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THE TREATMENT OF AQUEOUS SYSTEMS

The present invention relates to the treatment of aqueous systems and, more particularly, to reducing or eliminating corrosion in aqueous systems.

5           Many different types of material have been employed to prevent corrosion in aqueous systems. These include inorganic salts such as nitrites and chromates, inorganic mono- and polyphosphates and certain water-soluble polymers including naturally  
10           occurring materials such as lignins and starches as well as synthetic materials such as polyacrylates.

          Particular problems arise in cooling systems which are subject to intermittent operation or periodic shut-down. This is because the majority of corrosion  
15           inhibitors and the like only function effectively when the cooling system is in motion. Indeed, the only materials which have so far proved to be at all effective for systems involving periodic shut-down are the nitrites and, to a less extent, the chromates. Unfortunately,  
20           however, while nitrites are effective they have to be used in quite high concentrations; amounts as much as 1000 ppm are not uncommon. Such amounts present disposal

problems because these inorganic nitrites are quite toxic. Thus the maximum nitrogen content permitted by the World Health Organisation in drinking water is equivalent to only 45 mg/l of sodium nitrite.

5 However, such quantities of nitrite are ineffective for use as a corrosion inhibitor in cooling systems subject to intermittent operation.

It has now been found, according to the present invention, that it is possible to obtain effective  
10 corrosion inhibition if an inorganic nitrite, even in "non-toxic" amounts, that is to say less than 45 ppm, is used in combination in specific proportions and concentrations with a particular class of phosphonate. In fact, a synergistic effect has surprisingly been found.

15 According to the present invention there is provided a method of controlling inhibition in aqueous systems which comprises adding to the aqueous system at least one water soluble inorganic nitrite and at least one phosphonate as defined below, the concentration of phosphonate  
20 exceeding 5 ppm (wt/volume e.g. 5 mg/litre) and the weight ratio nitrite to phosphonate being from 90:10 to 5:95, in general from 80:20 to 10:90.

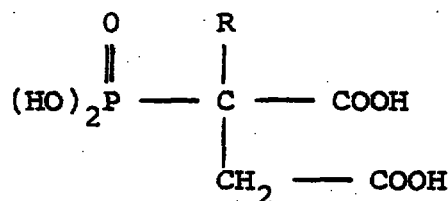
Preferred ratios are between 5:1 to 2:1, especially 4.5:1 to 3:1, and most especially about 4:1.

25 This combination is particularly useful where very corrosive conditions exist in the cooling system, for

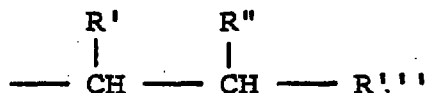
example in base exchanged water and very low water hardness systems.

The phosphonates for use in the present invention are those which contain at least 2 acid groups which are carboxylic and phosphonic acid groups, such that at least one acid group is a carboxylic acid group and at least one acid group is a phosphonic acid group, at least the said 2 acid groups being attached to carbon atoms.

The preferred phosphonates possess the general formula:



wherein R is hydrogen, alkyl, alkenyl or alkynyl having up to 4 carbon atoms; phenyl; cycloalkyl having 3 to 6 carbon atoms; benzyl; phenethyl or



wherein R' is hydrogen, alkyl having 1 to 4 carbon atoms or carboxyl, R'' is hydrogen or methyl and R''' is carboxyl or phosphonate. 2-Phosphonobutane-1,2,4-tricarboxylic acid, a commercially available material, is particularly preferred. Another preferred material is 2,4-diphosphonobutane-1,2-dicarboxylic acid. These phosphonates can be obtained by processes well known in the art, for example

as described in British Specification No 1 282 078.

While it is possible to add the materials separately it will generally be more convenient to incorporate them together in the form of a composition. Accordingly, the present invention also provides a composition suitable for addition to water to reduce or prevent corrosion which comprises at least one water soluble inorganic nitrite and at least one phosphonate as defined above, the weight ratio of nitrite to phosphonate being from 90:10 to 5:95, with the proviso that if the said ratio is from 90:10 to 5:1 the composition also contains at least one other water treatment additive.

Typically, the water-soluble nitrite is sodium nitrite but other alkali metal nitrites and also calcium nitrite are also suitable.

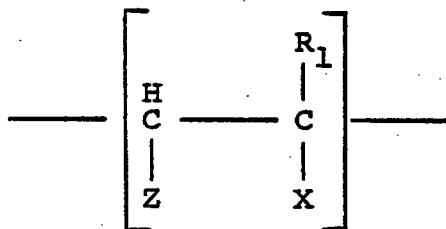
As indicated above, by incorporating the specified phosphonate with the inorganic nitrite in the specified amounts it is possible to obtain effective corrosion inhibition even though the concentration of nitrite is less than 45 ppm. Indeed, amounts as little as 10 ppm have been found to be effective. Preferably, the nitrite is present in the system in an amount from 10 to 45 ppm especially 30 to 45 ppm, and most preferably about 45 ppm. It will be appreciated, though, that in situations where health is not a factor concentrations

of up to 50 ppm or even, say, 100 ppm can be useful. The amount of phosphonate used will generally be less than that of the nitrite in order to keep costs down and, in general, amounts above 5 up to 50 ppm, particularly up to 30 ppm are suitable, amounts from 10 to 15 ppm, especially about 12 ppm, being preferred, thereby keeping down the phosphorus content in the water so as to reduce disposal problems. Amounts in excess of about 30 ppm are generally commercially unviable.

Phosphonates other than those of formula (I), in general, do not provide advantageous results and should, therefore, generally not be used in the system.

It has further been found that the presence of a water-soluble organic polymer in the system can further inhibit corrosion and, indeed, in certain cases an additional synergistic effect is found.

In general, the polymers suitable for use in the present invention are vinyl addition products possessing recurring units of the general formula:



wherein  $R_1$  represents hydrogen or alkyl of 1 to 4 carbon atoms, X represents COOH and Z represents hydrogen or COOH or X and Z together represent -CO-O-CO-.

The preferred polymers are those of methacrylic acid  
i.e. where  $R_1$  is methyl and Z is hydrogen and acrylic acid  
i.e. where  $R_1$  and Z are both hydrogen. In addition phosphinopol-  
-acrylates and methacrylates can be used; these materials can  
5 be obtained by polymerisation of (meth)acrylic acid with  
hypo-phosphorous acid. In general, the molecular weight of  
the polymers is from 500 to 100 000 and the preferred  
polymethacrylic acid has a molecular weight of about  
5 000 and the preferred polyacrylic acid a molecular weight  
10 of about 1 000. It will, of course, be appreciated that  
the polymers used may be copolymers containing recurring  
units derived from other vinyl monomers.

Not only does the presence of polymer further  
reduce corrosion but since the polymers are, in general,  
15 less expensive than the phosphonates used, by incorporating  
polymer and, in particular, by replacing some of the  
phosphonate by polymer it is possible further to reduce  
the cost of the additives. Of course, the polymer can  
be added to the system separately but it will, in general,  
20 be incorporated in a composition with the nitrite and  
phosphonate.

Although the formulae of the phosphonate and  
polymer have been given in terms of the free acid it is  
to be understood that these materials can be used in the  
25 form of an inorganic or organic salt, in particular an  
alkali metal salt such as sodium or potassium, ammonium or

a lower amine salt as well as zinc or other salts. In general, however, the use of alkali metal salts is preferred.

Typically, the polymer is used in an amount from 0.5 to 50 ppm, the preferred amount being from 2 to 10 ppm.

It will be appreciated that other low toxic materials conventionally used in water treatment can be added to the system and/or the composition including silicates, inorganic phosphates and polyphosphates and lignin derivatives as well as heterocyclic compounds for corrosion inhibition of yellow metals, such as benzotriazole, tolyltriazole and mercaptobenzothiazole.

The compositions of the present invention will normally be in the form of an aqueous solution but other possible forms include powders and briquettes.

Typically the solutions will contain 20 to 50 weight percent, especially 25 to 35 weight percent, nitrite, 2.5 to 20 weight percent, especially 5 to 10 weight percent, phosphonate and, optionally, 1 to 10 weight percent, especially 1.5 to 3 weight percent, polymer. Concentrations of other additives, such as benzotriazole, which can be present, are suitably from 0.1 to 5 weight percent, especially 0.5 to 1.5 weight percent; in order to bring the benzotriazole into solution the pH should be increased to, say, 12 to 12.5 with caustic soda. A particularly

preferred formulation contains: 30 weight % sodium  
nitrite, 16 weight % 2-phosphonobutane-1,2,4-tricarboxylic  
acid (50% active) i.e. 8 weight % of the acid, 5 weight %  
polyacrylic acid (33% active) i.e.  $1 \frac{2}{3}$  weight % of  
5 polyacrylic acid and 1 weight % benzotriazole with  
sufficient caustic soda to bring the pH of the aqueous  
solution to 12 to 12.5. Naturally the amount of the  
formulation used will depend upon the nature of the system  
and of the water but with this specific formulation  
10 amounts from 100 to 200, especially 150 to 200,ppm are  
generally suitable.

The following examples further illustrate the  
present invention. In these examples two different types  
of tests were employed, namely a circulatory test and a  
15 test to simulate intermittent flow operations.

In the circulatory test a laboratory test  
apparatus was used in which water is circulated etc by  
means of a pump from a reservoir maintained at a  
temperature of  $54^{\circ}\text{C}$  with a heater and thermostat. The  
20 water passes through a glass tube assembly holding the  
metal test specimens (flow rate 2 ft/sec; 0.61 m/sec) and  
then is returned to the reservoir entraining air as it  
does so in order to keep the water saturated with oxygen  
as it would be in a typical open recirculating cooling  
25 system.

Water lost by evaporation (concentration factor  
1.7) is replaced from an elevated tank through a float  
control to maintain a constant volume in the system.

In each test treatment is applied at three times normal dose for 24 hours in order to passivate the metals; then the water is diluted to the normal dose for the remainder of the test. Each test is for a minimum of 3 days, the test specimens being cleaned before and after each run to find the weight loss which is then calculated to show the average corrosion rate in mils (0.025 mm) per year.

The water used in the tests was Widnes mains water, 75 ppm calcium hardness, 90 ppm. M. alkalinity.

In the following tests the combined dosage of additives in the system was 30 ppm. "In line" or "High flow" represents the corrosion rate in the tube while "low flow/static areas" represents the corrosion rate in the body of the reservoir.

The results clearly show that the chosen phosphonates in combination with the nitrite do exhibit synergism.

Tests at 54°C

| Additive composition, % by weight |                                               | Corrosion rate, mils/year<br>(mm/year) |                                          |
|-----------------------------------|-----------------------------------------------|----------------------------------------|------------------------------------------|
| Sodium Nitrite                    | 2-Phosphonobutane<br>1,2,4-tricarboxylic acid | Mild Steel (in Line)                   | Mild Steel (in low<br>flow/static areas) |
| 100                               | -                                             | 17.0 (0.425)                           | 43.0 (1.075)                             |
| 85                                | 15                                            | 10.0 (0.25)                            | 32.0 (0.8)                               |
| 66.67                             | 33.33                                         | 5.0 (0.125)                            | 14.0 (0.35)                              |
| 33.33                             | 66.67                                         | 2.0 (0.05)                             | 2.0 (0.05)                               |
| 15                                | 85                                            | 2.0 (0.05)                             | 3.0 (0.075)                              |
| -                                 | 100                                           | 4.0 (0.1)                              | 6.0 (0.15)                               |

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Further tests were carried out in a similar manner, with the following results:

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| Ex. No.                   | Additive, ppm (in system) |      |     |      |      |      | Corrosion rate, mils/year (mm/year) |                            |                        |
|---------------------------|---------------------------|------|-----|------|------|------|-------------------------------------|----------------------------|------------------------|
|                           | NaNO <sub>2</sub>         | PBTC | PAA | BZT  | TTZ  |      | Mild Steel (High flow rate)         | Mild Steel (Low flow rate) | Brass (High flow rate) |
| Tests carried out at 54°C |                           |      |     |      |      |      |                                     |                            |                        |
| 1                         | -                         | -    | -   | -    | -    | -    | 56.0 (1.4)                          | 37.0 (0.925)               | 1.0 (0.025)            |
| 2                         | 25                        | 5    | -   | -    | -    | -    | 10.0 (0.25)                         | 32.0 (0.8)                 | -                      |
| 3                         | 20                        | 10   | -   | -    | -    | -    | 5.0 (0.125)                         | 14.0 (0.35)                | -                      |
| 4                         | 10                        | 20   | -   | -    | -    | -    | 2.0 (0.05)                          | 2.0 (0.05)                 | -                      |
| 5                         | 5                         | 25   | -   | -    | -    | -    | 2.0 (0.05)                          | 3.0 (0.075)                | -                      |
| 6                         | 40                        | 8    | -   | -    | -    | -    | 3.4 (0.085)                         | 6.2 (0.155)                | -                      |
| 7                         | 40                        | 8    | 3.0 | 0.75 | 0.75 | 0.75 | 3.1 (0.0775)                        | 5.4 (0.135)                | 0.4 (0.01)             |
| 8                         | 40                        | 6    | 3.0 | 0.75 | 0.75 | 0.75 | 5.3 (0.1325)                        | 21.4 (0.535)               | 0.2 (0.005)            |
| 9                         | 30                        | 4.5  | 3.0 | 0.75 | 0.75 | 0.75 | 17.5 (0.4375)                       | 31.5 (0.7875)              | 0.1 (0.0025)           |
| 10                        | 40                        | 8    | 2.5 | 0.75 | 0.75 | 0.75 | 3.4 (0.085)                         | 4.3 (0.1075)               | 0.1 (0.0025)           |
| 11                        | 45                        | 12   | 2.5 | 0.75 | 0.75 | 0.75 | 2.7 (0.0675)                        | 1.9 (0.0475)               | 0.1 (0.0025)           |

Continued

| Ex.                                                         | Additive, ppm (in system) |      |     |      | Corrosion rate, mils/year (mm/year) |                             |                            |                        |
|-------------------------------------------------------------|---------------------------|------|-----|------|-------------------------------------|-----------------------------|----------------------------|------------------------|
| No.                                                         | NaNO <sub>2</sub>         | PBTC | PAA | BZT  | TTZ                                 | Mild Steel (High flow rate) | Mild Steel (Low flow rate) | Brass (High flow rate) |
| Test at 60°C                                                |                           |      |     |      |                                     |                             |                            |                        |
| 12                                                          | 46                        | 13.5 | 2.5 | 1.5  | -                                   | 2.1 (0.0525)                | 2.5 (0.0625)               | 0.2 (0.005)            |
| Test at 60°C                                                |                           |      |     |      |                                     |                             |                            |                        |
| 13                                                          | 45                        | 12   | 2.5 | 0.75 | 0.75                                | 3.2 (0.08)                  | 4.1 (0.1025)               | 0.1 (0.0025)           |
| Test carried out at 54°C; base exchanged Widnes mains water |                           |      |     |      |                                     |                             |                            |                        |
| 14                                                          | 45                        | 12   | 2.5 | 0.75 | 0.75                                | 2.5 (0.0625)                | 1.7 (0.0425)               | 0.1 (0.0025)           |
| 15                                                          | -                         | -    | -   | -    | -                                   | 89.0 (2.225)                | 62.0 (1.55)                | 1.0 (0.025)            |

PBTC = 2-phosphobutane-1,2,4-tricarboxylic acid BZT = Benzotriazole

PAA = polyacrylic acid - molecular weight 1000 TTZ = Toly1 triazole

The above examples illustrate the usefulness of the present invention. Examples 7-11 (inclusive) show the effect of varying the phosphonate ratio and phosphonate concentration; it can be seen from Example 9 that when the concentration of phosphonate is reduced below the permitted minimum, the corrosion rate increases significantly. Examples 6 and 7 show the effect of the addition of other additives. Examples 12, 13 and 14 illustrate the effectiveness of the nitrite/phosphonate combination as a corrosion inhibitor under very severe corrosive conditions.



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CLAIMS

1. A method of controlling corrosion in an aqueous system which comprises adding to the system at least one water soluble inorganic nitrite and at least one phosphonate which contains at least two acid groups which are carboxylic and phosphonic acid groups such that at least one acid group is a carboxylic acid group and at least one acid group is a phosphonic acid group, at least the said two acid groups being attached to carbon atoms, the concentration of phosphonate exceeding 5 ppm weight per volume and the weight ratio of nitrite to phosphonate being from 90:10 to 5:95.

2. A method according to Claim 1 in which the weight ratio of nitrite to phosphonate is from 4.5:1 to 15:85.

3. A method according to Claim 1 in which the weight ratio of nitrite to phosphonate is from 80:20 to 10:90.

4. A method according to Claim 1 in which the weight ratio of nitrite to phosphonate is from 5:1 to 2:1.

5. A method according to Claim 1 in which the weight ratio of nitrite to phosphonate is from 4.5:1 to 3:1.

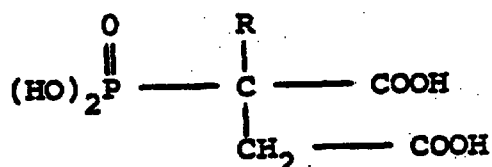
6. A method according to any one of the preceding claims in which the aqueous system is a base exchanged water or a water of very low water hardness.

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7. A method according to any one of the preceding claims in which the phosphonate has the general formula:



wherein R is hydrogen, alkyl, alkenyl or alkynyl having up to 4 carbon atoms; phenyl; cycloalkyl having 3 to 6 carbon atoms; benzyl; phenethyl or



wherein R' is hydrogen, alkyl having 1 to 4 carbon atoms or carboxyl, R'' is hydrogen or methyl and R''' is carboxyl or phosphonate.

10 8. A method according to Claim 7 in which the phosphonate is 2-phosphonobutane-1,2,4-tricarboxylic acid or 2,4-diphosphonobutane-1,2-dicarboxylic acid or a salt thereof.

9. A method according to any one of the preceding claims in which the concentration of nitrite is less than 45 ppm weight per volume.

10. A method according to Claim 9 in which the concentration of nitrite is from 10 to less than 45 ppm.

11. A method according to any one of the

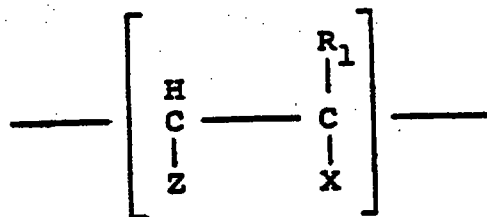


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preceding claims in which the concentration of phosphonate is from 10 to 15 ppm weight per volume.

12. A method according to any one of the preceding claims which comprises adding also a water soluble organic polymer.

13. A method according to Claim 12 in which the organic polymer possesses recurring units of the general formula:



wherein  $R_1$  represents hydrogen or alkyl of 1 to 4 carbon atoms, X represents COOH and Z represents hydrogen or COOH or X and Z together represent -CO-O-CO-.

14. A method according to Claim 13 in which the polymer is a polymer of acrylic or methacrylic acid.

15. A method according to Claim 12 in which the organic polymer is a phosphinopolyacrylate or methacrylate.

16. A method according to any one of Claims 12 to 15 in which the polymer has a molecular weight from 500 to 100 000.

17. A method according to any one of Claims 12 to 16 in which the polymer is added in an amount from 0.5



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to 50 ppm weight per volume.

18. A method according to Claim 17 in which the polymer is added in an amount from 2 to 10 ppm weight per volume.

5 19. A method according to any one of the preceding claims in which the aqueous system is a cooling water system.

20. A method according to Claim 1 substantially as hereinbefore described.

10 21. A method according to Claim 1 substantially as described in any one of Examples 3 to 8 and 10 to 14.

22. A composition suitable for addition to water which comprises at least one water soluble inorganic  
15 nitrite and at least one phosphonate as defined in Claim 1, the weight ratio of nitrite to phosphonate being from 90:10 to 5:95, with the proviso that if the said ratio is from 90:10 to 5 : 1 the composition also contains at least one other water treatment additive.

20 23. A composition according to Claim 22 in which the said other water treatment additive is a silicate, inorganic phosphate or polyphosphate, a lignin derivative or a heterocyclic compound.

24. A composition according to Claim 22 or 23  
25 which is in the form of an aqueous solution which contains 20 to 50 weight percent of nitrite and 2.5 to 20 weight



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percent of phosphonate.

25. A composition according to Claim 24 which contains 25 to 35 weight percent of nitrite and 5 to 10 weight percent of phosphonate.

5 26. A composition according to any one of Claims 22 to 25 in which the weight ratio of nitrite to phosphonate is as defined in any one of Claims 3 to 5.

27. A composition according to any one of Claims 22 to 25 in which the weight ratio of nitrite to  
10 phosphonate is as defined in Claim 2.

28. A composition according to any one of Claims 22 to 27 in which the phosphonate is as defined in Claim 7 or 8.

29. A composition according to any one of  
15 Claims 22 to 28 which also contains a water soluble organic polymer.

30. A composition according to Claim 29 in which the organic polymer is as defined in any one of Claims 13 to 15.

20 31. A composition according to Claim 29 or 30 which contains 1 to 10 weight percent of polymer.

32. A composition according to Claim 31 which contains 1.5 to 3 weight percent of polymer.

33. A composition according to any one of  
25 Claims 22 to 32 which comprises 30 weight percent sodium nitrite, 8 weight percent

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2-phosphonobutane-1,2,4-tricarboxylic acid, 1 2/3 weight percent polyacrylic acid and 1 weight percent benzotriazole, the composition being adjusted to a pH of 12 to 12.5 with caustic soda.

- 5                    34.    A composition according to Claim 22 substantially as hereinbefore described.
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