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(54) **COMPOSE PERMETTANT DE CONTROLER LA FORMATION
DE DEPOT CALCAIRE EN MILIEUX AQUEUX ET PROCEDE
CONNEXE**

(54) **SCALE CONTROL IN AQUEOUS SYSTEMS**

(57) A composition and process for preventing the deposition of scale and sludge in aqueous systems comprising adding to the system the combination of three or more additives selected from the group consisting of a) polyacrylic acid, copolymer of alkylsulfonate and maleic anhydride and mixtures thereof, b) hydroxy ethylidene diphosphonic acid, amino (trimethyl phosphonic acid), diethylenetriamine pentaacetic acid, and mixtures thereof, and c) copolymer of styrene sulfonate and maleic anhydride, copolymer of acrylic acid and acrylamide, poly(acrylic acid-co-hypophosphite) and mixtures thereof, and wherein the combination contains at least one additive selected from each of a), b) and c).

ABSTRACT

A composition and process for preventing the deposition of scale and sludge in aqueous systems comprising adding to the system the combination of three or more additives
5 selected from the group consisting of a) polyacrylic acid, copolymer of alkylsulfonate and maleic anhydride and mixtures thereof, b) hydroxy ethylidene diphosphonic acid, amino (trimethyl phosphonic acid), diethylenetriamine pentaacetic acid, and mixtures thereof, and c) copolymer of styrene
10 sulfonate and maleic anhydride, copolymer of acrylic acid and acrylamide, poly(acrylic acid-co-hypophosphite) and mixtures thereof, and wherein the combination contains at least one additive selected from each of a), b) and c).

BACKGROUND OF THE INVENTIONField of the Invention

5 This invention relates to compositions useful for
inhibiting the deposition of scale and sludge deposits
in aqueous systems particularly in steam generating
boilers, and more specifically this invention relates
to improved compositions comprising three or more
additives selected from the group consisting of a)
10 polyacrylic acid, copolymer of alkyl sulfonate and
maleic anhydride, and mixtures thereof, b) amino
(trimethylene phosphonic acid), hydroxyethylidene
diphosphonic acid, diethylenetriamine pentaacetic acid,
and mixtures thereof, and c) copolymer of styrene
15 sulfonate and maleic anhydride, copolymer of acrylic
acid and acrylamide, poly(acrylic acid- co-
hypophosphite) and mixtures thereof, wherein at least
one additive is selected from each of a), b) and c)
supra.

Description of Prior Art

20 The formation of scale and sludge deposits on
heating surfaces is the most serious problem
encountered in boiler operations. External water
softening only partially removes from the boiler
25 feedwater those scale-forming substances. In most
industrial boilers, internal chemical treatment is
applied to the boiler water to combat the scale-forming
tendency of entrained impurities, such as calcium,
30 magnesium salts, iron and silica. The internal
chemical treatment of boiler water can be accomplished
by either non-precipitation or precipitation treatment
programs. Under the non-precipitation treatment
program, chelants such as NTA (nitrilotriacetic acid)

and EDTA (ethylenediamine tetraacetic acid) are used. EDTA is capable of preventing calcium and magnesium deposits by solubilizing and moving these scale-forming substances through the boiler system until they are removed by blowdown. However, EDTA is known to be corrosive under certain conditions for example when there is excessive residual in the boiler.

Under the precipitation treatment program, commonly used precipitating chemicals include soda ash and sodium phosphates, e.g. disodium phosphate, trisodium phosphate and sodium metaphosphate. Thus, magnesium is precipitated as magnesium hydroxide by increasing the alkalinity of the boiler water. The precipitate or sludge, which can be made non-sticky and easily manageable by the addition of a dispersant or sometimes called sludge conditioner, is periodically or continuously removed from the boiler through blowdown. A wide variety of materials have been used as boiler dispersants such as sodium polyacrylates, sodium polymethacrylates, sodium carboxymethylcellulose, styrene-maleic anhydride copolymers, etc. However, the results of their dispersants have not been completely satisfactory.

Summary of the Invention

It is an object of this invention to provide improved compositions for inhibiting the deposition of scale and sludge in aqueous systems.

In accordance with this invention, there have been provided certain novel compositions which are comprised of a mixture of at least three additives selected from the group consisting of;

- 4 -

a) polyacrylic acid (PAA), copolymer of allyl sulfonate and maleic anhydride (ASMA) and mixtures thereof,

5 b) amino(trimethylene phosphonic acid) (AMP), hydroxyethylidene diphosphonic acid (HEDPA), diethylenetriamine pentaacetic acid (DTPA) and mixtures thereof, and

10 c) copolymer of styrene sulfonate and maleic anhydride (SMA), copolymer of acrylic acid and acrylamide (AAA), poly(acrylic acid-co-hypophosphite) (PAAHP) and mixtures thereof, wherein at least one additive is selected from each of a), b) and c) supra. The novel compositions of this invention exhibit surprising and unexpected activity in preventing and
15 controlling scale and sludge deposits in aqueous systems under both precipitation and non-precipitation treatment programs.

Detailed Description

20 The present invention is directed to compositions with improved effectiveness for inhibiting the deposition of scale and sludge in aqueous systems. The compositions of this invention comprise a combination of three or more additives selected from the group
25 consisting of;

a) polyacrylic acid (PAA), copolymer of allyl sulfonate and maleic anhydride (ASMA) and mixtures thereof,

30 b) hydroxyethylidene diphosphonic acid (HEDPA), amino(trimethylene phosphonic acid) (AMP) and diethylenetriamine pentaacetic acid (DTPA) and mixtures thereof, and

c) copolymer of styrene sulfonate and maleic anhydride (SMA), copolymer of acrylic acid and

- 5 -

acrylamide (AAA), poly(acrylic acid-co-hypophosphite) (PAAHP) and mixtures thereof, wherein at least one additive is selected from each of a), b) and c) supra.

5 The ratio of additives a:b:c is typically in the range (9-1):(9-1):5-0.5, preferably (6-2):(6-2):(3:1) respectively on an active basis. Mixtures within a group, for example in group a) polyacrylic acid together with copolymer of allyl sulfonate and maleic anhydride, are typically in the range (10-1):(1-10) and
10 are preferably 1:1 on an active basis.

The polyacrylic acid preferably has a low molecular weight in the range of 800 to 90,000, most preferably 1000 to 5000 on a weight average basis. The copolymer of allyl sulfonate and maleic anhydride
15 typically has a weight ratio of 10:1 to 1:10 respectively, preferably 1:1 and has a molecular weight in the 800 to 90,000 preferably 1000 to 10,000 on a weight average basis. The hydroxyethylidene diphosphonic acid and the amino(trimethylene phosphonic acid) are commercially available and conventional
20 procedures for preparation of these are described, for example, in U.S. Patent 3,214,454 and U.S. Patent 3,234,124 respectively. These phosphonates can be in potassium, sodium or ammonium salts. The
25 diethylenetriamine pentaacetic acid can be "as is" in acid form or in water soluble salts such as sodium, potassium and ammonium, most preferably the sodium salts. The DTPA is commercially available under the trademark of Hamp-EX Acid or Hamp-Ex 80 in sodium
30 salts, of W. R. Grace & Co.-Conn. The poly(acrylic acid-co-hypophosphite) can be in a weight ratio of 20:1 to 1:20 respectively, preferably 4:1 to 16:1 having a molecular weight in the range of 1000 to 20,000, preferably 1,000 to 5,000 on a weight average basis.

The copolymer of styrene sulfonate and maleic anhydride can be in a weight ratio of 10:1 to 1:10 respectively, preferably 1:1 having a molecular weight in the range 800 to 20,000, preferably 1000 to 5000 on a weight average basis. The copolymer of acrylic acid and acrylamide typically has a weight ratio of 1:10 to 10:1 and a molecular weight in the range 800 to 90,000 preferably 1000 to 10,000 on a weight average basis.

The combination of additives in accordance with this invention are capable of preventing and controlling scale in aqueous systems, such as steam generating boilers, under both the precipitation and non-precipitation treatment programs.

The total amounts of each additive can vary widely, provided it is in an amount effective to control the deposition of scale and sludge and in general, each additive is present in the range 0.1 ppm to 500 ppm, preferably 0.5 to 10 ppm and most preferably between 1 to 5 ppm.

The additives may be added to the aqueous system individually or they may be blended into uniform, homogeneous mixture, and optionally diluted with a suitable water-miscible diluents. In such mixtures, additives, (a) will normally be present in an amount from 15 to 90%, preferably 40 to 70%, and most preferably 45 to 55% by weight. The amount of the second additive, (b), will generally be in the range 5 to 45%, preferably 10 to 35 and most preferably 20 to 30% by weight. Thus, the amount of the third component is generally between 5 to 40%, preferably 10 to 25 and most preferably 15 to 20% by weight.

In addition to the instant composition, it is possible to incorporate into the composition or add to the aqueous system other materials used in the

treatment of aqueous systems. Such materials include, but are not limited to corrosion inhibitors.

5 The following examples are provided to illustrate the invention, but are not to be construed as limiting the invention in any way except as indicated on the appended claims. The examples provided herein include various embodiments of the invention. Other
10 embodiments will be apparent to those skilled in the art from a consideration of the specification or practice of the invention disclosed herein. It is understood that modifications and variations may be practiced without departing from the spirit and scope of the novel concepts of this invention.

15 The evaluation of the effectiveness of the additives under the non-precipitation and precipitation treatment programs was carried out in a small laboratory boiler. This boiler has been described previously in the proceedings of the Fifteenth Annual Water Conference, Engineers Society of Western
20 Pennsylvania, pages 87-102.

EXAMPLE 1

25 Using the laboratory boiler, the efficiency of the blended additives to transport calcium, magnesium and iron through the boiler system was tested at 200 psig for four days. The feedwater contained about 2 ppm as CaCO_3 of total hardness having a 2:1 (as CaCO_3) of calcium to magnesium ratio, 0.5 ppm as Fe of iron, 20 ppm as Cl of chloride, 35 ppm as SO_4 of sulfate and less
30 than 1 ppm as SiO_2 of silica. The boiler water concentration was about ten times. Sodium hydroxide and sodium sulfite were used to maintain a hydroxide alkalinity of 300-350 ppm as CaCO_3 and a residual sulfite of at least 20 ppm as SO_3 . The feedwater and

- 8 -

boiler water samples were analyzed for calcium, magnesium and iron by atomic absorption.

Various blended additives were tested using a dosage of 5:1 active additive per total hardness plus iron. The compositions tested have shown excellent total hardness recovery in the boiler.

1. Composition I - PAA + AMP + SMA
(6:3:2 active)
- 10 2. Composition II - PAA + DTPA + AAA
(6:3:2 active)
3. Composition III - AAA + AMP + ASMA
(6:6:2 active)
- 15 4. Composition IV - ASMA + AMP + AAA
(6:3:2 active)
5. Composition V - ASMA + HEDPA + SMA
(6:3:2 active)
6. Composition VI - PAA + AMP + SMA
(6:6:2 active)
- 20 7. Composition VII - ASMA + HEDPA + SMA
(6:3:4 active)
8. Composition VIII - PAA + AMP + AAA + PAAHP
(6:3:2:2 active)
- 25 9. Composition IX - PAA + AMP + SMA + ASMA
(6:3:2:2 active)
10. Composition X - PAA + HEDPA + AAA + PAAHP
(6:3:2:2 active)

The excellent total hardness transport performance of the 10 products is illustrated in the following table.

Table 1

Performance in % Transport
Total

	<u>Run No.</u>	<u>Additive</u>	<u>Hardness</u>	<u>Iron</u>
5	R-20	None (Blank)	15.3	0.8
	C-1429	Composition I	161.7	41.6
	C-1430	Composition II	127.4	66.2
	R-43	Composition III	111.0	81.5
10	C-1435	Composition IV	115.0	11.5
	R-23	Composition V	110.0	82.1
	R-42	Composition VI	89.0	86.4
	R-30	Composition VII	87.5	91.2
	R-32	Composition VIII	90.4	68.8
15	R-33	Composition IX	84.2	72.5
	R-38	Composition X	94.8	90.4

When the individual additives were evaluated for material transports at 200 psig, the following data were obtained.

Table 2

	<u>Run Nos.</u>	<u>Additive</u>	<u>% Total Hardness</u> <u>Transport</u>	<u>% Iron</u> <u>Transport</u>
	M-1911/R-11	None (Blank)	17.0	0.7
5	C-1416/R-12	PAA	77.9	3.4
	C-1417/C-1422	SMA	35.9	30.4
	M-1906/M-1913	AAA	71.8	23.5
	C-1415/R-12	ASMA	56.0	22.4
	R-48/R-49	PAAHP	74.4	14.9
10	M-1909/M-1914	HEDPA	24.7	22.0
	R-8/M-1916	AMP	39.2	17.5
	C-1418/R-21	DTPA	51.8	32.2
	R-7/R-10	EDTA	68.8	12.1

15

EXAMPLE 2

Using the same procedure as in Example 1, except the boiler pressure was 600 psig, the excellent total hardness transport performance of three products tested is shown as follows:

20

Table 3

	<u>Run No.</u>	<u>Additive</u>	<u>% Total Hardness Transport</u>
25	R-50	None (Blank)	20.2
	R-52	Composition VII	115.9
	R-51	Composition X	98.1
	R-81	Composition VIII	95.9

EXAMPLE 3

The scale preventing property of the blended additives on a precipitation boiler water treatment program was determined using the same small laboratory boiler. The boiler has three removable tubes. After the completion of a test, the boiler tubes were removed

from the boiler. The scale or deposit formed on the six inches of the central length of each tube was removed by scraping, collected in a tared vial and weighed. The scale scraped on the tubes on a blank test (no additive) and on a test with the additive being tested is compared.

The feedwater for the evaluation of additives was prepared by diluting Lake Zurich, Illinois tap water with distilled water to 40 ppm total hardness as CaCO_3 , followed by adjustment to a 6 to 1 elemental calcium to magnesium ratio using calcium chloride and/or magnesium chloride. The feedwater was fed to the boiler together with chemical treatment solutions (containing sodium sulfate, sodium sulfite, sodium hydroxide, sodium chloride, disodium phosphate and the additives for scale prevention) in a ratio of three volumes of feedwater to one volume of chemical treatment solution, giving a feedwater total hardness of 30 ppm as CaCO_3 . In the case of a blank test, no additive was added. All scaling tests, whether boiler water additive was present or absent (blank), were carried out in fixed manner as described as follows: Boiler blowdown was adjusted to 10% of the boiler feedwater, giving approximately 10 concentrations of the boiler water salines. Using the feedwater described previously in this paragraph, the composition of the chemical treatment solution was adjusted to give a boiler (after the 10 concentrations) of the following composition.

Table 4

	Sodium hydroxide as NaOH	258 ppm
5	Sodium carbonate as Na ₂ CO ₃	120 ppm
	Sodium chloride as NaCl	681 ppm
	Sodium sulfite as Na ₂ SO ₃	30-50 ppm
	Sodium sulfate as Na ₂ SO ₄	819 ppm
	Silica as SiO ₂	less than 1 ppm
10	Iron as Fe	less than 1 ppm
	Phosphate as PO ₄	20-40 ppm

All scaling tests were run for 47 hours each at a boiler pressure of 400 psig.

15 The effective scale inhibiting properties of the blended additive products are illustrated in the following table.

Table 5

5	Run No.	Additives	Active	Scaling	Scale
			Dosage in the Feed, ppm		
				Rate, g/ft ² /hr	Reduc- tion, %
	M-1947	None (Blank)	-	0.220	-
	M-1443	PAA	1	0.046	79.1
10	M-1703	SMA	1	0.010	95.4
	M-1716	AAA	1	0.061	72.3
	C-1138	ASMA	1	0.006	97.3
	C-1506	PAAHP	1	0.099	58.2
	M-398	HEDPA	1	0.145	34.1
15	M-372	AMP	1	0.074	66.4
	C-1439	Composition I	1	0.000	100.0
	M-1934	Composition V	1	0.002	99.1
	M-1936	Composition VII	1	0.004	98.2
20	M-1939	Composition X	1	0.009	95.9
	C-1441	Composition I	0.5	0.015	93.8
	M-1935	Composition V	0.5	0.128	39.4
	M-1938	Composition VII	0.5	0.042	80.1
	M-1940	Composition X	0.5	0.069	68.6
25	M-1950	Composition VI	0.5	0.019	90.9
	M-1946	Composition III	0.5	0.065	70.4

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A composition for inhibiting the deposition of scale and sludge in aqueous systems
 5 comprising the combination of three or more additives selected from the group consisting of:
 - a) polyacrylic acid (PAA), copolymer of allyl sulfonate and maleic anhydride (ASMA) and mixtures thereof,
 - b) hydroxyethylidene diphosphonic acid (HEDPA), amino(trimethylene
 10 phosphonic acid) (AMP), diethylenetriamine pentaacetic acid (DTPA), and mixtures thereof, and
 - c) copolymer of acrylic acid and acrylamide (AAA), and poly(acrylic acid-co-hyphosphite) (PAAHP) and mixtures thereof, and wherein the composition contains
 15 at least one additive selected from each of a), b) and c) supra, wherein the ratio additives a:b:c is from about 9-1:9-1:5-0.5, respectively on an active basis.
2. A composition according to claim 1 wherein the ratio of additives a:b:c is from
 20 about 6:3:2 respectively.
3. A composition according to claim 1 wherein (a) is polyacrylic acid and (b) is amino(trimethylene phosphonic acid).
- 25 4. A composition according to claim 1 wherein (a) is polyacrylic acid, (b) is diethylenetriamine pentaacetic acid and (c) is copolymer of acrylic acid and acrylamide.
5. A composition according to claim 1 wherein (a) is copolymer of allyl sulfonate and maleic anhydride, (b) is amino(trimethylene phosphonic acid) and (c) is copolymer of
 30 acrylic acid and acrylamide.

6. A composition according to claim 1 wherein (a) is copolymer of allyl sulfonate and maleic anhydride and (b) is hydroxyethylidene diphosphonic acid.

5 7. A composition according to claim 1 wherein (a) is polyacrylic acid, (b) is amino(trimethylene phosphonic acid), and (c) is a mixture of copolymer of acrylic acid and acrylamide, and poly(acrylic acid-co-hypophosphite).

8. A composition according to claim 1 wherein (a) is a mixture of polyacrylic acid
10 and copolymer of allyl sulfonate and maleic anhydride and (b) is amino(trimethylene phosphonic acid).

9. A composition according to claim 1 wherein (a) is polyacrylic acid, (b) is hydroxyethylidene diphosphonic acid, and (c) is a mixture of copolymer of acrylic acid
15 and acrylamide and poly(acrylic acid-co-hypophosphite).

10. A method for inhibiting the deposition of scale and sludge in aqueous systems comprising adding to the aqueous system the composition which further comprises the combination of three or more additives selected from the group consisting of:

20 a) polyacrylic acid (PAA), copolymer of allyl sulfonate and maleic anhydride (ASMA),

b) hydroxyethylidene diphosphonic acid (HEDPA), amino(trimethylene phosphonic acid) (AMP), and pentasodium diethylenetriamine pentaacetic acid (DTPA),
and

25 c) copolymer of acrylic acid and acrylamide (AAA), and poly(acrylic acid-co-hypophosphite) (PAAHP), and wherein the composition contains at least one additive selected from each of a), b) and c) supra wherein the ratio of additives a:b:c is from about 9-1:9-1:5-0.5 respectively on an active basis.

11. A method according to claim 10 wherein the amount of additive is in the range 1 ppm to 500 ppm.
- 5 12. A method according to claim 10 wherein the amount of additive is equal to the total hardness plus iron of the aqueous system.
13. A method according to claim 10 wherein the ratio of additives a:b:c is from about 6:3:2 respectively.
- 10 14. A method according to claim 10 wherein (a) is polyacrylic acid and (b) is amino(trimethylene phosphonic acid).
- 15 15. A method according to claim 10 wherein (a) is polyacrylic acid, (b) is diethylenetriamine pentaacetic acid and (c) is copolymer of acrylic acid and acrylamide.
- 20 16. A method according to claim 10 wherein (a) is copolymer of allyl sulfonate and maleic anhydride, (b) is amino(trimethylene phosphonic acid) and (c) is copolymer of acrylic acid and acrylamide.
- 25 17. A method according to claim 10 wherein (a) is copolymer of allyl sulfonate and maleic anhydride and (b) is hydroxyethylidene diphosphonic acid.
18. A method according to claim 10 wherein (a) is polyacrylic acid, (b) is amino(trimethylene phosphonic acid), and (c) is a mixture of copolymer of acrylic acid and acrylamide, and poly(acrylic acid-co-hypophosphite).
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19. A method according to claim 10 wherein (a) is a mixture of polyacrylic acid and copolymer of allyl sulfonate and maleic anhydride and (b) is amino(trimethylene phosphonic acid).
- 5 20. A method according to claim 10 wherein (a) is polyacrylic acid, (b) is hydroxyethylidene diphosphonic acid, and (c) is a mixture of copolymer of acrylic acid and acrylamide, and poly(acrylic acid-co-hypophosphite).
21. A composition according to claim 1 wherein the ratio of additives a:b:c is from (6-2):(6-2):(3-1).
22. A method according to claim 10 wherein the ratio of additives a:b:c is from (6-2):(6-2):(3-1).