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

(11) Publication number: **0 006 065**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **79400353.3**

(51) Int. Cl.²: **C 23 F 11/18**

(22) Date of filing: **01.06.79**

(30) Priority: **05.06.78 US 912616**

(43) Date of publication of application:
12.12.79 Bulletin 79/25

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

(71) Applicant: **CALGON CORPORATION**
Robinson Township Pennsylvania(US)

(72) Inventor: **Ralston, Paul Hotchkiss**
29 Santa Fe Drive
Bethel Pennsylvania 15102(US)

(74) Representative: **Corre, Jacques Dénis Paul et al,**
Cabinet Regimbeau 26, Avenue Kléber
F-75116 Paris(FR)

(54) **Composition and method for inhibiting corrosion.**

(57) A corrosion inhibitor composition and a method for its use in potable and industrial water treatment facilities for controlling corrosion encountered in water distribution systems such as turbine pump blades, the main distribution piping, their tributaries, and domestic and industrial piping comprises a weight ratio of $PO_4^{\equiv}$ to $Zn^{\#}$ of about 2:1 to 3:1. When added to the raw water intake or other suitable point in small but effective quantities, it passivates metal surfaces. The inhibitor is effective within a pH range of about 5-9 but is especially effective in waters having a pH of 6.5-8.

EP 0 006 065 A2

COMPOSITION AND METHOD FOR INHIBITING CORROSION

DISCLOSURE OF THE INVENTION:

This invention relates to compositions for inhibiting the corrosion of metal surfaces in contact with water, especially flowing water. More particularly, this invention relates to the prevention of corrosion of metal surfaces of equipment and piping employed in the purification and distribution of potable water supplies. This invention especially relates to a method and composition for the prevention of pitting and corrosion of metal particularly piping employed in water distribution systems.

It is known to those skilled in the art of corrosion inhibition that most commercial corrosion inhibitors exhibit one or more undesirable characteristics wholly apart from their abilities to inhibit corrosion. One of these weaknesses is a susceptibility to destruction by oxidizing or reducing agents present in the system. Another is the tendency of some corrosion inhibitors to encourage the growth of biological organisms because of their nutrient properties. Other corrosion inhibitors have the undesirable trait of depositing a relatively permanent stain on susceptible surfaces.

It is also known that iron when in contact with flowing water having a dissolved oxygen content

is prone to develop local electrolytic sites on its surface. These sites are a pecularity of the various impurities in iron either natural or introduced during the steel making process to impart desirable properties to the iron or steel. Similar corrosion mechanisms account for the dissipation of metal in contact with water. While the degree of corrosion encountered with soft aerated water or water having a high solids content may vary, the principles of this invention apply to all raw water sources.

Although the principle of employing phosphates and zinc to inhibit corrosion is not new, it was not heretofore known or appreciated that there was any criticality to the ratio of phosphate to zinc. In fact, the prior art taught away from the discovery set forth herein.

Now discovered is that a composition containing of about 2:1 to 3:1 by weight of phosphate to zinc in a concentration of a few parts per million is surprisingly successful in limiting corrosion. The satisfaction concentration range based on zinc ion content is about 0.2 to 5 ppm at the point of metering into the system. The corrosion inhibitor of this invention is further preferably injected as a liquid at the raw water intake and further it is preferred that the pH of the raw water be between 6.5 to 8, although the inhibitor is effective in waters having a pH of 5-9.

The liquid corrosion inhibitor composition comprises divalent zinc and trivalent phosphate (so-called orthophosphate PO_4^{-3}). The source of the zinc can be any non-toxic zinc salt, soluble in an aqueous carrier fluid, such as zinc oxide, zinc phosphate, zinc chloride, zinc carbonate, zinc sulfate. The phosphate is best obtained from orthophosphoric acid.

Solid sources of the orthophosphate ion may be supplied by any soluble orthophosphate salt, i.e., mono- and di-sodium acid phosphate (NaH_2PO_4, Na_2HPO_4), zinc orthophosphate, monopotassium phosphate, di-potassium phosphate and tripotassium phosphate and the like. Generally, the requisite quantities of salt comprising a source of zinc and phosphate to provide the necessary 2:1 to 3:1 ratio of phosphate to zinc is dissolved in water and the pH of the solution adjusted with a non-toxic acid such as phosphoric acid, sulfuric acid, or hydrochloric acid to solubilize the components. It should be noted that if adjusted with phosphoric acid the phosphate to zinc ratio should not depart from the critical ratio set forth herein. Also, the inhibitor content should preferably be as high as possible (40%-60%) so that shipping costs can be minimized and pumping costs reduced.

It should be understood that the composition need not be liquid but can comprise a mixture of dry salts, although the handling of this composition and its metering into the raw water intake or other suitable point is the distribution system is not believed as advantageous as a liquid.

The zinc content should be controlled so that it preferably is within the range of 0.5-2 parts per million when measured at a point remote from the injection point.

In the preferred method of employing the composition of this invention the composition is metered by any suitable equipment into the raw water immediately at the start of the treatment process. Of course, if flocculants are employed that remove the ions by precipitation or otherwise, the inhibitor composition is injected into the system subsequent to

the flocculation step. It is, however, desirable to inject the inhibitor composition as soon as practical so as to protect the downstream metals.

The details of the invention can be understood by the following illustrations which set forth the preferred mode of practicing this invention. Three zinc/orthophosphate composition with ratios of orthophosphate:Zn^{+2} of 3:1, 2:1 and 1:1 were investigated in the laboratory tests.

The steel corrosion rate data were obtained in a test unit which utilized 8 liters of Pittsburgh tap water (22 mg./l Ca^{+2}, 6 mg./l Mg^{+2}, 18 mg./l Cl^{-1}, 82 mg./l SO_4^{-2}, 10 mg./l HCO_3^{-1} at 30°C. (86°F.). The water was circulated, aerated and its temperature and pH maintained essentially constant.

The test panels were AISI 1010 steel with two 1 x 1" panels exposed in each test unit. These panels were cleaned and degreased by cleansing with a commercial detergent and rinsing in xylene and distilled water. The panels were dried, weighed on an analytical balance, and then rinsed with acetone and distilled water to yield a uniformly wetted surface. At the completion of the test, the steel panels were cleaned with inhibited acid, reweighed and the corrosion rate calculated in mils per year (mpy).

The corrosion test cycle used to evaluate the several corrosion inhibitors in the first series of investigations was a five-day laboratory test in which new inhibited Pittsburgh water was present at the beginning of the No. 1 and No. 2 days of testing while the fresh inhibited water used on the No. 3 day was not replaced during the remaining No. 4 and No. 5 days of testing. This test cycle will be referred to as the 1-1-3 cycle.

Later test cycles used a daily replacement of fresh inhibited Pittsburgh water over a four-day test period and are identified as the 1 x 4 cycle. Both of these cycles attempted to simulate many of the conditions which exist in municipal water treatment systems where large volumes of flowing water continually bring small concentrations of corrosion inhibitor to the metal pipe surfaces. However, in the laboratory test cycles, fresh inhibited water was not continually brought to the metal surface. Moreover, the ratio of metal surface to inhibited volume of water was higher than in municipal distribution systems. Therefore, these more aggressive conditions require that the laboratory inhibitor concentrations be several times higher than would be recommended for most field applications.

EXAMPLE I

A liquid containing 49.2% active components (2.9 PO_4:1 Zn^{+2}) with a specific gravity of 1.56 (at 25°C.), and a freeze point below -50°F. was prepared. The material of this example is made by mixing soft water, zinc chloride and phosphoric acid. For 1000 lbs. of product, 472 lbs. of 80% phosphoric acid are added slowly and with agitation to a mixture of 384 lbs. of $ZnCl_2$ (68.5%) and 144 lbs. of deionized water.

EXAMPLE II

Another liquid inhibitor composition was similarly prepared but adjusted in quantities of material so that a 2:1 weight ratio of $PO_4^{\equiv}$:Zn was obtained.

In Table 1, steel corrosion rate data are presented for the 1-1-3 cycle using Pittsburgh water at 30°C. and pH 6.5. Data for the five-day tests represent treatment of the water with 0, 6,

8, and 10 mg./l of the zinc/phosphate active components in the 2.9:1 and 2:1. An additional inhibitor with a weight ratio of 0.9 PO_4:1 Zn was also included in the test. As expected, all of the inhibitors were more effective in controlling corrosion at a 10 mg./l treatment rate as compared to 6 mg./l.

The corrosion rates of steel exposed to the several inhibitor systems were quite similar and ranged between 1.0-1.6 mpy for concentrations of 8 and 10 mg./l inhibitor. This represents 97.3%-98.5% inhibition compared to the untreated system. At a 6 mg./l treatment rate, corrosion rates for the several inhibitors were 2.7-3.9 mpy and represent 93.6%-95.5% inhibition of corrosion. Corrosion rates for steel exposed to the 2.9:1 and 2:1 compositions were lower than those for the 0.9:1 composition at two of the three inhibitor concentrations tested.

TABLE 1

Steel Corrosion Rates

1X Pittsburgh water-30°C. (86°F.) aerated, agitated 1-1-3 cycle-pH 6.5 ± 0.2

Inhibitor Concentration	Control	2.9:1	2:1	0.9:1
10 mg./l	56 mpy	1.2 mpy	1.3 mpy	1.5 mpy
8	67	1.6	----	1.0
6	61	2.7	2.7	3.9

Data collected at 6 mg./l (active) treatment rate of the several orthophosphate/Zn^{+2} inhibitors served as means of comparing the two laboratory test methods (the 1-1-3 cycle and the 1 x 4 cycle). The data in Table 2 does not indicate that the daily replacement of inhibitor solution (1 x 4 cycle) gave any better corrosion protection

than a test cycle that renewed the cycle only the first two days and then used the fresh third day solution for the balance of the five-day test.

The following table shows the steel corrosion rates for the two methods when the three inhibitors were evaluated at 6 mg./l of active Zn/phosphate and at a pH 6.5. Note that 0.9:1 composition performed slightly better than the others in the 1 x 4 cycle while the 2.9:1 composition appeared slightly more effective in the 1-1-3 cycle. The 2:1 composition peformed in a similar manner in both test cycles. In all cases, the experimental steel corrosion rates are in the 92.6%-95.5% inhibition range and both test methods would seem to give similar and useful corrosion rate data.

TABLE 2

Steel Corrosion Rates

pH 6.5-1X Pittsburgh water-30°C. (86°F.)-aerated, agitated 6 mg./l inhibitor (active)

Test Method	Control	2.9:1	2:1	0.9:1
1-1-3	61 mpy	2.7 mpy	2.7 mpy	3.9 mpy
1 x 4	51	3.8	2.8	2.7

It is believed an explanation for the importance of fresh inhibitor solutions in the early part of the test was found in an analytical study which followed the loss of PO_4 ion in the 1 x 4 cycle when the test waters were renewed each day. Samples of the inhibited waters were filtered through a Millipore filter (0.2 μ) daily, both before the steel panels were exposed to the new solution and after the panels had been exposed for 24 hours. Previous tests had shown that substantially all of the phosphate component was soluble at pH 6.5 so that

loss of phosphate during the test period could be related to the phosphate used in film formation and corrosion control.

In Table 3, the percent losses in phosphate (PO_4) at the end of each 24 hour period are shown for the several inhibitors.

TABLE 3

Percent Loss of PO_4

1X Pittsburgh water-30°C. (86°F.)-aerated, agitated
1 x 4 cycle, pH 6.5, 6 mg./l inhibitor (active)

Inhibitor	2.9:1	2:1	0.9:1
Day			
1	33%	45%	57%
2	17	25	23
3	10	13	15
4	11	14	15

Note that the highest amount of phosphate (and probably Zn^{+2}) were used in film formation (33%-57%) during the first 24 hour period. In the second day of testing, 17%-25% of the available phosphate was removed via film formation while 10%-15% orthophosphate was lost in the third and fourth days. In all cases, the amount of orthophosphate needed to maintain the protective film seems to be greatly reduced after two days of immersion in fresh inhibitor solutions. Thus, the daily renewal of inhibitor solution after three days would not appear to be particularly advantageous.

The higher daily percentage of PO_4 utilized (0.9:1 > 2:1 > 2.9:1) appears to be related to the lower initial PO_4 content of the inhibitor compositions 0.9:1 < 2:1 < 2.9:1.

The influence of solution pH on the effectiveness of the several Zn/orthophosphate inhibitors is shown in Table 4. These data were obtained in the 1 x 4 cycle test using 1X Pittsburgh water at 30°C.,

pH 6.5, and 6 mg./l of active Zn/orthophosphate solids.

TABLE 4

1X Pittsburgh water-30°C. (86°F.)-aerated, agitated, 1 x 4 cycle-6 mg./l inhibitor (active)

Inhibitor	Control	2.9:1	2:1	0.9:1
pH				
6.5	51 mpy	3.8 mpy	2.8 mpy	2.7 mpy
7.0	47.1	2.2	------	1.6
7.5	55.0	1.6	1.9	8.8

The corrosion rate data at the several pH levels indicate that the 0.9:1 composition is a considerably less effective corrosion inhibitor for steel in the pH 7.5 range as compared to the pH 6.5 range. On the other hand, the 2.9:1 and 2:1 compositions appear effective over the pH 6.5-7.5 range.

In preliminary screening tests, it was noted that the 0.9:1 solutions exhibited turbidity as the solution pH values approached the pH 7.5 range. Apparently, some of the zinc and/or orthophosphate present in 0.9:1 is precipitated from solution and this lower concentration of active, available inhibitor was related to the poor corrosion inhibitor performance that was noted at the pH 7.5.

To confirm this drop-out of active components of the 0.9:1 composition at pH 7.5, a series of analytical tests were conducted. Solutions containing 6 mg./l 0.9:1 (actives) were adjusted to pH 6.5 and 7.5 and filtered immediately through a 0.2 μ Millipore filter. These solutions were then analyzed for orthophosphate ion by the molybdenum blue-amino reduction method. Similar analytical data were collected for 2.9:1.

TABLE 5

Percent Orthophosphate (PO_4)

	0.9:1	2.9:1
Theoretical PO_4	2.8 mg./l	4.4 mg./l
pH 6.5	100%	100%
pH 7.5	66%	90%
PO_4 Loss	33%	10%

Many of the homes and apartment houses have water distribution lines of lead or lead alloys. Since lead is a toxic metal, corrosion inhibitors that would inhibit attack of this metal by soft, acid/neutral waters would be desirable. To determine the ability of the zinc/orthophosphate corrosion inhibitors to retard the attack on lead, we carried out continuous immersion tests.

The 8 liter system (Pittsburgh 1X water) was continually aerated and agitated at 30°C. (86°F.) and pH 6.5. The lead panels were 1 1/2 x 3" and were cleaned in 5% glacial acetic (15 min. at boil) and scrubbed lightly prior to weighing and testing.

The pick-up of lead ion in the test water was followed by atomic absorption analysis with test data collected at 10 mg./l active concentrations of the inhibitor. After five days of contact with the test water, both the 2.9:1 and the 0.9:1 compositions showed greater than 98% inhibition of lead attack (less than 0.1 mg./l Pb vs. 4.0 mg./l Pb for untreated). Thus, the increased inhibition of steel corrosion does not appear to be at the expense of a lessened inhibition of lead corrosion.

WHAT IS CLAIMED IS:

1. A method for inhibiting the corrosion of susceptible metal surfaces in contact with a stream of flowing water in potable or industrial water distribution systems comprising injecting a small but effective amount of a corrosion inhibitor upstream of the metal surfaces to be protected where said inhibitor comprises a source of zinc ions and a source of orthophosphate ions such that at the point of injection the ratio of orthophosphate to zinc ion by weight is from about 2:1 to 3:1.

2. A method according to claim 1 where said zinc ions are derived from a zinc salt selected from the group consisting of zinc chloride, zinc carbonate, zinc phosphate, zinc oxide or zinc sulfate.

3. A method according to claim 1 where said orthophosphate ions are derived from an orthophosphate containing compound selected from the group consisting of phosphoric acid, zinc orthophosphate, monosodium orthophosphate, disodium orthophosphate, trisodium orthophosphate or other soluble orthophosphate salt.

4. A method according to claim 1 where at the point of injection, the rate of injection is controlled so that in the water downstream of the injection site, the concentration of zinc ion is .2 to 10 ppm by weight of the corrosion inhibitor treated water.

5. A method according to claim 4 where the concentration is 0.5 to 2 ppm Zn^{+2}.

6. A method according to claim 1 where zinc chloride and phosphoric acid are admixed with water to provide a uniform corrosion inhibitor composition having active inhibitor components of from about 40% to 60% by weight.

7. A corrosion inhibitor composition comprising in combination a source of zinc ions derived from a zinc salt selected from the group consisting of zinc chloride, zinc phosphate, zinc oxide, zinc carbonate, and zinc sulfate and a source of orthophosphate ions derived from an orthophosphate compound selected from the group consisting of monosodium acid orthophosphate, disodium acid orthophosphate, trisodium orthophosphate, phosphoric acid and zinc orthophosphate wherein said ratio of orthophosphate to zinc is from 2:1 to 3:1 by weight.

8. A composition according to claim 7 where the zinc salt and the phosphate compound are in aqueous solution wherein the water content is from 40% to 60% by weight water, and the zinc ion is applied by zinc chloride and the phosphate ion is furnished by orthophosphoric acid.