

COMPOSITION AND METHOD FOR INHIBITING SCALE

This invention relates to the treatment of aqueous systems and, more particularly, to the inhibition and removal of solid deposits in industrial heating and cooling systems.

5 The water used in steam generating boilers, cooling towers, desalination units and other industrial aqueous systems contains various impurities. The impurities typically include alkaline earth cations such as calcium, barium, and magnesium and several anions such as
10 bicarbonate, carbonate, sulfate, oxalate, phosphate, silicate, and fluoride. These anions and cations combine and form precipitates due to the pH, pressure, or temperature in the system or the presence of additional ions with which they form insoluble products. The most
15 common impurities in industrial water supplies are the water-hardening calcium, magnesium and carbonate ions. In addition to precipitating as carbonates, calcium and magnesium as well as any iron or copper present can also react with phosphate, sulfate, and silicate ions and form
20 the respective complex insoluble salts. These solid reaction products accumulate on surfaces on the system and form scale. The water may also contain various solids such as mud, clay, iron oxides, silt, sand, and other mineral matter and microbiological debris that accumulate
25 as sludge deposits in the system. Iron oxides may be present in the feedwater and may be produced by corrosion of metal surfaces in contact with the water. The sludge may become incorporated in the scale deposits and the precipitates tend to cement the sludge particles and form
30 a strongly adherent scale.

Sludge and scale deposits greatly reduce heat transfer efficiency by settling at low flow points in the system and limiting the circulation of the water and insulating it from the heat transfer surfaces. In addition to interfering with heat transfer and fluid flow, corrosion of metal surfaces underneath the deposits is facilitated since corrosion control agents are unable to contact the surfaces effectively. The deposits also harbor bacteria. Removal of the deposits can cause expense delays and shutdown of the system. Water at the relatively high temperatures in steam generating boilers and hard waters are especially susceptible to scale formation. Extremely severe scale deposits can cause localized overheating and rupture in boilers.

15 Since external treatments such as softening, coagulation, and filtration do not adequately remove solids and solid-forming substances, various internal chemical treatments have been used to prevent and remove scale and sludge in aqueous systems. The chemical treatment for boilers generally involves the combined use of a precipitating agent and a solid conditioner to maintain the solids in the boiler water in a suspended state. The precipitating chemicals commonly employed for calcium salts are soda ash and sodium phosphates. 25 Magnesium is precipitated by the alkalinity of boiler water as magnesium hydroxide. The precipitate or sludge is periodically removed with the water drained from the boiler by blowdown. In blowdown, the sludge-containing boiler water is removed through a valve by rapidly 30 reducing the pressure within the boiler.

A variety of polycarboxylate and other soluble, polar polymers such as acrylate and methacrylate polymers have been used as solid conditioners in industrial water systems. The presence of small quantities of these

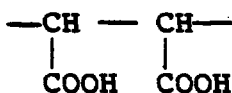
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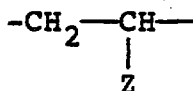
polymers improves the fluidity of sludge and results in the formation of amorphous, frangible and serrated precipitates instead of hard, dense crystals that form scale on surfaces.

Phosphonates are used extensively in water treatment 5 as precipitation inhibitors and are effective in threshold amounts that are markedly lower than the stoichiometric amount required for chelating or sequestering the scale forming action.

The composition for inhibiting formation of scale in 10 an aqueous system of the present invention comprises scale inhibiting amounts of a copolymer which possesses recurring units of the formula:



15 and of the formula



where Z represents $\text{---CH}_2\text{SO}_3\text{H}$

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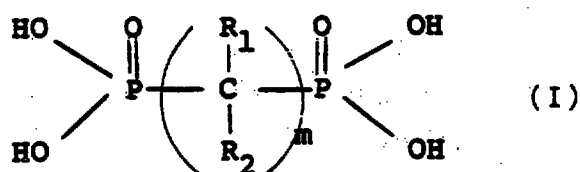
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or a water soluble salt thereof and a water soluble organic phosphonic acid or a water soluble salt thereof. The method of inhibiting the formation of scale in an aqueous system of the present invention comprises adding
5 to the system scale inhibiting amounts of the copolymer and the phosphonic acid.

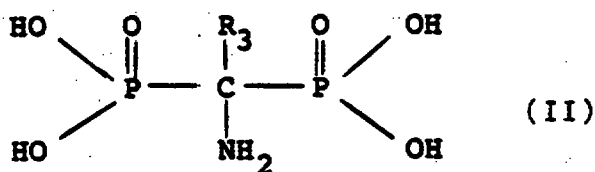
The present invention provides unexpectedly superior inhibition of deposition and formation of scale, particularly those containing calcium and magnesium
10 phosphates and silicates and iron oxide, on metallic surfaces of industrial water systems. The composition and method are effective when used at low treatment levels and in water at high temperatures and pressures in steam generating boilers and in water of high hardness and
15 alkalinity. Indeed, the present invention also provides the surprising additional advantage that, in pressurized boiler systems (which normally operate at an alkaline pH, generally from 9.5 to 12), an in-service cleaning effect can be obtained. In other words, the invention provides a
20 method of removing scale from a scaled pressurized boiler. Further, it has been found that the combination of the phosphonate and a copolymer having the recurring units specified above but with Z being $-SO_3H$, i.e., units derived from vinyl rather than allyl sulfonic acid
25 also provides this in-service cleaning effect in pressurized boilers and this forms another aspect of the present invention. It will be appreciated that by "pressurized boilers" we mean boilers operating at a pressure of at least 50 psig, generally at least 80 psig,
30 typically 80 to 150 psig, (low pressure), generally 150 to 600 psig (moderate pressure) and above 600 and up to, say, 2000 psig (high pressure). In such boilers, the water will be at its boiling point which will vary from about 298°F. at 50 psig, to about 324°F. at 80 psig, to about

366°F. at 150 psig, to about 489°F. at 600 psig, and to about 637°F. at 2000 psig.

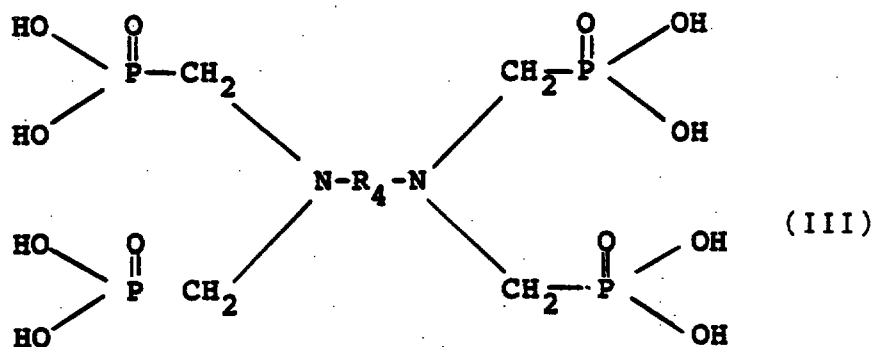
The present invention employs one or more water soluble organic phosphonic acids or water soluble salts thereof. The preferred organic phosphonic acids are alkylene phosphonic acids and phosphonocarboxylic acids. Suitable phosphonic acids have the general formula:



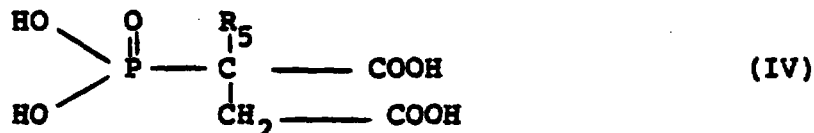
wherein m is an integer from 1 to 10, R₁ is hydrogen or an alkyl group having from 1 to 4 carbon atoms, R₂ is hydroxyl, hydrogen, or an alkyl group having from 1 to 4 carbon atoms; or the general formula:



wherein R₃ is an alkyl group having 1 to 10 carbon atoms, benzyl, or phenyl; or the general formula:



wherein R_4 is an alkylene group having from 1 to 10 carbon atoms; or the general formula:



wherein R_5 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_6 is hydrogen, alkyl having 1 to 4 carbon atoms or carboxyl, R_7 is hydrogen or methyl and R_8 is a carboxyl or phosphonate.

Water soluble amino alkylene phosphonic acids, hydroxy
10 alkylidene phosphonic acids, phosphonocarboxylic acids, or
water soluble salts thereof are especially preferred. The
most preferred compounds are aminotri(methylene phosphonic
acid), ethylenediaminetetra(methylene phosphonic acid),
hydroxyethylidene-1,1-diphosphonic acid, 2-phosphonobutane
15 tricarboxylic acid-1,2,4 and water soluble salts thereof.
The hydroxy alkylidene diphosphonic acid is commercially
available and conventional procedures for the preparation
of this and other such phosphonic acids are described, for
example, in U.S. Patents 3,214,454 and 3,297,578. The most
20 preferred aminophosphonic acid is commercially available
and the preparation of this and other such phosphonic acids
by conventional procedures is described for example, in
U.S. Patents 3,234,124 and 3,298,956. 2-phosphonobutane
tricarboxylic acid-1,2,4 is commercially available and
25 these and other such phosphonocarboxylic acids can be
prepared by conventional procedures such as those
described, for example, in U.S. Patent 4,020,101 of Geffers
et al. Other suitable phosphonic acids having these
formulas include, for example, diethylenetriamine
30 penta(methylene phosphonic acid), triethylenetetraamine
hexa(methylene phosphonic acid), hexamethylenediamine

tetra(methylene phosphonic acid), aminoethylidene
diphosphonic acid, aminopropylidene diphosphonic acid,
hydroxypropylidene diphosphonic acid, hydroxybutylidene
diphosphonic acid, hydroxyhexylidene diphosphonic acid,
5 1-phosphonoethane-1,2-dicarboxylic acid and
2-phosphonobutane-1,2,3,4-tetracarboxylic acid.

The composition of the present invention further
comprises an aliphatic copolymer of maleic acid or
anhydride or fumaric acid and allyl sulfonic acid or a
10 water soluble salt thereof. The copolymer may be prepared
by copolymerizing maleic acid or anhydride or fumaric acid
with allyl sulfonic acid or an alkali metal salt thereof
by following conventional procedures such as those
described in U.S. Patents 3,706,717 and 3,879,288 of
15 Siegele. Conventional additional polymerization methods
in the presence of light or free radical initiators may be
employed. Generally, the copolymerization may be effected
at from about 30 to about 120°C. using a peroxide in an
inert medium. The copolymer may be derived, for example,
20 by solution polymerization of maleic acid and sodium allyl
sulfonate in the presence of hydrogen peroxide. The
corresponding vinyl copolymers for use in the pressurised
boiler treatment method of the present invention may be
prepared in a similar manner from maleic acid or anhydride
25 or fumaric acid and vinyl sulfonic acid or a water soluble
salt thereof.

The relative proportions of sulfonate and carboxylate
depend upon the degree of scale inhibition needed. The
copolymer generally contains from about 10 to about 80
30 mole percent of sulfonate moieties and correspondingly
from about 90 to about 20 mole percent of the carboxylate

moieties. Preferably, the sulfonate moieties comprise about 25 to about 75 mole percent of the copolymer and the carboxylate moieties comprise from about 75 to about 25 mole percent. For the vinyl sulfonate copolymers, the
5 sulfonate moieties especially comprise about 50 to 75 mole percent of the copolymer and the carboxylate moieties from about 50 to about 25 mole percent.

The average molecular weight of the copolymer is not critical so long as the polymer is water soluble.

10 Generally, the weight average molecular weight ranges from about 500 to about 100,000. The molecular weight is preferably from about 800 to about 25,000 and especially is from about 1,000 to about 15,000. A copolymer having a mole ratio of maleic acid or anhydride to allyl sulfonic
15 acid of about 1:1 and a molecular weight of about 2,000 is especially preferred. Preferred vinyl sulfonate copolymers include those having a weight ratio of maleic acid or anhydride to vinyl sulfonic acid of about 1:1.5 or about 1:3 and a molecular weight of about 7,000 to about
20 9,000. Although the best results are generally obtained with the 1:3 mole ratio, in practice because of the relatively high cost of the vinyl sulfonic acid, a mole ratio of 1:1.5 is generally preferred even though the results are not quite so good.

25 The phosphonic acids and the copolymers are generally used in the form of an alkali metal salt and usually as the sodium salt. Other suitable water soluble salts include potassium, ammonium, zinc, and lower amine salts. The free acids may also be used and all of the acidic
30 hydrogens need not be replaced nor need the cation be same for those replaced. Thus, the cation may be any one of or a mixture of NH_4 , H, Na, K, etc. The copolymer is converted into the water soluble salts by conventional methods.

While it is possible to add the phosphonic acid and the copolymer separately to an aqueous system, it is generally more convenient to add them together in the form of a composition. The composition of the present invention generally comprises from about 0.1 to about 100, preferably about 2 to 6, parts by weight of the copolymer and from about 0.1 to about 100, preferably about 0.5 to 5, parts by weight of the phosphonic acid. Generally, the polymer and phosphonic acid are present in the composition in a weight ratio of about from 10:1 to about 1:10, preferably of from about 4:1 to about 1:4, and especially of about 1:1.

The compositions may be added as dry powders and permitted to dissolve during use but normally are used in the form of aqueous solutions. The solutions generally contain from about 0.1 to about 70 weight percent of the composition and preferably contain from about 1 to about 40 weight percent. The solutions can be made by adding the ingredients to water in any order.

The amount of the composition added to the water is a substoichiometric amount that is effective to inhibit, control, and/or remove scale and sludge and depends on the nature of the aqueous system to be treated. The phosphonic acid dosage depends to some extent on the amounts of hardness causing scale forming compounds present in the system. Generally, the amount is calculated from the calcium concentration and consequent water hardness. The copolymer dosage depends to some extent on the concentration of suspended solids and existing levels of solids buildup in the system. The composition generally is added to the aqueous system in an amount of from about 0.01 to about 500 parts per million (p.p.m.) and preferably of from about 0.1 to about 100 ppm, and especially of from about 5 to about 50 ppm.

The compositions of this invention may include or be added to water containing other ingredients customarily employed in water treatment such as alkalies, lignin derivatives, other polymers, tannins, other phosphonates, biocides, and corrosion inhibitors. In particular, for pressurized boiler water treatment, it may be convenient to add the copolymer and phosphonate in combination with a water-soluble hardness precipitating agent, typically a phosphate such as sodium phosphate, e.g., disodium phosphate or trisodium phosphate, potassium phosphate or other phosphate including polyphosphates, e.g., sodium hexametaphosphate or a fluorophosphate, or a carbonate, typically sodium carbonate. The pH in the pressurized boiler will normally be adjusted, if necessary, to about 9.5 to about 12, preferably about 10 to about 11. This pH can be achieved by maintaining the recommended alkalinity value for the particular boiler employed by adding appropriate quantities of caustic soda. This alkalinity value can be determined using well known methods, such as by titration against standard acid. Typically, the copolymer is added as an aqueous solution generally containing about 0.1 to about 50%, preferably about 2.5 to 10%, especially about 3 to about 5% by weight (active) of the copolymer. The amount of hardness precipitating agent in the solution is suitably from about 5 to about 50% (or solubility limit), preferably from about 15 to about 35%, especially about 25 to about 35%, by weight. Thus, the relative weight proportions of the copolymer and hardness precipitating agent are suitably from 0.1:50 to 10:1, preferably from 1:15 to 2:3 (i.e. 0.1 to 500, preferably 1.5 to 15, parts by weight of hardness precipitating agent per part by weight of copolymer), especially from 1:11 to 1:13. In an especially preferred method, the total amount of the copolymer, phosphonate, and precipitating agent added to the system is from about 20 to about 2500 ppm of system water.

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The composition may be introduced at any location where it will be quickly and efficiently mixed with the water of the system. The treatment chemicals are customarily added to the makeup or feed water lines 5 through which water enters the system. Typically, an injector calibrated to deliver a predetermined amount periodically or continuously to the makeup water is employed. The present invention is especially useful in the treatment of the feed or makeup water in a steam 10 generating boiler. Such boiler systems are generally operated at a temperature of from about 298 to about 637°F. and a pressure of from about 50 to about 2,000 psig.

The composition and method of this invention are illustrated by the following examples in which all parts 15 are by weight unless otherwise indicated.

EXAMPLES

Aqueous solutions of a composition containing equal parts of hydroxyethylidene diposphonic acid, aminotri(methylene phosphonic acid), ethylenediaminetetra 20 (methylene phosphonic acid), or 2-phosphonobutane tricarboxylic acid-1,2,4 and of a copolymer of allyl sulfonic acid and maleic acid having a molecular weight of about 2,000 and a allyl sulfonic acid to maleic acid mole ratio of 1:1 were prepared. The treatment solutions also 25 contain sodium phosphate, sodium sulfate, sodium sulfite, sodium hydroxide, and sodium chloride in amounts sufficient to provide the boiler water composition shown in Table I. A solution containing the identical amounts of the treatment chemicals except for the composition of 30 the present invention and solutions containing the identical amounts of the treatment chemicals and equivalent amounts of each component of each of the compositions were also prepared.

The sludge conditioning and scale inhibiting properties of these solutions were evaluated in a small laboratory boiler which had three removable tubes as described in the Proceedings of the Fifteenth Annual Water 5 Conference, Engineers Society of the Western Pennsylvania, pp. 87-102 (1954). The feedwater for the laboratory boiler was prepared by diluting Lake Zurich, Illinois tap water with distilled water to 40 ppm total hardness as CaCO_3 and adding calcium chloride to provide a 6 to 1 10 elemental calcium to magnesium ratio. The feedwater and chemical treatment solutions were fed to the boiler in a ratio of 3 volumes of feedwater to 1 volume of solution giving a feedwater total hardness of 30 ppm of CaCO_3 . The scaling tests for all the treatment solutions were 15 conducted by adjusting boiler blowdown to 10 percent of the boiler feedwater giving an approximately 10-fold concentration of the boiler water salines and adjusting the composition of the treatment solution to give a boiler water after the 10-fold concentration having the 20 composition shown in Table I.

TABLE I

	Sodium Hydroxide as NaOH	258 ppm
	Sodium Carbonate as Na_2CO_3	120 ppm
	Sodium Chloride as NaCl	681 ppm
25	Sodium Sulfite as Na_2SO_3	50 ppm
	Sodium Sulfate as Na_2SO_4	819 ppm
	Silica as SiO_2	less than 1 ppm
	Iron as Fe	less than 1 ppm
	Phosphate as PO_4	10-20 ppm

30 The scaling tests were run for 45 hours each at a boiler water pressure of 400 psig. At the completion of a test, the boiler tubes were individually removed from the boiler and the scale or deposit present on 6 inches of the

central length of each tube was removed by scraping, collected in a tared vial, and weighed. The results of the tests are shown in Table II.

TABLE II

5			Additive Dosage in the Boiler Water (ppm)	Scaling Rate Rate (g/ft ² /hr)	Scale Reduction (%)
	Run No.	Additive(s)			
		<u>Comparative Runs</u>			
10	1	None (Blank)	-	0.213	-
	2	Allyl sulfonic acid and maleic acid copolymer (1:1; weight average molecular weight of about 2,000) (I)	5	0.063	70.4
15					
	3	Hydroxyethylidene diphosphonic acid (II)	5	0.148	30.5
20	4	Aminotri(methylene phosphonic acid) (III)	5	0.105	50.7
	5	Ethylenediamine- tetra(methylene phosphonic acid) (IV)	5	0.143	32.9
25					
	6	2-Phosphonobutane tricarboxylic acid 1,2,4 (V)	5	0.167	21.6
30					
		<u>Examples</u>			
	1	I + II (1:1 active)	5	0.007	96.7
	2	I + III (1:1 active)	5	0.005	97.7
	3	I + IV (1:1 active)	5	0.010	95.3
	4	I + IV (1:1 active)	5	0.010	95.3

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The comparative results on scale formation shown in Table II demonstrate that the composition and method of the present invention provide scale inhibition that unexpectedly is very considerably superior to that of the 5 components added alone.

In a second series of tests, the system used in Examples 1 - 4 was first run for 45 hours without any addition of copolymer and then one of the three tubes was taken out and replaced by a clean tube. The system was 10 then run for a further 45 hours but this time with a copolymer of sodium vinyl sulfonate and maleic acid added. After this further period of 45 hours, the scale in the three tubes was weighed as before. Thus, comparison of the results of this test with those of an 15 untreated blank (no polymer added during the second 45 hour period) enables one to assess whether the polymer was capable of removing scale and also preventing the formation of scale on a clean tube. The results obtained are shown in the following Table III.

20

TABLE III

<u>Example</u>	<u>Additives</u>	<u>Active Dosage in the Boiler Water, (ppm)</u>	<u>Scale Reduction (%)</u>
Comparative II		30	77.8
5	I + II (1:1 active)	30	115.1
25 6	VI + II (1:1 active)	30	110.1

VI = copolymer of sodium vinyl sulfonate and maleic acid (1.5:1; weight average molecular weight of about 7,000 - 9,000).

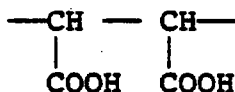
30 It can be seen that, in Examples 5 and 6 where the combination of phosphonate and vinyl or allyl copolymer was used, the scale reduction was greater than 100%, thus indicating the removal of existing scale.



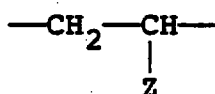
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CLAIMS

1. A composition suitable for controlling scale in an aqueous system which comprises a copolymer which possesses recurring units of the formula:



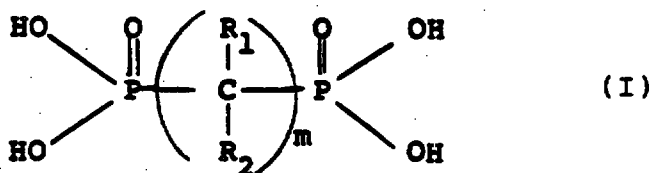
5 and of the formula:



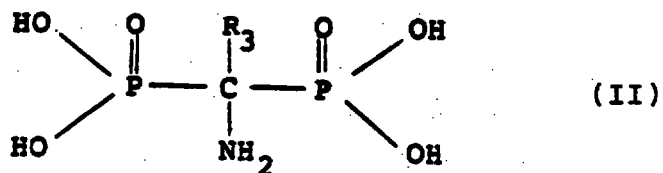
wherein Z represents $\text{---CH}_2\text{SO}_3\text{H}$

or a water soluble salt thereof, and a water soluble organic phosphonic acid or a water soluble salt thereof.

10 2. A composition according to claim 1 in which the phosphonic acid has the general formula



wherein m is an integer from 1 to 10, R_1 is hydrogen or an alkyl group having from 1 to 4 carbon atoms, R_2 is
15 hydroxyl, hydrogen, or an alkyl group having from 1 to 4 carbon atoms; or the general formula:

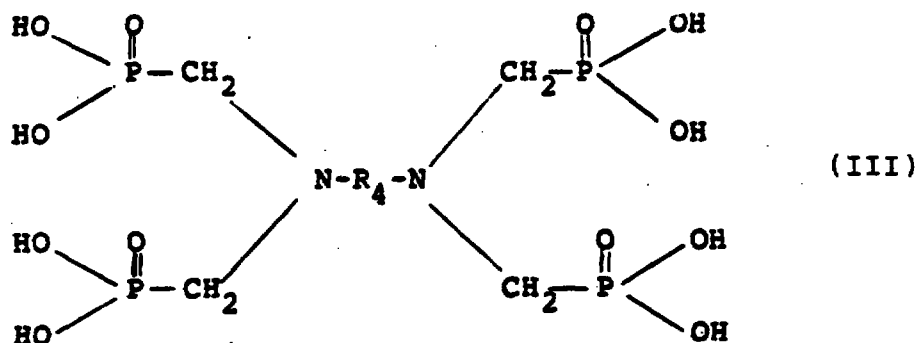


wherein R_3 is an alkyl group having 1 to 10 carbon atoms, benzyl, or phenyl; or the general formula:

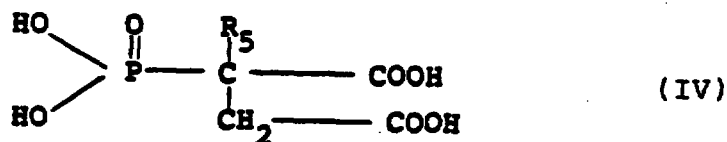


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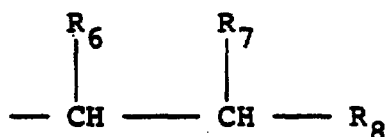
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wherein R_4 is an alkylene group having from 1 to 10 carbon atoms; or the general formula:



5 wherein R_5 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_6 is hydrogen, alkyl having 1 to 4 carbon atoms or 10 carboxyl, R_7 is hydrogen or methyl and R_8 is a carboxyl or phosphonate.

3. A composition according to claim 2 in which the phosphonic acid is an amino alkylene phosphonic acid or a water soluble salt thereof.

15 4. A composition according to claim 2 in which the phosphonic acid is aminotri(methylene phosphonic acid).

5. A composition according to claim 2 in which the phosphonic acid is ethylenediaminetetra(methylene phosphonic acid).



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6. A composition according to claim 2 in which the phosphonic acid is a hydroxy alkylidene phosphonic acid or a water soluble salt thereof.

7. A composition according to claim 6 in which the phosphonic acid is hydroxyethylidene-1,1-diphosphonic acid.

8. A composition according to claim 2 in which the phosphonic acid is a phosphonocarboxylic acid or a water soluble salt thereof.

9. A composition according to claim 2 in which the phosphonic acid is 2-phosphonobutane tricarboxylic acid-1,2,4.

10. A composition according to claims 1 to 9 in which the copolymer and the phosphonic acid are present in a weight ratio of from 10:1 to 1:10.

11. A composition according to claim 10 in which the copolymer and the phosphonic acid are present in a weight ratio of from 4:1 to 1:4.

12. A composition according to claim 11 in which the copolymer and the phosphonic acid are present in a weight ratio of about 1:1.

13. A composition according to any one of the preceding claims in which the copolymer comprises from 10 to 80 mole percent of allyl sulfonic acid moieties and from 90 to 20 mole percent of maleic acid moieties.

14. A composition according to claim 13 in which the copolymer comprises from 25 to 75 mole percent of allyl sulfonic acid moieties and from 75 to 25 mole percent of maleic acid moieties.

15. A composition according to any one of the preceding claims in which the molecular weight of the copolymer is from 500 to 100,000.

16. A composition according to claim 15 in which the molecular weight of the copolymer is from 800 to 25,000.

17. A composition according to claim 16 in which the molecular weight of the copolymer is 1,000 to 15,000.



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18. A composition according to any one of the preceding claims which further comprises a water soluble hardness precipitating agent.

19. A composition according to claim 18 in which the hardness precipitating agent is disodium or trisodium phosphate or sodium hexa metaphosphate.

20. A composition according to claim 18 or 19 which contains 0.1 to 500 parts by weight of hardness precipitating agent per part by weight of copolymer.

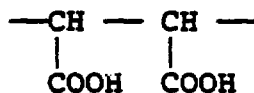
21. A composition according to claim 20 which contains 1.5 to 15 parts by weight of hardness precipitating agent per part by weight of copolymer.

22. A composition according to any one of the preceding claims which is aqueous.

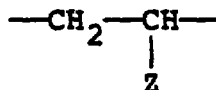
23. A composition according to claim 1 suitable for inhibiting formation of scale in an aqueous system comprising an aqueous solution of a copolymer of maleic acid and allyl sulfonic acid, said copolymer having a molecular weight of from 800 to 25,000 and an allyl sulfonic acid to maleic acid mole ratio of about 1:1 and hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylene phosphonic acid), ethylenediamine tetra(methylene phosphonic acid), or 2-phosphonobutane tricarboxylic acid 1,2,4; said copolymer and said phosphonic acid being present in a weight ratio of about 1:1.

24. A composition according to claim 1 substantially as described in any one of the Examples.

25. A method for controlling scale in an aqueous system comprising adding to the system a copolymer which possesses recurring units of the formula:



and of the formula:

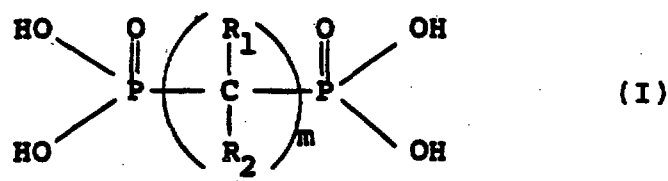


wherein Z represents $\text{---CH}_2\text{SO}_3\text{H}$

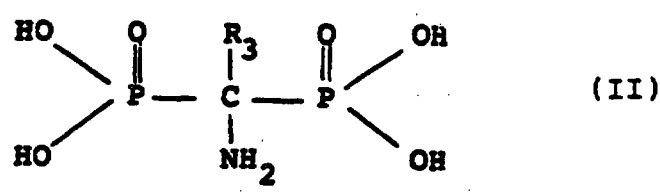
or a water soluble salt thereof, and a water soluble organic phosphonic acid or a water soluble salt thereof.

26. A method according to claim 25 in which the phosphonate has the general formula:

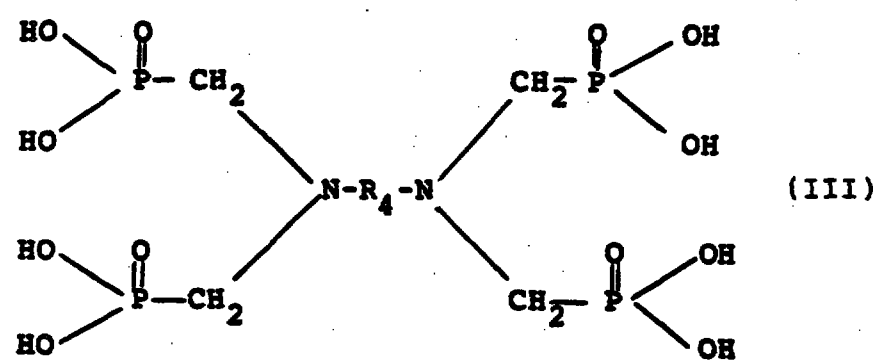
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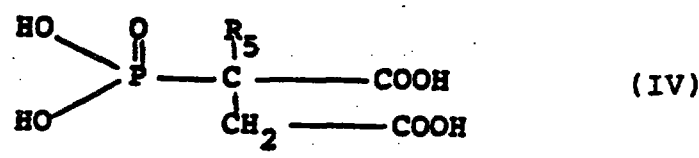
wherein m is an integer from 1 to 10, R₁ is hydrogen or an alkyl group having from 1 to 4 carbon atoms, R₂ is hydroxyl, hydrogen, or an alkyl group having from 1 to 4 carbon atoms; 5 or the general formula:



wherein R₃ is an alkyl group having 1 to 10 carbon atoms, benzyl, or phenyl; or the general formula:



10 wherein R₄ is an alkylene group having from 1 to 10 carbon atoms; or the general formula:



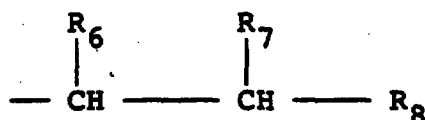
wherein R₅ is hydrogen, alkyl, alkenyl or alkynyl having



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up to 4 carbon atoms; phenyl; cycloalkyl having 3 to 6 carbon atoms; benzyl; phenethyl or



wherein R_6 is hydrogen, alkyl having 1 to 4 carbon atoms or 5 carboxyl, R_7 is hydrogen or methyl and R_8 is a carboxyl or phosphonate.

27. A method according to claim 26 in which the phosphonic acid is an amino alkylene phosphonic acid or a water soluble salt thereof.
- 10 28. A method according to claim 26 in which the phosphonic acid is aminotri(methylene phosphonic acid).
29. A method according to claim 28 in which the phosphonic acid is ethylenediaminetetra(methylene phosphonic acid).
- 15 30. A method according to claim 28 in which the phosphonic acid is a hydroxy alkylidene phosphonic acid or a water soluble salt thereof.
31. A method according to claim 26 in which the phosphonic acid is hydroxyethylidene-1,1-diphosphonic acid.
- 20 32. A method according to claim 26 in which the phosphonic acid is a phosphonocarboxylic acid or a water soluble salt thereof.
33. A method according to claim 26 in which the phosphonic acid is 2-phosphonobutane tricarboxylic acid-1,2,4.
- 25 34. A method according to any one of claims 22 to 30 in which the copolymer comprises from 10 to 80 mole percent of allyl sulfonic acid moieties and from 90 to 20 mole percent of maleic acid moieties.
- 30 35. A method according to claim 34 in which the copolymer comprises from 25 to 75 mole percent of allyl sulfonic acid moieties and from 75 to 25 mole percent of maleic acid moieties.



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36. A method according to any one of claims 25 to 35 in which the molecular weight of the copolymer is from 500 to 100,000.

37. A method according to claim 36 in which the molecular weight of the copolymer is from 800 to 25,000.

38. The method according to claim 36 in which the molecular weight of the copolymer is 1,000 to 15,000.

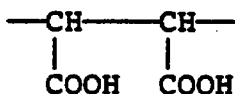
39. A method according to any one of claims 22 to 35 in which the copolymer and phosphonic acid are added as a composition as claimed in any one of claims 1 to 24.

40. A method according to claim 39 in which the composition is added to the aqueous system in an amount of from 0.01 to 500 parts per million in system water.

41. A method of inhibiting formation of scale in a steam generating boiler according to claim 25 which comprises adding to the boiler water an aqueous solution of a copolymer of maleic acid and allyl sulfonic acid, said copolymer having a molecular weight of from 1,000 to 15,000 and an allyl sulfonic acid to maleic acid mole ratio of about 1:1 and hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylene phosphonic acid) ethylenediamine tetra(methylene phosphonic acid), or 2-phosphonobutane tricarboxylic acid, 1,2,4; said copolymer and said phosphonic acid being present in a weight ratio of about 1:1 and said composition being added in an amount of from 0.1 to 100 parts per million of water in the boiler.

42. A method according to claim 25 substantially as described in any one of the Examples.

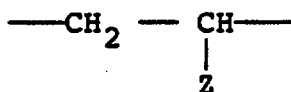
43. A method for the treatment of scale in a pressurised boiler water system which comprises adding to the system a copolymer which possesses recurring units of the formula:





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and of the formula:



wherein Z represents $\text{-SO}_3\text{H}$ or $\text{-CH}_2\text{SO}_3\text{H}$ or a water soluble salt thereof, and of a water soluble organic phosphonic acid or a water soluble salt thereof.

5 44. A method according to claim 43 in which the copolymer is one defined in any one of claims 13 to 17.

45. A method according to claim 43 or 44 in which the phosphonic acid is one defined in any one of claims 2 to 9.

10 46. A method according to any one of claims 25 to 40 and 43 to 45 in which a water soluble hardness precipitating agent is also added to the system.

15 47. A method according to claim 46 in which a water soluble hardness precipitating agent is also added to the system in an amount from 0.1 to 500 parts by weight per part by weight of the copolymer.

20 48. A method according to claim 47 in which the hardness precipitating agent is added to the system in an amount from 1.5 to 15 parts by weight per part by weight of the copolymer.

49. A method according to any one of claims 46 to 48 in which the hardness precipitating agent is sodium phosphate.

25 50. A method according to any one of claims 46 to 48 in which the hardness precipitating agent is disodium or trisodium phosphate or sodium hexa metaphosphate.

30 51. A method according to any one of claims 25 to 40 and 43 to 50 in which the total amount of copolymer, phosphonate and precipitating agent added to the system is from 20 ppm to 2500 ppm of system water.

52. A method according to claim 43 substantially as hereinbefore described.
