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Description

The present invention is related to zinc-containing corrosion inhibitor treatments and treatment compositions. The ability of zinc to inhibit the corrosion of ferrous metals is, indeed, well known. Accordingly, soluble zinc salts are vital ingredients of many corrosion treatment programs. For example, U.S. 4,089,796 to *Harris et al* discloses a corrosion inhibiting composition comprising zinc and hydrolyzed polymaleic anhydride or soluble salt thereof and benzotriazole. Other exemplary patents disclosing such zinc containing treatments are U.S. 3,432,428 to *Wirth et al* and U.S. 4,120,655 to *Crambes et al*.

10 An art-recognized major problem encountered with zinc-containing treatments, particularly in cooling water, is the uncontrolled precipitation of zinc salts; because, to be effective, the zinc must reach the surfaces to be protected in a soluble form. For example, the use of orthophosphate in combination with zinc as a cooling water treatment is well known as evidenced by U.S. 2,900,222 to *Kahler et al* wherein phosphate, chromate and zinc are used in combination. The orthophosphate can
15 be provided as an actual addition, or as a reversion product from any one of complex inorganic phosphate, organic phosphate or organic phosphonate. When orthophosphate and zinc are both present in the water, zinc phosphate precipitation becomes a concern. Whether or not orthophosphate is present, the zinc could precipitate in other forms, for example, as zinc hydroxide or zinc silicate. The solubility of the various salts, that is, the retention of the respective salt constituents in ionic form,
20 depends on such factors as water temperature and pH and ion concentrations. *Wirth et al* states that although water temperatures can vary from 32° to 200°F (0 to 93.3°C), lower temperatures of 32° to 80°F (0 to 26.7°C) are preferred because "zinc tends to remain in solution better in cooler waters." This patent further states that alkaline waters, particularly above about pH 7.5, are relatively undesirable because "the dissolved zinc tends to deposit out or drop out much more rapidly in alkaline
25 water". Similarly, *Crambes et al* points out that zinc salts are unstable in neutral or alkaline water and will precipitate with phosphates. Thus, if any of these conditions are present, the aqueous medium becomes prone to zinc precipitation. Because of the formation of this zinc scale, many of the surfaces in contact with the aqueous medium will foul and the amount of effective (soluble) corrosion inhibitor present in the aqueous medium can be significantly reduced.

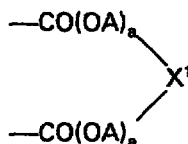
30 DE—A—2643242 (Kutita Water Industries Ltd) is directed to an improved method of inhibiting scale employing polymers containing a structural unit that is derived from a monomer having an ethylenically unsaturated bond and which has one or more carboxyl radicals, at least a part of said carboxyl radicals being modified as represented by the general formula:—

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or

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45 wherein OA is an oxyalkylene radical having 2 to 4 carbon atoms, X is a hydroxyl radical, an alkoxy radical having 1 to 4 carbon atoms or a monovalent phosphate radical, X¹ is a bivalent phosphate radical and a is a positive integer. When corrosion resistance is also required, conventional water treating agents are also required, such as polyphosphoric acids, phosphonic acids, orthophosphoric acid, organic phosphoric esters or polyvalent metal salts such as zinc or nickel salts, are also necessary.

50 A very wide range of polymers is included within the scope of DE—A—2643242. Thus the polymer may be derived from acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, cinnomic acid or vinylbenzoic acid, preferably acrylic acid, methacrylic acid, maleic acid and fumaric acid. The specific polymers illustrated are generally terpolymers composed of optional units such as esters of (meth)acrylic acid such as methyl(meth)acrylate, ethyl(meth)acrylate,
55 butyl(meth)acrylate, diethylamino ethyl(meth)acrylate etc; styrene compounds such as styrene, methyl styrene, etc; fatty acid esters of vinyl alcohols, etc; etc.

The specific examples of DE—A—2643242 illustrate the use of six terpolymers in conjunction either with one of the aforementioned phosphorus compounds or with both such a phosphorus compound and a zinc salt. These specifically exemplified terpolymers have been found not to be
60 efficacious in retaining a corrosion-inhibiting amount of zinc in soluble form in an aqueous system.

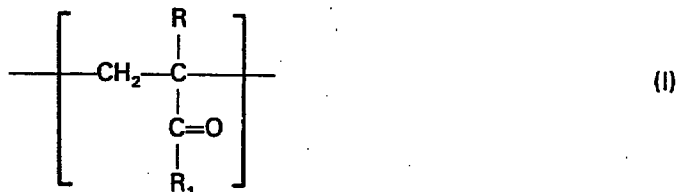
There has existed for a long time the need for a zinc-containing corrosion inhibitor treatment which overcomes the above-noted problems, and the present invention is considered to fulfill that need.

Although the present invention is considered to have general applicability to any aqueous system where zinc precipitation is a problem, it is particularly useful in cooling water systems. Accordingly, the
65 invention will hereinafter be described as it relates to cooling water systems.

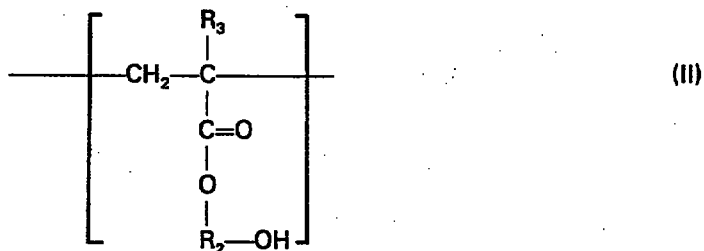


According to the present invention, a corrosion inhibitor treatment for metal surfaces exposed to an aqueous medium comprises (i) water-soluble zinc compound and (ii) a particular type of water-soluble polymer comprising moieties derived from an acrylic acid compound and moieties of hydroxylated lower alkyl acrylate (HAA). The treatment could additionally comprise (iii) water-soluble orthophosphate and (iv) water-soluble chromate. It was discovered that, although the polymer demonstrated no significant activity alone as a corrosion inhibitor, when it was combined with a zinc-containing treatment the various ionic constituents of the treatment were unexpectedly retained in their soluble form and a corresponding increase in corrosion inhibiting activity was observed. The present invention is accordingly also considered to be related to a method for inhibiting the formation of zinc scale in an aqueous medium.

The polymers according to the present invention are those effective for the purpose which comprise moieties derived from an acrylic acid compound (AA), i.e.,



where R is hydrogen or a lower alkyl of from 1 to 3 carbon atoms and $\text{R}_1 = \text{OH}$, NH_2 or OM , where M is a water-soluble cation, e.g., NH_4 , alkali metal (K, Na), etc; and moieties of an hydroxylated lower alkyl ($\text{C}_2 - \text{C}_6$) acrylate (HAA) as represented, for example, by the formula:



where R_3 is H or lower alkyl of from 1 to 3 carbon atoms, and R_2 is a lower alkylene having from 2 to 6 carbon atoms.

In terms of mole ratios, the polymers are considered, most broadly, to have a mole ratio of AA:HAA of from 1:4 to 36:1. This mole ratio is preferably 1:1 to 11:1, and most preferably 1:1 to 5:1. The only criteria that is considered to be of importance with respect to mole ratios is that it is desirable to have a copolymer which is water-soluble. As the proportion of hydroxylated alkyl acrylate moieties increases, the solubility of the copolymer decreases. It is noted that, from an efficacy point of view, the polymers having a mole ratio of AA:HAA of 1:1 to 5:1 were considered the best.

The polymers could have a molecular weight of from 1,000 to 50,000 with from 2,000 to 6,000 being preferred.

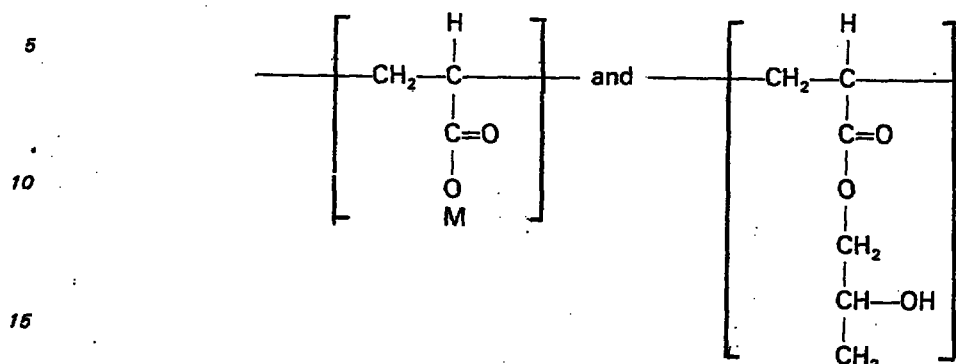
The polymers utilized in accordance with the invention can be prepared by vinyl addition polymerization or by treatment of an acrylic acid or salt polymer. More specifically, acrylic acid or derivatives thereof or their water soluble salts, e.g., sodium, potassium, ammonium, etc. can be copolymerized with the hydroxy alkyl acrylate under standard copolymerization conditions utilizing free radical initiators such as benzoyl peroxide, azobisisobutyronitrile or redox initiators such as ferrous sulfate and ammonium persulfate. The molecular weights of the resulting copolymer can be controlled utilizing standard chain control agents such as secondary alcohols (isopropanol), mercaptans, halocarbons, etc. Copolymers falling within the scope of the invention are commercially available from, for example, National Starch Company.

The hydroxy alkyl acrylate can be prepared by the addition reaction between the acrylic acid or its derivatives or water soluble salts and the oxide of the alkyl derivative desired. For example, the preferred monomer of the present invention is the propyl derivative. Accordingly, to obtain the hydroxylated monomer, acrylic acid is reacted with propylene oxide to provide the hydroxypropyl acrylate monomer.

The polymers of the invention may also be prepared by reacting a polyacrylic acid or derivatives thereof with an appropriate amount of an alkylene oxide having from 2 to 6 carbon atoms such as ethylene oxide, propylene oxide and the like. The reaction takes place at the COOH or COM group of the moieties to provide the hydroxylated alkyl acrylate moiety.

The polymer prepared either by copolymerization of AA with hydroxy propyl acrylate (HPA) or

reaction of AA with propylene oxide would be composed of units or moieties having the structural formulas:



where M is as earlier defined.

20 Illustrative water-soluble zinc compounds which are considered to be suitable for use in accordance with the present invention are zinc oxide, zinc acetate, zinc chloride, zinc formate, zinc nitrate, zinc sulphate, zinc borate, zinc chromate, zinc dichromate, etc.

As already noted above, the treatment could further comprise orthophosphate. Indeed, the use of zinc and orthophosphate together as a corrosion inhibition treatment is well known. It has also already been noted that the orthophosphate could be provided as an actual addition product, e.g., sodium

25 orthophosphate, or as a precursor compound such as complex inorganic phosphates, organic phosphates or organic phosphonates which revert to orthophosphate in the water.

Illustrative examples of orthophosphate as an actual addition are monosodium phosphate, and monopotassium phosphate. Any other water-soluble orthophosphate or phosphoric acid would also be considered to be suitable.

30 The complex inorganic phosphates are exemplified by sodium pyrophosphate, sodium tripolyphosphate, sodium tetrphosphate, sodium septaphosphate, sodium decaphosphate and sodium hexametaphosphate. Either the corresponding potassium or ammonium salts or the corresponding molecularly dehydrated phosphoric acids such as metaphosphoric acid or pyrophosphoric acid are considered to be suitable.

35 The organic phosphonates are exemplified by aminotrimethylene phosphonic acid, hydroxyethylidene diphosphonic acid and the water-soluble salts thereof.

Organic phosphates are exemplified in U.S. 3,510,436.

The amount of each constituent added to the cooling water will, of course, be an effective amount for the purpose and will depend on such factors as the nature and severity of the corrosion problem

40 being treated, the temperature and pH of the cooling water and the type and amount of precipitation-prone ions present in the water.

In terms of active zinc ion, as little as 0.5 parts of zinc per million parts (ppm) of cooling water are believed to be effective in certain instances, with 2 ppm being preferred. Based on economic considerations, the amount of zinc ion added could be as high as 25 ppm, with 10 ppm representing

45 the preferred maximum.

In terms of active polymer, as little as 0.5 ppm polymer is considered to be effective, while 2 ppm is the preferred minimum. Based on economic considerations, the polymer could be fed in amounts as high as 200 ppm, with 50 ppm representing the preferred maximum.

50 In terms of active product added, the orthophosphate or precursor compound thereof could be fed in an amount as low as 1 ppm, with 2 ppm representing the preferred minimum. Based on economic considerations, the maximum amount is considered to be 200 ppm. However, 50 ppm is considered to be the preferred maximum.

Methods for feeding corrosion inhibitors to cooling water are well known in the art such that details thereof are not considered necessary. However, due to rather severe stability problems experienced when the polymer was stored at high concentrations with the remaining components, a

55 two or three-barrel treatment is recommended.

Compositions according to the present invention could comprise on a weight basis:

- (i) 1 to 95% of water-soluble zinc compound, and
- 60 (ii) 5 to 99% AA/HAA polymer of the total amount of zinc compound and polymer. The preferred relative proportions are 4 to 85% water-soluble zinc compound and 15 to 96% polymer; while it is most preferred that the compositions comprise 5 to 70% zinc compound and 30 to 95% polymer.

65 In those instances where orthophosphate is also present, compositions according to the present invention could comprise on a weight basis:

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- (i) 1 to 95% water-soluble zinc compound
 (ii) 5 to 99% AA/HAA polymer, and
 (iii) 1 to 95% orthophosphate (or precursor thereof) of the total amount of zinc compound, polymer and orthophosphate.

The preferred relative proportions are 5 to 85% zinc compound, 15 to 95% polymer and 5 to 85% orthophosphate. The most preferred relative proportions are 10 to 60% zinc compound, 15 to 80% polymer and 10 to 60% orthophosphate.

The cooling water preferably will have a pH of 6.5 to 9.5. Since zinc precipitation problems most commonly occur at pH's above about 7.5, the most preferred pH range is from 7.5 to 9.5.

Examples

Illustration of zinc precipitation problem

Example 1

As noted above, an art-recognized major problem encountered with zinc-containing treatments, particularly in cooling water, is the uncontrolled precipitation of zinc salts from the water. Even in the absence of orthophosphate in the water, the zinc can form precipitates such as zinc hydroxide.

This point is illustrated by the zinc-solubility results of several tests conducted in water containing no orthophosphate. The tests were conducted, inter alia, to determine the solubility of zinc in the test water as a function of pH.

The following aqueous test solutions were first prepared:

Solution A: 1,000 ppm Zn^{++} obtained from
 0.27 gram $Zn \cdot SO_4 \cdot H_2O$ 100 ml

SCW₇: 170 ppm Ca as $CaCO_3$,
 110 ppm Mg as $CaCO_3$,
 15 ppm SiO_2

The tests were conducted using the following procedure:

1. Prepare SCW₇ (detailed in Example 5 below) and adjust its pH to 4 with concentrated HCl.
2. To 2,000 ml of the above solution, add the required amount of Solution A with stirring.
3. Add 100 ml of the solution from step 2 to a bottle and agitate.
4. Slowly adjust the pH to the desired value with dilute NaOH solution and record pH.
5. Place the samples in an oven at the required temperature for 24 hours, after which time, filter through a 0.2 micron millipore filter.
6. Analyze the filtrate for soluble zinc and record final pH.

The results of these tests are reported below in Tables 1 and 2 in terms of soluble zinc (ppm) remaining after 24 hours at various final pH values.

TABLE 1
 Zinc precipitation as function of pH

Conditions: Initial Zinc=2 ppm as Zn^{++}
 $T=120^\circ F$ ($48.9^\circ C$)
 Time=24 hours

	pH	Soluble zinc (ppm)
50	7.62	0.8
	7.70	0.5
55	7.92	0.5
	8.12	0.2
	8.21	0.1
60	8.35	0.2
	8.42	0.1
65	8.76	0.0

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TABLE 2
Zinc precipitation as function of pH

Conditions: Initial Zinc=10 ppm as Zn^{++}
T=120°F (48.9°C)
Time=24 hours

	pH	Soluble zinc (ppm)
5	7.15	8.2
10	7.25	7.8
15	7.36	8.2
	7.46	8.0
20	7.50	7.8
	7.56	5.4
	7.67	1.8
25	7.70	1.6
	8.05	0.4
30	8.10	0.2
	8.22	0.4
	8.65	0.2
35	9.06	0.0

Example 2

The problem of zinc precipitation in cooling water is further illustrated by the zinc-solubility results of additional tests similar to those in Example 1, but conducted in water containing both zinc ions and orthophosphate ions.

The following aqueous test solutions were first prepared:

Solution A: 1,000 ppm PO_4^{-3} , obtained from
0.400 gram $Na_3PO_4 \cdot 12H_2O$ /100 ml

Solution B: 1,000 ppm Zn^{+2} , obtained from
0.27 gram $ZnSO_4 \cdot H_2O$ /100 ml

SCW₇: Same as Example 1

The following procedure was used:

1. Prepare SCW₇ and adjust its pH to 4 with HCl solution.
2. To 2,000 ml of the above solution, add the appropriate amount of Solution A, followed by the appropriate amount of Solution B with agitation.
3. Add 100 ml of the solution from step 2 to a bottle and adjust the pH to 7.5 with dilute NaOH with agitation.
4. Place the samples in an oven for 24 hours at the appropriate temperature.
5. After the 24 hour period, filter the solution through a 0.2 micron millipore filter.
6. Analyze the filtrate for Zn^{+2} and PO_4^{-3} .

The results of these tests are reported below in Tables 3 and 4 in terms of ppm soluble zinc and ppm soluble phosphate remaining after 24 hours at various final pH values.

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TABLE 3
Zinc precipitation as function of pH

Conditions: Initial Zinc=5 ppm as Zn^{++}
Initial $o-PO_4$ =10 ppm
T=120°F (48,9°C)
Time=24 hours

	pH	Soluble zinc (ppm)	Soluble PO_4 (ppm)
10	7.0	3	6
	7.5	0.5	5
15	8.0	0.1	3.7
	8.5	0.1	2.4
20	9.0	0.1	1.2

TABLE 4
Zinc precipitation as function of pH

Conditions: Initial Zinc=10 ppm as Zn^{++}
Initial $o-PO_4$ =5 ppm
T=120°F (48,9°C)
Time=24 hours

	pH	Soluble zinc (ppm)	Soluble PO_4 (ppm)
30	7.5	3.3	0.8
	8.0	0.2	0.7
35	9.0	0.1	0.1

Efficacy in retaining soluble zinc-containing treatments Example 3

A series of tests were conducted to determine the efficacy of various materials in retaining zinc-containing corrosion inhibition treatments in a soluble form. After all, the corrosion inhibition efficacy of such treatments will, for the most part, depend on the constituents remaining soluble.

The test water contained both zinc and orthophosphate ions, and the test procedures were the same as in Example 2 but for a few different steps as follows:

1. Solution C comprising 1,000 ppm of active treatment was also used.
3. Add 100 ml of solution from step 2 to a bottle, add the appropriate quantity of treatment solution (1 ml=10 ppm), and adjust pH to appropriate value with dilute NaOH with agitation.

The results of the tests were calculated in terms of % increase in retention of soluble zinc ions and soluble phosphate ions vs. an untreated solution using the following equation:

$$\% \text{ Retention} = \frac{100 \times \text{Sol. } PO_4 \text{ at } T=24 \text{ hrs} - \text{Sol. } PO_4 \text{ in control at } T=24 \text{ hrs.}}{\text{Sol. } PO_4 \text{ in control at } T=0 \text{ hrs} - \text{Sol. } PO_4 \text{ in control at } T=24 \text{ hrs.,}}$$

where Sol. PO_4 =soluble PO_4 in ppm. Of course, a similar equation was used for zinc calculations.

The results of these tests are reported below in Tables 5 and 6. In addition to testing various AA/HPA copolymers in accordance with the present invention, various commercial polyacrylic acids (PAA) were also tested.

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TABLE 5
Zinc and phosphate retention
Conditions: Initial Zinc=10 ppm as Zn^{++}
Initial $o-PO_4=5$ ppm
 $T=120^\circ F$ (48.9°C)
Time=24 hours

Treatment	Mole ratio AA:HPA	Molecular weight	Water pH	Dosage (ppm actives)	Soluble zinc retained (ppm)	Soluble PO_4 retained (ppm)	% Increase in zinc retention (vs. control)	% Increase in PO_4 retention (vs. control)
None	—	—	7.5	—	3.3	0.8	—	—
PAA-Commercial	—	5,000	7.5	5	2.3	0.8	-15	0
"	—	5,000	7.5	10	2.3	1.0	-15	5
"	—	5,000	7.5	20	2.4	1.2	-13	10
PAA-Commercial	—	90,000	7.5	5	2.2	0.7	-16	0
"	—	90,000	7.5	10	2.5	1.0	-12	5
"	—	90,000	7.5	20	1.9	1.4	-21	14
PAA-Commercial	—	<1,000	7.5	5	2.9	0.9	-6	2
"	—	<1,000	7.5	10	3.4	1.4	1	14
"	—	<1,000	7.5	20	3.0	1.2	-4	10
AA/HPA	1.8:1	6,000	7.5	2.5	3.7	1.2	6	10
"	1.8:1	6,000	7.5	5	8.6	4.2	79	81
AA/HPA	3:1	6,000	7.5	2.5	1.3	1	-30	5
"	3:1	6,000	7.5	5	8.6	4.4	79	86
AA/HPA	9.9:1	1K-2K*	7.5	5	6.8	4.7	52	93
"	9.9:1	1K-2K	7.5	10	8.6	5.1	79	102
AA/HPA	9.9:1	6K-10K	7.5	5	8.8	4.7	82	93
"	9.9:1	6K-10K	7.5	10	7.2	4.8	58	95
"	19.8:1	2K-6K	7.5	5	5.4	2.8	31	48
"	19.8:1	2K-6K	7.5	10	5.6	3.2	34	57
"	36:1	2K-6K	7.5	5	6.8	4.3	52	83
"	36:1	2K-6K	7.5	10	8.8	4.8	82	95

*K=1,000



TABLE 6
Zinc and phosphate retention

Conditions: Initial Zinc=5 ppm as Zn^{++}
Initial $o-PO_4=10$ ppm
 $T=120^\circ F$ ($48.9^\circ C$)
Time=24 hours

Treatment	Mole ratio AA:HPA	Molecular weight	Water pH	Dosage (ppm actives)	Soluble zinc retained (ppm)	Soluble PO_4 retained (ppm)	% Increase in zinc retention (vs. control)	% Increase in PO_4 retention (vs. control)
None	—	—	7.0	—	3	6	—	—
AA/HPA	1.8:1	6,000	7.0	2.5	4.6	9.2	80	80
"	1.8:1	6,000	7.0	5	4.9	9.5	95	87
"	3:1	6,000	7.0	2.5	4.2	8.9	60	72
"	3:1	6,000	7.0	5	5	9.4	100	85
"	9.9:1	1K-2K*	7.0	2.5	4.9	9.3	95	82
"	9.9:1	1K-2K	7.0	5	5.0	9.4	100	85
"	9.9:1	6K-10K	7.0	2.5	3.2	6.8	10	20
"	9.9:1	6K-10K	7.0	5	5.0	9.3	100	82
"	19.8:1	2K-6K	7.0	2.5	4.3	8.3	65	57
"	19.8:1	2K-6K	7.0	5	4.7	8.9	85	72
"	36:1	2K-6K	7.0	2.5	4.3	8.5	65	62
AA/HPA	36:1	2K-6K	7.0	5	4.4	8.5	70	62
None	—	—	8.0	—	0.1	3.7	—	—
AA/HPA	1.8:1	6,000	8.0	2.5	1.8	5.7	35	32
"	1.8:1	6,000	8.0	5	3.8	8.8	75	81
"	3:1	6,000	8.0	10	3.8	8.8	75	81
"	9.9:1	1K-2K	8.0	10	3.8	9.1	75	86
"	19.8:1	1K-2K	8.0	10	3.7	9.1	73	86
"	36:1	1K-2K	8.0	10	3.9	9.1	77	86
None	—	—	9.0	—	0.1	1.2	—	—

TABLE 6 (continued)

Treatment	Mole ratio AA:HPA	Molecular weight	Water pH	Dosage (ppm actives)	Soluble zinc retained (ppm)	Soluble PO ₄ retained (ppm)	% Increase in zinc retention (vs. control)	% Increase in PO ₄ retention (vs. control)
AA/HPA	1.8:1	6,000	9.0	30	4.5	8.4	90	82
"	1.8:1	6,000	9.0	20	4.5	8.4	90	82
"	3:1	6,000	9.0	30	4.6	8.5	92	83
"	3:1	6,000	9.0	20	4.7	8.7	94	85
"	9.9:1	1K-2K	9.0	15	3.5	7.6	69	73
"	9.9:1	1K-2K	9.0	20	4.4	7.4	88	70
"	9.9:1	6K-10K	9.0	30	3.0	6.3	59	58
"	9.9:1	6K-10K	9.0	20	4.3	8.4	86	82
"	19.8:1	2K-6K	9.0	20	2.4	6.7	47	62
"	36:1	2K-6K	9.0	30	4.1	7.9	82	76
"	36:1	2K-6K	9.0	15	2.9	6.7	57	62
"	36:1	2K-6K	9.0	20	3.9	7.4	77	70

*K=1,000

Example 4

A further series of tests were conducted to demonstrate the efficacy of various AA/HPA polymers in retaining soluble zinc in an aqueous medium. The tests were the same as those of Example 3 except for the absence of orthophosphate from the test solutions.

5 The results of these tests are reported below in Tables 7—13 in terms of ppm soluble zinc retained in solution. For purposes of comparison with untreated test solution, Table 7 should be compared with the results of Table 1 and Tables 8—13 should be compared with the results of Table 2.

Visual comparisons of Table 7 with Table 1 and Tables 8—13 with Table 2 are provided in the accompanying drawing.

10 In Figure 1 are presented a series of graphs which contain comparisons of Table 7 with Table 1 in terms of soluble zinc remaining in solution after 24 hours vs. pH of the test water. As can be seen from the figure, the lowermost graph represents a no treatment test wherein the zinc readily precipitates. In comparison, the higher graphs represent various test solutions to which have been added the noted AA/HPA polymers. The polymers were all considered to be efficacious in retaining soluble zinc in
15 solution.

Remaining Figures 2—7 provide visual comparisons of respective ones of Tables 8—13 with Table 2. Figure 2 compares Table 8, Figure 3 compares Table 9, Figure 4 compares Table 10, Figure 5 compares Table 11, Figure 6 compares Table 12, and Figure 7 compares Table 13, all with Table 2 in terms of plots of soluble zinc remaining in solution after 24 hours vs. pH at various indicated treatment
20 levels. The line marked "No Treatment" in each figure represents the results of Table 2.

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TABLE 7
Zinc retained as compared to Table 1

Conditions: Initial Zinc=2 ppm as Zn^{++}
 $T=120^{\circ}F$ ($48.9^{\circ}C$)
 Time=24 hours
 Treatment=AA/HPA
 Dosage=5 ppm actives

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Mole ratio AA:HPA	Molecular weight	Water pH	Soluble zinc retained (ppm)
1.8:1	6,000	8.27	1.8
"	"	8.42	1.7
"	"	8.78	1.8
"	"	8.86	1.7
"	"	9.10	0.9
9.9:1	6,000—10,000	7.59	1.7
"	"	7.85	1.7
"	"	7.95	1.7
"	"	8.00	1.8
"	"	8.45	1.6
"	"	8.72	1.6
"	"	8.94	1.5
3:1	6,000	7.50	1.8
"	"	7.85	1.8
"	"	8.21	1.9
"	"	8.54	1.8
"	"	8.67	1.6
"	"	8.94	1.5
"	"	9.06	1.2
9.9:1	1,000—2,000	7.68	1.9
"	"	8.06	1.8
"	"	8.21	1.7
"	"	8.38	1.8
"	"	8.51	1.5
"	"	8.88	1.7

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TABLE 7 (Continued)

Mole ratio AA:HPA	Molecular weight	Water pH	Soluble zinc retained (ppm)
19.8:1	2,000—6,000	7.79	1.7
"	"	7.92	1.8
"	"	8.25	1.4
"	"	8.50	1.4
"	"	8.67	1.1
"	"	8.92	0.7
36:1	2,000—6,000	7.84	1.7
"	"	8.05	1.8
"	"	8.65	1.7
"	"	8.88	1.6
"	"	8.95	1.6

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TABLE 8
Zinc retained as compared to Table 2

Conditions: Initial Zinc=10 ppm as Zn^{++}
T=120°F (48.9°C)
Time=24 hours
Treatment=AA/HPA, Mole Ratio AA:HPA=1.8:1, Molecular Weight=6,000

	Water pH	Treatment dosage (ppm actives)	Soluble zinc retained (ppm)
5	7.50	5	8.6
10	7.60	5	10.0
15	7.75	5	5.4
20	7.79	5	6.6
	7.92	5	5.0
	7.96	5	4.4
25	8.26	5	0.2
	8.30	5	0.6
	8.42	5	0.4
30	8.48	5	1.6
	8.60	5	0.8
35	7.61	10	8.0
	7.70	10	8.4
	7.90	10	8.0
40	8.00	10	8.2
	8.27	10	8.4
45	8.75	10	8.0
	8.90	10	8.6
50	9.02	10	7.4
	9.18	10	6.8
	9.23	10	3.4
55	8.82	20	9.4
	8.88	20	9.8
60	9.13	20	10.0

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TABLE 9
Zinc retained as compared to Table 2

Conditions: Initial Zinc=10 ppm as Zn^{++}
T=120°F (48.9°C)
Time=24 hours
Treatment=AA/HPA, Mole Ratio AA:HPA=3:1, Molecular Weight=6,000

	Water pH	Treatment dosage (ppm actives)	Soluble zinc retained (ppm)
5	7.27	5	10
10	7.54	5	10
15	7.77	5	10
	8.02	5	8.4
20	8.08	5	8.0
	8.20	5	0.8
25	8.37	5	2.0
	8.45	5	0.8
	8.55	5	0.0
30	7.62	10	7.8
	7.90	10	7.6
35	8.00	10	8.0
	8.29	10	7.0
	8.34	10	8.4
40	8.41	10	7.4
	8.56	10	7.2
45	8.60	10	8.4
	8.97	10	6.6
	9.14	10	7.0
50	9.30	10	4.8
	8.58	20	9.0
55	8.80	20	9.4
	9.31	20	8.8

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TABLE 10
Zinc retained as compared to Table 2Conditions: Initial Zinc=10 ppm as Zn^{++}

T=120°F (48.9°C)

Time=24 hours

Treatment=AA/HPA, Mole Ratio AA:HPA=9.9:1, Molecular Weight=1,000—2,000

	Water pH	Treatment dosage (ppm actives)	Soluble zinc retained (ppm)
5	7.60	5	8.6
10	7.72	5	8.0
15	7.80	5	6.6
	7.93	5	5.0
20	8.04	5	3.2
	8.27	5	1.2
25	8.35	5	1.0
	7.53	10	9.0
	7.75	10	10.0
30	7.97	10	10.0
	8.15	10	9.4
35	8.30	10	6.6
	8.48	10	8.4
	8.65	10	6.8
40	8.72	10	5.6
	8.92	10	6.0
45	9.10	10	5.0
	9.25	10	4.4
	8.65	20	7.6
50	8.90	20	7.2
	9.10	20	7.6
55	9.30	20	3.2

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TABLE 11
Zinc retained as compared to Table 2

Conditions: Initial Zinc=10 ppm as Zn^{++}

T=120°F (48.9°C)

Time=24 hours

Treatment=AA/HPA, Mole Ratio AA:HPA=9.9:1, Molecular Weight=6,000—10,000

Water pH	Treatment dosage (ppm actives)	Soluble zinc retained (ppm)
7.50	5	7.6
7.68	5	8.2
7.74	5	2.4
7.80	5	2.0
7.86	5	2.8
7.88	5	0.8
8.20	5	0.6
8.27	5	0.2
8.58	5	0.2
8.10	10	8.4
8.13	10	8.4
8.20	10	8.2
8.25	10	8.6
8.50	10	7.2
8.74	10	6.0
9.01	10	7.4
9.14	10	7.6
9.32	10	3.8

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TABLE 12
Zinc retained as compared to Table 2

Conditions: Initial Zinc=10 ppm as Zn^{++}

T=120°F (48.9°C)

Time=24 hours

Treatment=AA/HPA, Mole Ratio AA:HPA=19.8:1, Molecular Weight=2,000—6,000

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Water pH	Treatment dosage (ppm actives)	Soluble zinc retained (ppm)
7.80	10	2.4
7.83	10	2.4
7.95	10	1.2
8.08	10	1.0
8.12	10	1.2
8.25	10	1.2
8.35	10	1.4
8.15	20	4.6
8.35	20	4.8
8.52	20	5.2
8.78	20	4.0
8.62	30	8.4
8.83	30	8.6
8.88	30	8.2
8.95	30	8.4
9.02	30	7.4
9.11	30	5.2

TABLE 13
Zinc retained as compared to Table 2

Conditions: Initial Zinc=10 ppm as Zn^{++}

T=120°F (48.9°C)

Time=24 hours

Treatment=AA/HPA, Mole Ratio AA:HPA=36:1, Molecular Weight=2,000—6,000

	Water pH	Treatment dosage (ppm actives)	Soluble zinc retained (ppm)
5	7.75	5	5.8
10	7.79	5	2.6
15	8.02	5	1.0
20	8.34	5	0.2
	8.66	5	0.0
25	8.27	10	7.0
	8.40	10	5.8
	8.50	10	7.6
30	8.62	10	6.6
	8.87	10	6.6
35	8.90	10	7.2
	9.03	10	7.8
	9.40	10	5.2
40	8.79	20	9.0
	8.95	20	8.6
45	9.05	20	8.6
	9.11	20	7.0
	9.21	20	7.8
50	9.23	20	7.2

Efficacy as corrosion inhibitor

Example 5

Having already demonstrated both the zinc precipitation problem related to zinc-containing corrosion inhibitor treatments in aqueous mediums and the resolution of this problem by combining the treatment with AA/HAA polymer, the following test results are presented to demonstrate, from a corrosion inhibition point of view, the benefits of the combined treatments.

The tests were each conducted with two non-pretreated low carbon steel coupons which were immersed and rotated in aerated synthetic cooling water for a 3 or 4 day period. The water was adjusted to the desired pH and readjusted after one day if necessary; no further adjustments were made. Water temperature was 120°F (48.9°C). Rotational speed was maintained to give a water velocity of 1.3 feet per second (0.396 ms^{-1}) past the coupons. The total volume of water was 17 liters. Cooling water was manufactured to give the following conditions:

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	SCW ₇ (pH=7)	SCW ₈ (pH=8)
ppm Ca as CaCO ₃	170	170
ppm Mg as CaCO ₃	110	110
ppm SiO ₂	15	15
ppm Na ₂ CO ₃	0	100

Corrosion rate measurement was determined by weight loss measurement. Prior to immersion, coupons were scrubbed with a mixture of trisodium phosphate-pumice, rinsed with water, rinsed with isopropyl alcohol and then air dried. Weight measurement to the nearest milligram was made. At the end of one day, a weighed coupon was removed and cleaned. Cleaning consisted of immersion into a 50% solution of HCl for approximately 20 seconds, rinsing with tap water, scrubbing with a mixture of trisodium-pumice until clean, then rinsing with tap water and isopropyl alcohol. When dry, a second weight measurement to the nearest milligram was made. At the termination of the tests, the remaining coupon was removed, cleaned and weighed.

Corrosion rates were computed by differential weight loss according to the following equation:

$$\text{Corrosion Rate} = \frac{N^{\text{th}} \text{ Day Weight Loss} - 1^{\text{st}} \text{ Day Weight Loss}}{N-1}$$

where N=3 or 4.

The cooling water was prepared by first preparing the following stock solutions:

Solution A—212.4 g CaCl₂ · 2H₂O/l

Solution B—229.9 g MgSO₄ · 7H₂O/l

Solution C—25.5 g NaSiO₃ · 9H₂O/l

Solution D—85 g Na₂CO₃/l

Treatment Solutions—1.7% solutions (1.7 g/100 ml)

Then, these solutions were combined using the following order of addition:

1. To 17 l of de-ionized water add, with stirring, (a) 20 ml of Solution A, (b) 20 ml of Solution B and (c) 20 ml of Solution C.
2. Adjust pH to 6.
3. With stirring add treatment (except Zn⁺²).
4. Add o-PO₄ Solution (if used).
5. Adjust pH to 7.0 if necessary.
6. Add Zn⁺² Solution (if used).
7. (a) for SCW₇ adjust pH to 7.0.
- (b) For SCW₈ add 20 ml of Solution D and adjust pH to 8.0.

The results of these tests are reported below in Table 14 in terms of corrosion rates in mils per year (mpy).

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TABLE 14
Corrosion inhibition

	Polymer (ppm)	AA:HPA	Molecular weight	o-PO ₄ (ppm)	Zinc (ppm as Zn ⁺⁺)	pH	Corrosion rate (mpy)
5	5	3:1	6,000	—	—	7	155
	50	3:1	6,000	—	—	7	35
10	—	—	—	10	2	7	2.8
	5	3:1	6,000	10	2	7	2.5
15	—	—	—	5	2	7	8
	5	3:1	6,000	5	2	7	3
	5	1.8:1	6,000	10	2	7	2.1
20	None	—	—	—	—	8	82
	30	3:1	6,000	—	—	8	86
25	—	—	—	—	10	8	84
	5	3:1	6,000	—	5	8	13.6
	15	3:1	6,000	—	10	8	13.4
30	—	—	—	5	2	8	21.5
	5	3:1	6,000	5	2	8	1.5
35	5	1.8:1	6,000	5	2	8	0
	—	—	—	3	2	8	76
	5	3:1	6,000	3	2	8	1.6
40	5	1.8:1	6,000	3	2	8	8.6

While the comparative test results were not so pronounced at pH=7, the comparative results at pH=8 were considered to be rather dramatic. Even though the AA/HPA polymer alone demonstrated little, if any, efficacy as a corrosion inhibitor, when combined with the zinc-containing treatments, the combined treatments demonstrated significantly enhanced results as corrosion inhibitors. For example, at pH=8, the corrosion inhibition efficacy of 30 ppm active polymer alone (86 mpy) and 10 ppm Zn⁺² alone (84 mpy) appeared to be non-existent as compared to the untreated system (82 mpy); however, when only 5 ppm polymer were combined with only 5 ppm Zn⁺², the corrosion rate decreased to 13.6 mpy.

Illustrative examples of stable aqueous compositions made in accordance with the present invention are presented in Table 15 in terms of relative proportions (in weight percent) of the various constituents. In these compositions, the water-soluble zinc compound was ZnSO₄ · H₂O and the orthophosphate was Na₃PO₄ · 12H₂O. Since calculations were rounded-off to two places, not all compositions added up to 100%. Stability is defined in terms of soluble constituents in solution after 24 hours at 120°F.

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TABLE 15
Illustrative examples of compositions

	Mole ratio AA:HPA	Molecular weight	Water pH	Weight % polymer	Weight % zinc	Weight % PO ₄
5	1.8:1	6,000	7.5	34	50	16
	1.8:1	6,000	7.5	28	48	24
10	3:1	6,000	7.5	52	27	21
	3:1	6,000	7.5	28	48	24
15	9.9:1	1K-2K	7.5	30	41	28
	9.9:1	1K-2K	7.5	42	36	22
	9.9:1	6K-10K	7.5	27	48	25
20	9.9:1	6K-10K	7.5	45	33	22
	19.8:1	2K-6K	7.5	38	41	21
25	19.8:1	2K-6K	7.5	53	30	17
	36:1	2K-6K	7.5	31	42	27
	36:1	2K-6K	7.5	42	37	20
30	1.8:1	6,000	7.0	15	28	56
	3:1	6,000	7.0	16	27	57
35	3:1	6,000	7.0	26	26	48
	9.9:1	1K-2K	7.0	15	29	56
	19.8:1	2K-6K	7.0	27	25	48
40	36:1	2K-6K	7.0	28	25	47
	1.8:1	6,000	8.0	25	18	57
45	3:1	6,000	8.0	44	17	39
	19.8:1	1K-2K	8.0	44	16	40
	1.8:1	6,000	9.0	70	10	20
50	1.8:1	6,000	9.0	61	14	26
	3:1	6,000	9.0	70	11	20
55	9.9:1	1K-2K	9.0	57	13	29
	9.9:1	1K-2K	9.0	63	14	23
	9.9:1	6K-10K	9.0	76	8	16
60	9.8:1	2K-6K	9.0	69	8	23
	36:1	2K-6K	9.0	71	10	19
65	1.8:1	6,000	8.27	74	26	—

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TABLE 15 (Continued)
Illustrative examples of compositions

	Mole ratio AA:HPA	Molecular weight	Water pH	Weight % polymer	Weight % zinc	Weight % PO ₄
5	1.8:1	6,000	8.42	75	25	—
	1.8:1	6,000	9.10	85	15	—
10	9.9:1	6K-10K	7.59	75	25	—
	9.9:1	6K-10K	8.45	76	24	—
15	9.9:1	6K-10K	8.94	77	23	—
	3:1	6,000	7.50	74	26	—
	3:1	6,000	8.54	74	26	—
20	3:1	6,000	9.06	81	19	—
	9.9:1	1K-2K	7.68	72	28	—
25	9.9:1	1K-2K	8.88	75	25	—
	19.8:1	2K-6K	8.92	88	12	—
	36:1	2K-6K	7.84	75	25	—
30	36:1	2K-6K	8.65	75	25	—
	36:1	2K-6K	8.95	76	24	—
35	1.8:1	6,000	7.50	37	63	—
	1.8:1	6,000	7.60	33	67	—
	1.8:1	6,000	7.75	48	52	—
40	1.8:1	6,000	7.92	50	50	—
	1.8:1	6,000	7.96	53	47	—
45	1.8:1	6,000	8.26	96	4	—
	1.8:1	6,000	8.30	89	11	—
	1.8:1	6,000	8.60	86	14	—
50	1.8:1	6,000	9.23	75	25	—
	1.8:1	6,000	8.88	67	33	—
55	1.8:1	6,000	8.12	89	11	—
	1.8:1	6,000	8.62	78	22	—

60 Claims

1. A composition comprising an aqueous solution of a water-soluble zinc compound, characterised in that the solution also contains as a stabilizer a water-soluble polymer comprising moieties derived from an acrylic acid compound and moieties of hydroxylated lower alkyl acrylate, wherein the moieties of said polymer have the following formulas:

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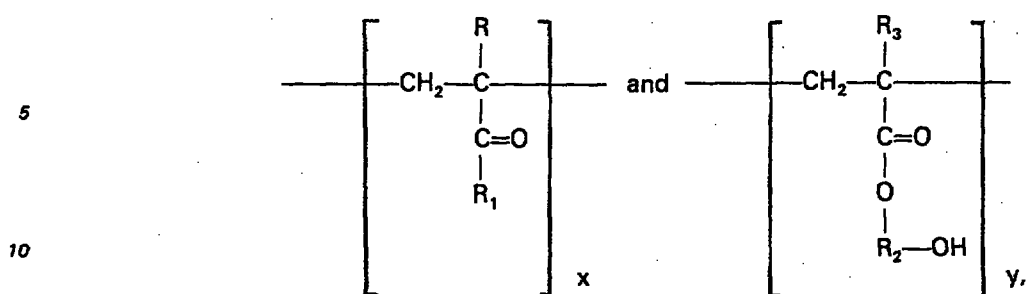
TABLE 15 (Continued)
Illustrative examples of compositions

	Mole ratio AA:HPA	Molecular weight	Water pH	Weight % polymer	Weight % zinc	Weight % PO ₄
5	1.8:1	6,000	8.42	75	25	—
10	1.8:1	6,000	9.10	85	15	—
	9.9:1	6K-10K	7.59	75	25	—
	9.9:1	6K-10K	8.45	76	24	—
15	9.9:1	6K-10K	8.94	77	23	—
	3:1	6,000	7.50	74	26	—
20	3:1	6,000	8.54	74	26	—
	3:1	6,000	9.06	81	19	—
	9.9:1	1K-2K	7.68	72	28	—
25	9.9:1	1K-2K	8.88	75	25	—
	19.8:1	2K-6K	8.92	88	12	—
30	36:1	2K-6K	7.84	75	25	—
	36:1	2K-6K	8.65	75	25	—
	36:1	2K-6K	8.95	76	24	—
35	1.8:1	6,000	7.50	37	63	—
	1.8:1	6,000	7.60	33	67	—
40	1.8:1	6,000	7.75	48	52	—
	1.8:1	6,000	7.92	50	50	—
	1.8:1	6,000	7.96	53	47	—
45	1.8:1	6,000	8.26	96	4	—
	1.8:1	6,000	8.30	89	11	—
50	1.8:1	6,000	8.60	86	14	—
	1.8:1	6,000	9.23	75	25	—
	1.8:1	6,000	8.88	67	33	—
55	1.8:1	6,000	8.12	89	11	—
	1.8:1	6,000	8.62	78	22	—

60 Claims

1. A composition comprising an aqueous solution of a water-soluble zinc compound, characterised in that the solution also contains as a stabilizer a water-soluble polymer comprising moieties derived from an acrylic acid compound and moieties of hydroxylated lower alkyl acrylate, wherein the moieties of said polymer have the following formulas:





15 where R is hydrogen or a lower alkyl of from 1 to 3 carbon atoms; R₁ is OH, NH₂ or OM where M is a water-soluble cation; R₂ is a lower alkylene of 2 to 6 carbon atoms, R₃ is H or lower alkyl of from 1 to 3 carbon atoms and the mole ratio of x:y is 1:4 to 36:1, and further characterised in that on a weight basis said zinc compound comprises 1 to 95% and said polymer comprises 5 to 99% of the total amount of water-soluble zinc compound and water-soluble polymer.

20 2. A composition as claimed in claim 1, characterised in that on a weight basis said zinc compound comprises 4 to 85% and said polymer comprises 15 to 96% of the total amount of water-soluble zinc compound and water-soluble polymer.

3. A composition as claimed in claim 1, characterised in that on a weight basis said zinc compound comprises 5 to 70% and said polymer comprises 30 to 95% of the total amount of water-soluble zinc compound and water-soluble polymer.

25 4. A composition as claimed in any one of claims 1 to 3, characterised in that said polymer has a molecular weight of 1,000 to 50,000.

5. A composition as claimed in claim 4, characterised in that said polymer has a molecular weight of 2,000 to 6,000.

30 6. A composition as claimed in any one of claims 1 to 5, characterised in that the pH of said aqueous solution is 6.5 to 9.5

7. A composition as claimed in any one of claims 1 to 6, characterised in that the mole ratio of x:y is 1:1 to 11:1.

8. A composition as claimed in claim 7, characterised in that the mole ratio x:y is 1:1 to 5:1.

35 9. A composition as claimed in any one of claims 1 to 8, characterised in that the polymer is a copolymer of acrylic acid or water soluble salt thereof and hydroxy propyl acrylate.

10. A composition as claimed in any one of claims 1 to 9, characterised in that it also contains a water-soluble orthophosphate or a precursor thereof.

11. A composition as claimed in any one of claims 1 to 10, characterised in that it additionally comprises water-soluble chromate.

40 12. A composition as claimed in claim 10, characterised in that on a weight basis, said zinc compound comprises 1 to 95%, said orthophosphate comprises 1 to 95% and said polymer comprises 5 to 99% of the total amount of water-soluble zinc compound, water-soluble orthophosphate or precursor and water-soluble polymer.

45 13. A composition as claimed in claim 10, characterised in that said zinc compound comprises 5 to 85%, said orthophosphate comprises 5 to 85% and said polymer comprises 15 to 95% of the total amount of water-soluble zinc compound, water-soluble orthophosphate or precursor and water-soluble polymer.

50 14. A method for reducing the amount of corrosion of metal surfaces in contact with an aqueous medium prone to zinc precipitation characterised by adding to said aqueous medium in addition to a water-soluble zinc compound an effective amount of a water-soluble polymer as defined in any one of claims 1, 5, 6, 8, 9 and 10, wherein said zinc compound is added in an amount sufficient to provide from 0.5 to 25 parts of zinc ion per million parts of aqueous medium, and wherein said polymer is added in an amount of from 0.5 to 200 parts of polymer per million parts of aqueous medium.

55 15. A method as claimed in claim 14, characterised in that said zinc compound is added in an amount sufficient to provide from 2 to 10 parts of zinc ion per million parts of aqueous medium, and said polymer is added in an amount of from 2 to 50 parts of polymer per million parts of aqueous medium.

16. A method as claimed in any one of claims 14 to 15, characterised in that said aqueous medium is cooling water.

60 17. A method as claimed in any one of claims 14 to 16, characterised in that said aqueous medium has a pH of from 6.5 to 9.5.

18. A method as claimed in any one of claims 14 to 17, characterised in that water-soluble orthophosphate, or a precursor thereof, is also added to said aqueous medium in an amount of from 1 to 200 parts per million.

65 19. A method as claimed in any one of claims 14 to 18, characterised in that the aqueous medium additionally comprises water soluble chromate.



20. A method as claimed in claim 18, wherein said orthophosphate or precursor thereof is added in an amount of from 2 to 50 parts per million.

21. A method of inhibiting the formation of zinc scale in an aqueous medium containing zinc ions under scale forming conditions, which method is characterised by adding to said aqueous medium an effective amount for the purpose, of effective water-soluble polymer as defined in any one of claims 1, 5, 6, 8, 9 and 10, and wherein said polymer is added in an amount of from 0.5 to 200 parts per million parts of aqueous medium.

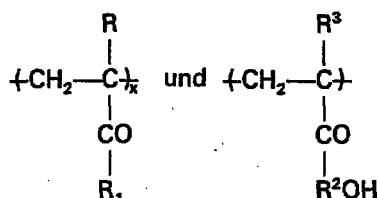
22. A method as claimed in claim 21, characterised in that said aqueous medium is cooling water.

23. A method as claimed in claim 22, characterised in that said aqueous medium contains phosphate ions which have been added as a treatment.

24. A method as claimed in any one of claims 21 to 23, characterised in that said zinc scale comprises at least one member selected from zinc hydroxide and zinc phosphate.

Patentansprüche

1. Zusammensetzung in Form einer wäßrigen Lösung einer wasserlöslichen Zinkverbindung, dadurch gekennzeichnet, daß die Lösung als Stabilisator ein wasserlösliches Polymer enthaltend Einheiten abgeleitet von einer Acrylsäureverbindung und Einheiten von hydroxyliertem niederen Alkylacrylat der Formeln



aufweist, worin R und R³ H oder eine niedere Alkylgruppe mit 1 bis 3 C-Atomen, R¹ OH, NH₂ oder OM ist und M ein wasserlösliches Kation bedeutet und R² eine niedere Alkylengruppe mit 2 bis 6 C-Atomen ist und die Einheiten mit den Indices x und y in einem Molverhältnis 1:4 bis 36:1 stehen, und die Lösung 1 bis 95 Gew.-% Zinkverbindung und 99 bis 5 Gew.-% Polymer, bezogen auf Gesamtmenge Zinkverbindung und Polymer, enthält.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie 4 bis 85% Zinkverbindung und 96 bis 15% Polymer enthält.

3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie 5 bis 70% Zinkverbindung und 95 bis 30% Polymer enthält.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Polymere ein Molekulargewicht von 1000 bis 50000 besitzt.

5. Zusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß das Polymere ein Molekulargewicht von 2 000 bis 6 000 besitzt.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der pH-Wert der wäßrigen Lösung 6,5 bis 9,5 beträgt.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Molverhältnis der Einheiten 1:1 bis 11:1 beträgt.

8. Zusammensetzung nach Anspruch 7, dadurch gekennzeichnet, daß das Molverhältnis 1:1 bis 5:1 beträgt.

9. Zusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das Polymere ein Copolymer von Acrylsäure oder deren wasserlöslichen Salze und Hydroxypropylacrylat ist.

10. Zusammensetzung nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß sie zusätzlich ein wasserlösliches Orthophosphat oder dessen Vorläufer enthält.

11. Zusammensetzung nach einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß sie zusätzlich ein wasserlösliches Chromat enthält.

12. Zusammensetzung nach Anspruch 10, dadurch gekennzeichnet, daß sie 1 bis 95% Zinkverbindung, 1 bis 95% Orthophosphat und 99 bis 5% Polymer, bezogen auf die Summe der Gewichte Zinkverbindung, Orthophosphat oder dessen Vorläufer und Polymeres enthält.

13. Zusammensetzung nach Anspruch 10, dadurch gekennzeichnet, daß sie 5 bis 85% Zinkverbindung, 5 bis 85% Orthophosphat und 95 bis 15% Polymeres, bezogen auf die Gesamtmenge Zinkverbindung, Orthophosphat oder dessen Vorläufer und Polymer, enthält.

14. Verfahren zur Verringerung der Korrosion von Metalloberflächen, die mit einem wäßrigen Medium in Berührung stehen, welches einer Zinkausfällung zugänglich ist, dadurch gekennzeichnet, daß man dem wäßrigen Medium außer einer wasserlöslichen Zinkverbindung, das in den Ansprüchen 1, 5, 6, 8, 9 und 10 definierte Polymere zusetzt, und zwar die Zinkverbindung in einer Menge



entsprechend 0,5 bis 25 ppm Zinkionen und Polymeres entsprechend 0,5 bis 200 ppm, bezogen auf wäßriges Medium.

15. Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß man die Zinkverbindung in einer Menge entsprechend 2 bis 10 ppm Zinkionen und das Polymere in einer Menge entsprechend 2 bis 50 ppm zusetzt.

16. Verfahren nach Anspruch 14 oder 15, dadurch gekennzeichnet, daß das wäßrige Medium Kühlwasser ist.

17. Verfahren nach einem der Ansprüche 14 bis 16, dadurch gekennzeichnet, daß das wäßrige Medium einen pH-Wert von 6,5 bis 9,5 hat.

18. Verfahren nach einem der Ansprüche 14 bis 17, dadurch gekennzeichnet, daß man dem wäßrigen Medium 1 bis 200 ppm eines wasserlöslichen Orthophosphats oder dessen Vorläufer zusetzt.

19. Verfahren nach einem der Ansprüche 14 bis 18, dadurch gekennzeichnet, daß man dem wäßrigen Medium ein wasserlösliches Chromat zusetzt.

20. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß man Orthophosphat oder dessen Vorläufer in einer Menge von 2 bis 50 ppm zusetzt.

21. Verfahren zur Verhinderung von Zinkabscheidungen aus einem wäßrigen Medium enthaltend Zinkionen unter ansatzbildenden Bedingungen, dadurch gekennzeichnet, daß man dem wäßrigen Medium wasserlösliches Polymeres entsprechend der Ansprüche 1, 5, 6, 8, 9 oder 10 in einer Menge von 0,5 bis 200 ppm, bezogen auf wäßriges Medium, zusetzt.

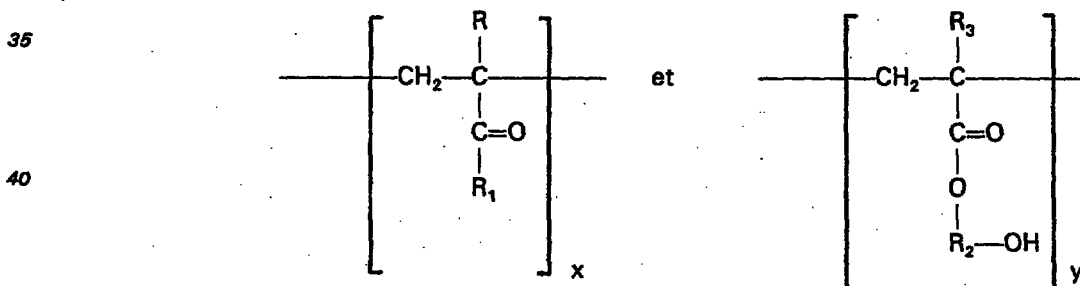
22. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß das wäßrige Medium Kühlwasser ist.

23. Verfahren nach Anspruch 22, dadurch gekennzeichnet, daß das wäßrige Medium Phosphationen, die zu einer Behandlung zugesetzt worden sind, enthält.

24. Verfahren nach einem der Ansprüche 21 bis 23, dadurch gekennzeichnet, daß der Ansatz Zinkhydroxid und/oder Zinkphosphat enthält.

Revendications

1. Composition comprenant une solution aqueuse d'un composé de zinc soluble dans l'eau, caractérisée en ce que cette solution contient aussi comme stabilisant un copolymère hydrosoluble comprenant des motifs d'un composé d'acide acrylique et des motifs d'un acrylate d'alkyle inférieur hydroxylé, motifs représentés par les formules:



(dans lesquelles R représente l'hydrogène ou un alkyle en C₁ à C₃; R₁ un groupe OH, NH₂ ou OM, M étant un cation hydrosoluble, R₂ est un alkylène en C₂ à C₆, R₃ l'hydrogène ou un alkyle en C₁ à C₃ et le rapport molaire X:Y est compris entre 1:4 et 36:1), et caractérisée en outre en ce que, en poids, le composé de zinc représente de 1 à 95% et le polymère 5 à 99% du total des deux.

2. Composition selon la revendication 1 caractérisée en ce que le composé de zinc représente 4 à 85% en poids, et le polymère 15 et 96% en poids, du total des deux.

3. Composition selon la revendication 1 caractérisée en ce que le composé de zinc représente 5 à 70% en poids, et le polymère 30 à 95% en poids, du total des deux.

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le polymère a une masse moléculaire de 1.000 à 50.000.

5. Composition selon la revendication 4, caractérisée en ce que le polymère a une masse moléculaire de 2.000 à 6.000.

6. Composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce que le pH de la solution aqueuse est compris entre 6,5 et 9,5.

7. Composition selon l'une quelconque des revendications 1 à 6, caractérisée en ce que le rapport molaire x:y est compris entre 1:1 et 11:1.

8. Composition selon la revendication 7, caractérisée en ce que le rapport molaire x:y est compris entre 1:1 et 5:1.

9. Composition selon l'une quelconque des revendications 1 à 8, caractérisée en ce que le polymère est un copolymère d'acide acrylique ou d'un sel hydrosoluble de cet acide et d'acrylate d'hydroxypropyle.





10. Composition selon l'une quelconque des revendications 1 à 9, caractérisée en ce qu'elle contient aussi un orthophosphate hydrosoluble ou un précurseur de celui-ci.

11. Composition selon l'une quelconque des revendications 1 à 10, caractérisée en ce qu'elle comprend en outre un chromate hydrosoluble.

12. Composition selon la revendication 10, caractérisée en ce que, en poids, le composé de zinc représente 95%, l'orthophosphate ou son précurseur 1 à 95% et le polymère 5 à 99%, du total des trois.

13. Composition selon la revendication 10, caractérisée en ce que le composé de zinc représente 5 à 85%, l'orthophosphate ou son précurseur 5 à 85% et le polymère 15 à 95%, du total des trois.

14. Procédé pour diminuer le degré de corrosion de surfaces métalliques qui sont en contact avec un milieu aqueux ayant tendance à laisser précipiter du zinc, procédé caractérisé en ce que l'on ajoute au milieu aqueux, en plus d'un composé de zinc hydrosoluble, une proportion appropriée d'un polymère hydrosoluble tel que défini à l'une quelconque des revendications 1, 5, 6, 8, 9 et 10, le composé de zinc étant ajouté dans une proportion donnant 0,5 à 25 parties d'ion zinc par million de parties du milieu aqueux, et le polymère dans une proportion de 0,5 à 200 parties par million de parties du milieu aqueux.

15. Procédé selon la revendication 14, caractérisé en ce que le composé de zinc est ajouté dans une proportion donnant 2 à 10 parties d'ion zinc par million de parties du milieu aqueux, et le polymère dans une proportion de 2 à 50 parties par million de parties du milieu aqueux.

16. Procédé selon la revendication 14 ou 15, caractérisé en ce que le milieu aqueux est une eau de refroidissement.

17. Procédé selon l'une quelconque des revendications 14 à 16, caractérisé en ce que le pH de milieu aqueux est compris entre 6,5 et 9,5.

18. Procédé selon l'une quelconque des revendications 14 à 17, caractérisé en ce que l'on ajoute également au milieu aqueux un orthophosphate soluble dans l'eau ou un précurseur de celui-ci dans une proportion de 1 à 200 parties par million.

19. Procédé selon l'une quelconque des revendications 14 à 18, caractérisé en ce que le milieu aqueux comprend en outre un chromate soluble dans l'eau.

20. Procédé selon la revendication 18, dans lequel l'orthophosphate ou son précurseur est ajouté dans une proportion de 2 à 50 parties par million.

21. Procédé pour empêcher la formation d'incrustations de zinc dans un milieu aqueux contenant des ions zinc dans des conditions entraînant la formation d'incrustations, procédé caractérisé en ce que l'on ajoute au milieu aqueux une proportion appropriée à cette fin d'un polymère hydrosoluble tel que défini à l'une quelconque des revendications 1, 5, 6, 8, 9 et 10, polymère qui est ajouté dans une proportion de 0,5 à 200 parties par million de parties du milieu aqueux.

22. Procédé selon la revendication 21 caractérisé en ce que le milieu aqueux est une eau de refroidissement.

23. Procédé selon la revendication 22 caractérisé en ce que le milieu aqueux contient des ions phosphate qui ont été ajoutés pour le traitement.

24. Procédé selon l'une quelconque des revendications 21 à 23, caractérisé en ce que les incrustations de zinc comprennent de l'hydroxyde ou du phosphate de zinc ou les deux à la fois.

