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METHOD OF INHIBITING CORROSION WITH AMINOMETHYLPHOSPHONIC ACID COMPOSITIONS

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18 Claims

ABSTRACT OF THE DISCLOSURE

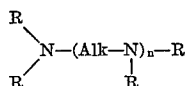
Aminomethylphosphonic acid compounds and soluble salts thereof, alone or in combination with zinc, dichromate, certain thiols and 1,2,3-triazoles and mixtures thereof, are disclosed as inhibiting the corrosion of metals by oxygen bearing waters.

This invention is a continuation-in-part of our copending application Ser. No. 534,947, filed Jan. 24, 1966, and now abandoned.

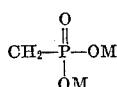
This invention relates to the use of aminomethylphosphonic acid compounds and salts thereof for inhibiting the corrosion of metals by oxygen-bearing waters. It also relates to aminomethylphosphonic acid compositions containing zinc, dichromate, certain thiols and 1,2,3-triazoles, and mixtures thereof and to corrosion inhibition therewith.

Oxygen corrosion is, of course, a serious problem in any metal-containing water system. The corrosion of iron and steel is of principal concern because of their extensive use in many types of water systems. Copper and its alloys, aluminum and its alloys, and galvanized steel are also used in water systems and are subject to corrosion. We have discovered novel corrosion inhibitors which will inhibit oxygen corrosion in water systems containing such metals.

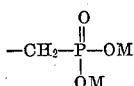
We have found that aminomethylphosphonic acid compounds and soluble salts thereof (hereinafter referred to as the phosphonates) make effective corrosion inhibitors. These phosphonates include aminomethylphosphonic acid, amino bis (methylphosphonic acid), amino tris (methylphosphonic acid), compounds containing the above amino forms, and salts of any of the above acids. Such compounds include compounds of the general formula:



(See U.S. Patents 2,599,807 and 2,609,390) where Alk is any alkylene carbon group ($\text{C}_{n\text{H}_{2n}}$) containing 2 to 6 carbon atoms, each R may be H, $-\text{CH}_2\text{COOM}$, or

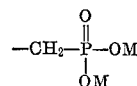


M is H or a cation forming a water-soluble salt and $n=0$ to 14 provided, however, that where $n=0$ at least one of the radicals represented by R are

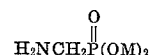


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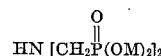
and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are



Ethylene diamine tetrakis (methylphosphonic acid) and its water-soluble salts are preferred; amino tris (methylphosphonic acid) and its water-soluble salts are also preferred compositions. Of the monoamines containing only one or two methylphosphonate groups, we prefer the primary and secondary amines containing no other groups, i.e., those of the formula



and



although we may also use substituted amines, such as, for example, diethanol amino (methyl phosphonates). Lower alkanol substituted monoamines having at least one methyl phosphonate group are contemplated in our invention. We have also successfully used compounds over the range $n=0$ to 14, including as representative compounds nitrilotris (methylphosphonic acid) in which $n=0$; ethylenediamine tetrakis (methyl phosphonic acid) in which $n=1$; diethylenetriamine pentakis (methyl phosphonic acid) in which $n=2$; pentamethylenhexamine octakis (methylphosphonic acid) in which $n=5$; and polyethyleneimine polykis (methylphosphonic acid) in which $n=14$.

We have performed numerous experiments which demonstrate the effectiveness of those phosphonates in inhibiting metallic corrosion. In these experiments $1\frac{1}{2}'' \times 1\frac{1}{2}''$ No. 1010 AISI steel coupons were weighed and placed in beakers containing 1000 ml. water at 35°C . and various amounts of corrosion inhibitor. The water contained 11 p.p.m. bicarbonate, 18 p.p.m. chloride, 78 p.p.m. sulfate, 20 p.p.m. calcium, and 6 p.p.m. magnesium, and had a total hardness as CaCO_3 of 76 p.p.m. The coupons were gently agitated for five days, after which they were removed, cleaned, and reweighed. The amount of corrosion that had taken place was determined by the loss in weight and expressed in terms of milligrams of steel consumed per square decimeter of surface per day (m.d.d.). Results of tests with several phosphonates are given in Table I.

TABLE I.—INHIBITION OF CORROSION OF STEEL WITH AMINO METHYL PHOSPHONATES

Inhibitor Conc., p.p.m.	Amino tris (methyl phosphonic acid), m.d.d.	Ethylenediamine tetrakis (methyl phosphonic acid), m.d.d.	Disodium diethanolamino methylphosphonate, m.d.d.
0	206	206	206
10	170	125	125
20	14.5	66	66
30	9.7	15	15
50	3.3	1.1	1.1
100	2.4	1.0	1.0
200			30

Our phosphonates will inhibit corrosion of ferrous metals when maintained in a water system at a concentration of at least about 20 p.p.m., and preferably about 50 p.p.m.; maximum concentrations are determined by economics. Because they attack copper to some degree, use of the phosphonates by themselves is recommended only in water systems which do not contain copper.

As with all concentration ranges given throughout this patent, the concentrations of inhibitor needed to inhibit corrosion effectively will depend on the characteristics of the water system being treated and the particular phosphonates used. The ranges given are a general indication

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of the concentrations needed; exact concentrations must be determined by examination of the water system to be treated.

We have discovered a synergistic effect on corrosion inhibition between phosphonates and the zinc ion; that is, the use of the phosphonates with the zinc ion more effectively inhibits corrosion than does an equal concentration of either the phosphonate or the zinc ion alone. Experiments to show the synergism between the phosphonates and zinc were performed in the same manner as those previously described for Table I. Table II gives the results of these experiments. The zinc ion was introduced as zinc sulfate. In all tables, the heading (m.d.d.) means mg./square decimeter/day.

TABLE II.—INHIBITION OF CORROSION OF STEEL WITH ZINC ION AND AMINO TRIS (METHYLPHOSPHONIC ACID)

Inhibitor Composition, Wt. Percent		Corrosion Rate (m.d.d.)				
Amino tris (methylene phosphonic acid)	Zinc++	10 p.p.m.	15 p.p.m.	20 p.p.m.	30 p.p.m.	50 p.p.m.
0	100	112	104	93	80	7.0
20	80	69	38	14	0.9	1.4
40	60	42	1.3	1.2	0.8	0.6
60	40	30	1.5	1.0	0.9	0.6
80	20	108	6.3	5.0	4.1	3.6
100	0	117	110	34	8.8	3.2

Similar experiments with other phosphonates were also performed. Tables III and IV show large decreases in corrosion when small amounts of zinc were present with ethylenediamine tetrakis (methylphosphonic acid) and with disodium diethanolamine methyl phosphonate.

TABLE III

Influence of zinc (sulfate) on inhibition of corrosion of steel with ethylenediamine tetrakis (methylphosphonic acid) (10 p.p.m.)

Zn++ (p.p.m.)	Corrosion rate (m.d.d.)
0	127
2	65
4	1.5
6	0.6
8	0.3
10	0.3

TABLE IV

Influence of zinc ion on inhibition of corrosion of steel with disodium diethanolamine methyl phosphonate (50 p.p.m.)

Zn++ (p.p.m.)	Corrosion rate (m.d.d.)
0	163
10	46
20	17
30	11
40	7.9
50	5.2

A combination of about 3 to 100 p.p.m. amino phosphonate and about 2 to 100 p.p.m. zinc ion will inhibit corrosion in most water systems; the preferred concentration range is about 5 to 25 p.p.m. phosphonate and about 5 to 25 p.p.m. zinc ion.

Amino phosphonate and a zinc salt may be mixed as a dry composition can be fed into a water system. Such a composition having maximum synergism between the amino phosphonate and the zinc ion comprises about 10% to 80% soluble zinc salt and about 20% to 90% amino phosphonate; preferably it comprises about 20% to 60% soluble zinc salt and about 40% to 80% amino phosphonate.

We have also found synergism between the amino phosphonates and chromate or dichromate. Because chromate and dichromate are each readily converted into the other by a change in pH, it is understood that both will be simultaneously present at most pH's even though only one is mentioned, Tables V, VI, and VII give the results of

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experiments similar to those already described and show the synergism between the amino phosphates and chromate or dichromate.

Tables V, VI, and VII each use different amino phosphonate compounds; Table V illustrates results with total inhibitor mixtures of 10 and 20 parts per million, Table VI illustrates results at 50 parts per million total inhibitor mixture, and Table VII employs an inhibitor mixture at 10 parts per million.

TABLE V.—INHIBITION OF CORROSION OF STEEL WITH SODIUM DICHROMATE-AMINO TRIS (METHYLPHOSPHONIC ACID) MIXTURES

[35° C.; pH 6.5]

Inhibiting Composition, Wt. percent		Corrosion Rate (m.d.d.)	
Amino Tris (Methylphosphonic Acid)	Na ₂ Cr ₂ O ₇	10 p.p.m.	20 p.p.m.
100	0	96	12
80	20	4.6	4.8
60	40	6.8	7.5
40	60	7.2	7.4
20	80	9.8	4.8
0	100	23	8.7

TABLE VI.—INHIBITION OF CORROSION OF STEEL WITH SODIUM DICHROMATE-DISODIUM DIETHANOLAMINO METHYL PHOSPHATE

[35° C.; pH 6.5]

Disodium Diethanolamino Methyl Phosphonate (Weight percent)	Na ₂ Cr ₂ O ₇ (Weight percent)	Weight Loss at 50 p.p.m. Inhibitor Level (m.d.d.)
100	0	163
80	20	5.1
60	40	7.7
40	60	1.2
20	80	4.7
0	100	5.2

TABLE VII.—INHIBITION OF CORROSION OF STEEL WITH SODIUM DICHROMATE ETHYLENEDIAMINE TETRAKIS (METHYLPHOSPHONIC ACID) 10 P.P.M. INHIBITOR

E (ethylenediamine Tetrakis (Methylphosphonic Acid) Wt. percent)	Na ₂ Cr ₂ O ₇ (Wt. percent)	Weight Loss (m.d.d.)
100	0	108
80	20	9.2
60	40	9.7
40	60	13
20	80	20
0	100	14

Corrosion in most water systems may be inhibited by adding about 1 to 100 p.p.m. amino phosphonate and about 1 to 100 p.p.m. chromate or dichromate; preferably about 5 to 25 p.p.m. amino phosphonate and about 5 to 25 p.p.m. chromate or dichromate is added.

We have also found that compositions of amino phosphonates, zinc iron, and chromate or dichromate are useful in inhibiting the corrosion of metals. The inhibiting action of zinc and dichromate compositions has been shown in Hatch U.S. Patent 3,022,133; thus, all three components of this composition are mutually synergistic. The co-action of zinc and dichromate illustrated in U.S. Patent 3,022,133 remains unaffected by the presence of amino phosphonates and the other ingredients of our inhibitors mentioned herein. Tables VIII and IX give the results of experiments conducted as previously described using these corrosion inhibiting compositions.

TABLE VIII.—INHIBITION OF CORROSION OF STEEL WITH AMINO TRIS (METHYLPHOSPHONIC ACID)—SODIUM DICHROMATE—ZINC (SULFATE) MIXTURES

[pH=8]

Concentration (p.p.m.)			Weight Loss (m.d.d.)
Amino Tris Methylphosphonic Acid	Sodium Dichromate	Zinc++	
0	0	0	208
5	1.25	1.25	6.1
10	2.5	2.5	2.6
15	3.75	3.75	1.7
20	5	5	1.2
25	6.25	6.25	0.8
2.5	2.5	2.5	3.4
5	2.5	2.5	2.4
15	2.5	2.5	2.1
20	2.5	2.5	1.9
5	5	5	1.9

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TABLE IX.—INHIBITION OF CORROSION OF STEEL WITH ETHYLENEDIAMINE TETRAKIS (METHYLPHOSPHONIC ACID)—SODIUM DICHROMATE—ZINC (SULFATE) MIXTURES

[pH=8]			
Concentration (p.p.m.)			Weight Loss (m.d.d.)
Ethylenediamine Tetakis (Methylphosphonic Acid)	Sodium Dichromate	Zinc++	
0.....	0	0	208
2.5.....	1.25	1.25	13
5.....	2.5	2.5	1.5
7.5.....	3.75	3.75	1.0
10.....	5	5	0.7

Especially useful combinations of amino phosphonate, chromate, and zinc exist in the range of about 1 to 100 phosphonate of the type described, about ½ to 50 p.p.m. chromate or dichromate, and about ½ to 50 p.p.m. zinc ion. The preferred range is about 2 to 30 p.p.m. phosphonate, and about 1 to 15 p.p.m. chromate or dichromate, and about 1 to 15 p.p.m. zinc ion.

TABLE X.—INHIBITION OF CORROSION OF STEEL WITH DIETHYLENTRIAMINE PENTAKIS (METHYL PHOSPHONIC ACID) ALONE AND IN THE PRESENCE OF ZINC (SULFATE)

[pH=6.8]		
DTPMP Conc. (p.p.m.)	Wt. Loss (m.d.d.)	
	Alone	With Zinc (30% of DTPMP Conc.)
0.....	180	83.0
5.....	120	6.8
10.....	103	3.4
20.....	2.0	2.0
30.....	56.8	2.7
50.....	17.0	1.5
100.....		

TABLE XI.—INHIBITION OF CORROSION OF STEEL WITH PENTAMETHYLENEHEXAMINE OCTAKIS (METHYL PHOSPHONIC ACID) ALONE AND IN THE PRESENCE OF ZINC (SULFATE)

[pH=6.9]		
PMHOMP Conc. (p.p.m.)	Wt. Loss (m.d.d.)	
	Alone	Plus Zn (30% of the Phosphonic Acid)
0.....	188	62.0
5.....	97.4	52.2
10.....		5.1
20.....	55.5	3.5
30.....	41.6	5.3
50.....	15.7	3.7
100.....		

TABLE XII.—INHIBITION OF CORROSION OF STEEL WITH POLYETHYLENEIMINE POLYKIS (METHYL PHOSPHONIC ACID) ALONE AND IN THE PRESENCE OF ZINC (SULFATE)

[pH=6.9]		
PEPMP Conc. (p.p.m.)	Wt. Loss (m.d.d.)	
	Alone	Plus 30% (of PEPMP Conc.) Zn
0.....	186	62.6
10.....	104	64.0
20.....	91.2	7.8
30.....	80.0	3.8
50.....	60.9	3.1
100.....	9.4	

TABLE XIII.—INFLUENCE OF ZINC (SULFATE) ON CORROSION OF COPPER IN PRESENCE OF 50 P.P.M. NITRILOTRIS (METHYL PHOSPHONIC ACID)

[pH=7.0]		
Zinc Conc. (p.p.m.)	Percent of NTMP Conc.	Wt. Loss (m.d.d.)
0.....	0	7.3
5.....	10	4.5
10.....	20	1.9
15.....	30	1.0
20.....	40	0.3
25.....	50	0.07

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TABLE XIV.—INFLUENCE OF ZINC (SULFATE) ON CORROSION OF COPPER IN PRESENCE OF 50 P.P.M. DIETHYLENTRIAMINE PENTAKIS (METHYL PHOSPHONIC ACID)

[pH=7.0]		
P.p.m.	Percent of DTPMP Conc.	Wt. Loss (m.d.d.)
0.....	0	5.7
5.....	10	2.6
10.....	20	0.6
15.....	30	0.3
20.....	40	0
25.....	50	0.1

TABLE XV.—INFLUENCE OF ZINC (SULFATE) ON CORROSION OF ARSENICAL ADMIRALTY BRASS IN PRESENCE OF 50 P.P.M. NITRILOTRIS (METHYL PHOSPHONIC ACID)

[pH=6.9]		
P.p.m.	Percent of NTM Conc.	Wt. Loss (m.d.d.)
0.....	0	10.5
5.....	10	7.4
10.....	20	3.6
15.....	30	2.3
20.....	40	1.6
25.....	50	1.0

TABLE XVI.—INFLUENCE OF ZINC (SULFATE) ON CORROSION OF ARSENICAL ADMIRALTY BRASS IN PRESENCE OF 50 P.P.M. DIETHYLENTRIAMINE PENTAKIS (METHYL PHOSPHONIC ACID)

[pH=6.9]		
P.p.m.	Percent of DTPMP Conc.	Wt. Loss (m.d.d.)
0.....	0	7.2
5.....	10	4.0
10.....	20	1.2
15.....	30	0.8
20.....	40	0.7
25.....	50	0.6

TABLE XVII.—EFFECT OF pH ON CORROSION OF COPPER IN PRESENCE OF 50 P.P.M. DIETHYLENTRIAMINE PENTAKIS (METHYL PHOSPHONIC ACID) AND INFLUENCE THEREON OF 15 P.P.M. ZINC

pH	Wt. Loss (m.d.d.)	
	Alone	With Zinc
4.0.....	16.3	14.4
5.0.....	9.2	6.9
6.0.....	7.1	2.2
7.0.....	6.0	0.3
8.0.....	5.4	0.1
9.0.....	5.1	0.3

We have found that the amino phosphonate inhibitors are effective over a rather wide pH range although below a pH of about 3 their inhibitive action decreases considerably. If the pH of the water being treated is too low, it may be necessary to raise it by the addition of alkali in order to achieve effective corrosion inhibition. Generally, slightly lesser amounts of corrosion inhibitor are needed for effective inhibition at higher pH levels. Best results are obtained at a pH between about 5 and about 9.

Table XIII shows the influence of zinc on the corrosion of copper in the presence of nitrilotris (methyl phosphonic acid). Table XIV contains similar data for diethylenetriamine pentakis (methyl phosphonic acid). The addition of zinc causes a pronounced decrease in the attack on copper in each case. Between 30 and 40% zinc is required with nitrilotris (methyl phosphonic acid), while somewhat less (i.e., 20 to 30% zinc) suffices with diethylenetriamine pentakis (methyl phosphonic acid).

Zinc exerts a similar inhibitive action on the corrosion of arsenical admiralty brass in the presence of these amino-methyl phosphonates. This is illustrated by the data for nitrilotris (methyl phosphonic acid) in Table XIV and those for diethylenetriamine pentakis (methyl phosphonic

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acid) in Table XVI. Again, a somewhat greater quantity of zinc is required for the nitrilotris (methyl phosphonic acid) than for the diethylenetriamine pentakis (methyl phosphonic acid).

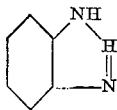
The range of pH over which zinc provides adequate protection of copper and its alloys in solutions of these aminomethyl phosphonic acid compounds is rather restricted. This is illustrated by the data in Table XVII which shows the influence of pH on the corrosion of copper in the presence of 50 p.p.m. diethylenetriamine pentakis (methyl phosphonic acid) plus 15 p.p.m. zinc. Adequate protection is not attained when the pH drops much below 7.

The inclusion of a 1,2,3-triazole or a thiol of a thiazole, oxazole or imidazole will afford greater protection of copper and its alloys over a considerably expanded pH range. Two p.p.m. 2-mercaptobenzothiazole sufficed to reduce the attack of copper in solutions of 50 p.p.m. of either nitrilotris (methyl phosphonic acid) or diethylenetriamine pentakis (methyl phosphonic acid) containing 15 p.p.m. zinc to a level such that no detectable weight loss was observed at pH values as low as 4.

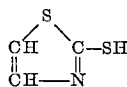
These copper inhibitors are also effective for prevention of attack on copper and its alloys by high levels of these aminomethylene phosphonates. Five p.p.m. 2-mercaptobenzotriazole sufficed to prevent detectable weight loss of copper strips or pickup of copper in 2000 p.p.m. diethylenetriamine pentakis (methyl phosphonic acid) over the pH range of 3 to 8.

Concentrated solutions of chromate and amino phosphonate should be avoided because at high concentrations chromate or dichromate will tend to oxidize the phosphonates and thereby render them ineffective. Thus, when a corrosion inhibitor which employs both chromate and amino phosphonate is used, the chromate and amino phosphonate should be fed separately into the water system.

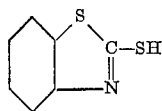
We have found that the inclusion in an amino phosphonate corrosion inhibitor of 1,2,3-triazoles or a thiol of a thiazole, an oxazole, or an imidazole as described respectively in Hatch U.S. Patents 2,941,953 and 2,742,369 (hereinafter referred to as thiols and 1,2,3-triazoles) will inhibit the phosphonate attack on copper. This composition makes a phosphonate corrosion inhibitor useful in an iron or steel water system containing copper; zinc ion may also be present in the inhibitor. The preferred 1,2,3-triazole is 1,2,3-benzotriazole of the formula



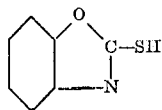
The preferred thiols of a thiazole, an oxazole, or an imidazole are 2-mercaptobenzothiazole



2-mercaptobenzothiazole

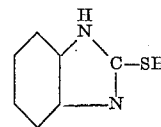


2-mercaptobenzoxazole



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and 2-mercaptobenzimidazole



Tables X and XI give the results of experiments performed as previously described and show that the amino phosphonates and water-soluble 1,2,3-triazoles or a thiol of a thiazole will inhibit the corrosion of copper.

TABLE XVIII

Influence of 1,2,3-benzotriazole on corrosion of copper in water treated with 100 p.p.m. amino tris (methylphosphonic acid) pH=8	
1,2,3-benzotriazole concentration (p.p.m.)	Weight loss (m.d.d.)
0	8.6
0.1	0.07
0.2	0
0.5	0
1	0

TABLE XIX

Influence of 2-mercaptobenzothiazole on corrosion of copper in water treated with 100 p.p.m. amino tris (methylphosphonic acid) pH=8	
2-mercaptobenzothiazole concentration (p.p.m.)	Weight loss (m.d.d.)
0	8.6
0.1	0
0.2	0
0.5	0
1	0

Where the water system containing copper is an open or once through system about 3 to 100 p.p.m. amino phosphonate, about 0.05 to 5 p.p.m. thiol or 1,2,3-triazole, and up to about 100 p.p.m. zinc ion are generally satisfactory concentrations; preferably the concentrations are about 5 to 25 p.p.m. amino phosphonate, about 0.5 to 2 p.p.m. triazole or thiol, and about 5 to 25 p.p.m. zinc ion.

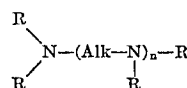
A dry composition may be made which may be fed into the water system containing copper. Such a composition would consist of about 20% to 90% amino phosphonate, about 1% to 10% thiol or 1,2,3-triazole, and up to about 79% soluble zinc salt; preferably, it would consist of about 38% to 90% amino phosphonate, about 2% to 10% thiol or 1,2,3-triazole, and up to about 60% soluble zinc salt.

It should be noted that the corrosion inhibitors of this invention may be used in conjunction with various well-known inhibitors such as the molecularly dehydrated phosphates.

Thus, it may be seen that this invention relates to amino methylphosphonic acid compounds and salts thereof as corrosion inhibitors. We do not intend to be limited to any compounds, composition, or methods disclosed herein for illustrative purposes. Our invention may be otherwise practiced and embodied within the scope of the following claims.

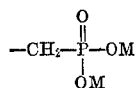
We claim:

1. A composition useful for inhibiting the corrosion of metals in a water system consisting essentially of about 10% to 80% of a water soluble zinc salt and about 20% to 90% of a compound of the general formula

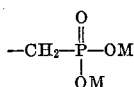


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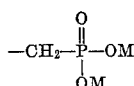
where Alk is any alkylene carbon group containing 2 to 6 carbon atoms, R may be a member selected from the group consisting of H, $-\text{CH}_2\text{COOM}$ and



M is a member selected from the group consisting of H and a cation forming a water soluble salt, $n=0-14$ provided, however, that where $n=0$ at least one of the radicals represented by R is



and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are



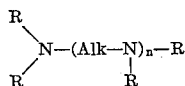
2. The composition of claim 1 wherein said compound is selected from the group consisting of ethylenediamine tetrakis (methylphosphonic acid) and water soluble salts thereof.

3. The composition of claim 1 wherein said compound is selected from the group consisting of amino tris (methylphosphonic acid) and water soluble salts thereof.

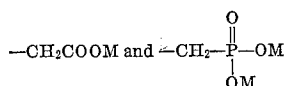
4. Composition of claim 1 wherein said zinc compound is zinc sulfate.

5. A composition useful for inhibiting the corrosion of metals in a water system which contains cuprous metals consisting essentially of:

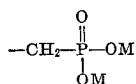
(a) about 20% to 90% of a compound of the general formula



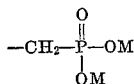
where Alk is any alkylene carbon group containing 2 to 6 carbon atoms, R may be a member selected from the group consisting of H,



M is a member selected from the group consisting of H and a cation forming a water soluble salt, $n=0-14$ provided, however, that where $n=0$ at least one of the radicals represented by R is



and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are



(b) about 1% to 10% of a compound selected from the group consisting of 1,2,3-triazoles, thiols of triazoles, thiols of oxazoles, and thiols of imidazoles, and

(c) up to about 79% water soluble zinc salt.

6. The composition of claim 5 wherein (b) is selected from the group consisting of 1,2,3-benzotriazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, and 2-mercaptobenzimidazole.

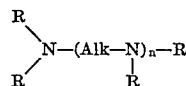
7. Composition of claim 5 wherein the amino methylphosphonic acid of (a) is ethylene diamine tetrakis (methylphosphonic acid).

8. Composition of claim 5 wherein the amino methyl-

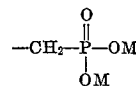
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phosphonic acid of (a) is amino tris (methylphosphonic acid).

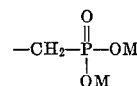
9. A method of inhibiting the corrosion of non-cuprous metals in a water system comprising maintaining in the water of said system at least about 20 p.p.m. of a compound of the general formula



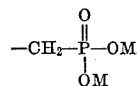
where Alk is any alkylene carbon group containing 2 to 6 carbon atoms, R may be a member selected from the group consisting of H, $-\text{CH}_2\text{COOM}$ and



M is a member selected from the group consisting of H and a cation forming a water soluble salt, $n=0-14$ provided, however, that where $n=0$ at least one of the radicals represented by R is



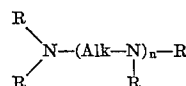
and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are



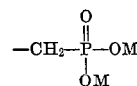
10. The method of claim 9 wherein said compound is selected from the group consisting of ethylenediamine tetrakis (methylphosphonic acid) and water soluble salts thereof.

11. The method of claim 9 wherein said compound is selected from the group consisting of amino tris (methylphosphonic acid) and water soluble salts thereof.

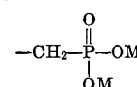
12. A method of inhibiting the corrosion of ferrous metals in a water system comprising maintaining in the water of said system about 2 to 100 p.p.m. zinc ion derived from water soluble zinc salts and about 3 to 100 p.p.m. of a compound of the general formula



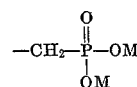
where Alk is any alkylene carbon group containing 2 to 6 carbon atoms, R may be a member selected from the group consisting of H, $-\text{CH}_2\text{COOM}$ and



M is a member selected from the group consisting of H and a cation forming a water soluble salt, $n=0-14$ provided, however, that where $n=0$ at least one of the radicals represented by R is



and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are



13. The method of claim 12 wherein said compound is selected from the group consisting of ethylenediamine tetrakis (methylphosphonic acid) and soluble salts thereof.

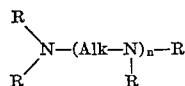
14. The method of claim 12 wherein said compound

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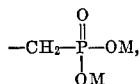
is selected from the group consisting of amino tris (methylphosphonic acid) and soluble salts thereof.

15. A method of inhibiting the corrosion of metal in a water system comprising maintaining in the water of said system:

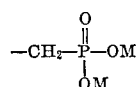
(a) about 1 to 100 p.p.m. of a compound of the general formula



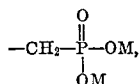
where Alk is any alkylene carbon group containing 2 to 6 carbon atoms, R may be a member selected from the group consisting of H, $-\text{CH}_2\text{COOM}$ and



M is a member selected from the group consisting of H and a cation forming a water soluble salt, $n=0-14$ provided, however, that where $n=0$ at least one of the radicals represented by R is



and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are

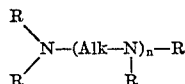


(b) about $\frac{1}{2}$ to 50 p.p.m. of a water soluble compound selected from the group consisting of chromates and dichromates, and

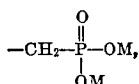
(c) about $\frac{1}{2}$ to 50 p.p.m. zinc ion derived from water soluble zinc salts.

16. A method of inhibiting metal corrosion in open, once-through water systems containing cuprous metals comprising maintaining in the water of said system:

(a) about 3 to 100 p.p.m. of a compound of the general formula

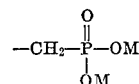


where Alk is any alkylene carbon group containing 2 to 6 carbon atoms, R may be a member selected from the group consisting of H, $-\text{CH}_2\text{COOM}$ and

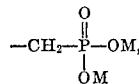


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M is a member selected from the group consisting of H and a cation forming a water soluble salt, $n=0-14$ provided, however, that where $n=0$ at least one of the radicals represented by R is



and where n is greater than zero at least $\frac{1}{2}$ of the radicals represented by R are



(b) about 0.05 to 5 p.p.m. of a compound selected from the group consisting of 1,2,3-triazoles, thiols of thiazoles, thiols of oxazoles, and thiols of imidazoles, and

(c) up to about 100 p.p.m. zinc ion derived from water soluble zinc salts.

17. A method of inhibiting metal corrosion in closed recirculating water systems containing cuprous metals comprising maintaining in the water of said system:

(a) about 500 to 5,000 p.p.m. of a compound selected from the group consisting of amino methylphosphonic acids and water soluble salts thereof, and

(b) about 0.1 to 10 p.p.m. of a compound selected from the group consisting of 1,2,3-triazoles, thiols of thiazoles, thiols of oxazoles, and thiols of imidazoles.

18. The composition of claim 1 wherein said compound is selected from the group consisting of ethylenetriamine tetrakis (methylphosphonic acid) and water soluble salts thereof.

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LEON D. ROSDOL, Primary Examiner

I. GLUCK, Assistant Examiner

U.S. Cl. X.R.

21—2.7; 106—14; 252—8.5, 387, 390, 391

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,483,133

December 9, 1969

George B. Hatch et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 33, "those" should read -- these --. Column 3, line 63, after "composition" insert -- which --. Column 4, TABLE VI, in the heading, line 3 thereof, "PHOSPHATE" should read -- PHOSPHONATE --; TABLE VII, in the heading to the first column, line 1 thereof, "E(thylenediamiue" should read -- (Ethylenediamine --; same table, in the heading to the first column, line 3 thereof, "Wt. percent)" should read -- (Wt. percent) --; same column 4, line 47, "5" should read -- 2 --; line 49, "iron" should read -- ion --; line 58, "resuls" should read -- results --. Column 7, line 15, "thiazone" should read -- thiazole --.

Signed and sealed this 3rd day of November 1970.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

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