate, zinc chloride, zinc nitrate, alkali metal-zinc phosphate glasses, crystalline alkali metal-zinc polyphosphates, and the like.

Aqueous systems can be treated with aqueous solutions containing from 1 to 70 percent and preferably from 1 to 10 percent of the compositions of this invention. These solutions can be made by premixing the ingredients of this composition and then adding the mixture to water, or by adding the individual ingredients of the composition of this invention separately to water. These aqueous feed solutions are stable and can be stored prior to use.

In the methods of this invention for preventing corrosion of metals in contact with aqueous liquids, from 1 to 10,000 ppm. and preferably from 1 to 100 of the organophosphonic acid compounds, and from 1 to 10,000 ppm. and preferably from 2 to 200 ppm. of the water-soluble zinc salts are maintained in aqueous liquid.

The aqueous corrosion resistant solutions of this invention are solutions of at least 1 and preferably from 5 to 200 ppm. of the compositions of this invention. The ingredients can be added to the aqueous solution either in premixed solid or solution or individual solids or solutions to form this aqueous solution composition.

The compositions of this invention are non-toxic and prevent corrosion of metals in contact with aqueous liquids. These compositions can be substituted for chromate base corrosion inhibitors previously used where the toxicity of the chromate makes its use undesirable or where disposal of corrosion inhibiting solutions containing chromates raises serious water pollution problems requiring extensive pretreatment to remove the chromates prior to disposal of such solutions. The compositions of this invention in aqueous solutions prevent corrosion of metal parts such as heat exchangers, engine jackets, and pipes and particularly prevent metal loss, pitting, and tuberculation of iron base alloys, copper alloys, and aluminum alloys in contact with water.

This invention is further illustrated by the following specific but non-limiting examples.

EXAMPLE 1

This example demonstrates the synergistic reduction in corrosion rates obtained with the compositions of this invention.

In this test, circulating water having the following composition was used:

Calcium sulfate dihydrate	445 ppm.
Magnesium sulfate heptahydrate	519 ppm.
Sodium bicarbonate	185 ppm.
Calcium chloride	136 ppm.

During the test, the circulating water was fed to a closed circulating test system at a rate of 5 gallons per day, the overflow from the test system being discharged to waste.

In the closed circulating system, circulating water having a temperature of 130° F. and pH of 6.5-7.0 was fed at a rate of one gallon per minute to a coupon chamber containing test coupons for the corrosion test. Water from the coupon chamber was then passed through an arsenical admiralty brass tube surrounded by a jacket through which a heating fluid having an initial temperature of 240° F. was countercurrently passed. The circulating water was then cooled to 130° F. and recirculated through the system. The total circulating time for each test was 10 days.

Mild steel coupons having an average area of 26.2 cm.² were used in the test chamber. The coupons were carefully cleaned and weighed before use. Following the test, each coupon was cleaned with inhibited hydrochloric acid, rinsed, dried and weighed to determine the corrosion rate in mils per year. A comparison of the corrosion rates of the individual ingredients of the composition of this invention with combination of these ingredients according to this invention were found to be as shown in Table A.

TABLE A

Example No.	Additive	Corrosion Rate of Steel In Mils per Year
1	Blank (No Treatment)	15.0
2	Zn ⁺⁺ , 10 ppm	15.3
3	Hydroxy ethylidene diphosphonic acid, 10 ppm	11.1
4	Zn ⁺⁺ , 10 ppm, hydroxy ethylidene diphosphonic acid, 10 ppm	8.4

As shown in Table A, Example 4 corresponding to the composition of this invention provides a corrosion protection far greater than would be expected in view of the effects of the individual components thereof.

Examples of other compositions accordong to this invention are shown in Table B.

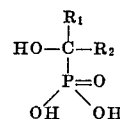
TABLE B

Example No.	Ingredients - wt. %
5	Zinc chloride — 40.0%; hydroxy ethylidene diphosphonic acid — 60.0%
6	Magnesium methylenediphosphonate — 30%; zinc sulfate monohydrate — 70%
7	Zinc isopropylidenediphosphonate — 30%; zinc sulfate monohydrate — 70%
8	Sodium trimethylenediphosphonate — 30%; zinc sulfate monohydrate — 70%
9	Decamethylenediphosphonic acid — 30%; zinc sulfate monohydrate — 70%
10	Sodium 1,6-dihydroxy, 1,6-dimethyl, hexamethylene-diphosphonate — 30%; zinc sulfate monohydrate — 70%
11	1-amino-2-phenylethane-1,1-diphosphonic

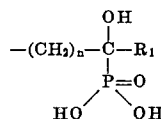
- acid — 30%; zinc sulfate monohydrate — 70%
- 12 Sodium 1,3-dihydroxy, 1,3-dipropyl, trimethylene-diphosphonate — 30%; zinc sulfate monohydrate — 70%
- 13 Zinc 1-aminoethane-1,1-diphosphonate — 30%; zinc sulfate monohydrate — 70%
- 5 14 1-aminoethane-1,1-diphosphonic acid monoethyl ester — 30%; zinc sulfate monohydrate — 70%
- 15 Tin methylenediphosphonate — 30%; zinc sulfate monohydrate — 70%
- 16 Butylidenediphosphonic acid — 30%; zinc sulfate monohydrate — 70%
- 10 17 1-aminobenzyl-1,1-diphosphonic acid — 30%; zinc sulfate monohydrate — 70%
- 18 Sodium dihydroxy, diethyl, ethylenediphosphonate — 30%; zinc sulfate monohydrate — 70%
- 19 1-hydroxy ethylidene diphosphonic acid — 50%; zinc chloride — 50%
- 15 20 1-hydroxy propylidene diphosphonic acid — 40%; zinc sulfate monohydrate — 60%
- 21 1-hydroxy ethylidene diphosphonic acid — 25%; zinc nitrate — 75%
- 22 1-hydroxy butylidene diphosphonic acid — 30%; zinc sulfate monohydrate

What is claimed is:

1. A composition useful for inhibiting corrosion in aqueous systems, said composition consisting essentially of one part by weight zinc in the form of a water-soluble zinc salt and from 0.02 to about 300 parts by weight of a water-soluble organic phosphonate compound having the formula



where R₁ is independently selected from the group consisting of alkyl groups up to four carbon atoms, and phosphonate groups, and R₂ is selected from the group consisting of alkyl groups having up to four carbon atoms, when R₁ is a phosphonate group; and



where n is 0 to 6, when R₁ is an alkyl group; and water-soluble salts and esters thereof.

2. The composition of claim 1 in which the water-soluble zinc salt is zinc sulfate.

3. The composition of claim 1 in which the phosphonate compound is ethanol 1,1-diphosphonic acid or water-soluble salt thereof.

4. A method of inhibiting corrosion in aqueous systems comprising adding to said aqueous systems at least about one part per million of the composition of claim 1.

5. A method of inhibiting corrosion in aqueous systems comprising adding to said aqueous system at least about one part per million of the composition of claim 2.

6. A method of inhibiting corrosion in aqueous systems comprising adding to said aqueous system at least about one part per million of the composition of claim 3.

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