

PATENT SPECIFICATION

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(54) CONTROL OF SCALING IN AN AQUEOUS MEDIUM

(71) We, BETZ INTERNATIONAL, INC., a corporation organized and existing under the laws of the State of Pennsylvania, United States of America, of 4636 Somerton Road, Trevose, State of Pennsylvania, United States of America, (assignee of IRENE THERESA GODLEWSKI, JOSEPH JOHN SCHUCK and ANDREW STEPHAN CHISARIK), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of controlling the formation and deposition of deposits on the structural parts of a system containing an aqueous medium. More particularly it relates to a method of controlling the formation and deposition of deposits such as calcium phosphate on the structural parts of a system containing an aqueous medium having the tendency for the formation of such deposits. It also relates to a method of dispersing a compound such as iron oxide and/or clay contained in an aqueous medium. Although the invention has general applicability to any given system where the formation and deposition of deposits, such as calcium phosphate, is a potential problem, it will be discussed in detail as it concerns boiler water systems.

As is well known and comprehensively described and discussed in the *Betz Handbook of Industrial Water Conditioning*, 6th Edition, 1968, Betz Laboratories, Inc., Trevose, Pennsylvania, pages 151—171, the formation of scale and sludge deposits on boiler heating surfaces is the most serious water problem encountered in steam generation. Although current industrial steam producing systems make use of sophisticated external treatments of the boiler feed water, e.g., coagulation, filtration, softening of water prior to its feed into the boiler system, those operations are only moderately effective. In all cases, external treatment does not in itself provide adequate treatment since muds, sludge, silts and hardness-imparting ions escape the treatment, and eventually are introduced into the steam generating system.

The problems which result from their introduction into the steam generating system are apparent. Since the deposit forming materials are present, they have a tendency to accumulate upon concentration of the water and to settle at points in the system where there is low flow and therefore restrict water circulation. The baking of mud and/or sludge on tubes and sheets will result in overheating and failure, thereby requiring down time for repair or replacement of the structural parts. In addition, mud, sludge, and silts may become incorporated in scale deposits adding to their volume and heat insulating effect.

Accordingly, internal treatments have been necessary to maintain the mud and silts in a suspended state. These internal treatments have been generally referred to in the industry as sludge conditioning agents.

In addition to the problems caused by mud, sludge or silts, the industry has also had to contend with boiler scale. Although external treatment is utilized specifically in an attempt to remove calcium and magnesium from the feed water, scale formation due to residual hardness, i.e., calcium and magnesium salts or the breakdown of calcium carbonate, is always experienced. Accordingly, internal treatment, i.e., treatment of the water fed to the system, is necessary to prevent, reduce and/or retard formation of the scale-imparting compounds and their deposition. The carbonates of magnesium and calcium are not the only problem compounds as regards scale, but also waters having high contents of phosphate,

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5 sulfate and silicate ions either occurring naturally or added for other purposes
cause problems since calcium and magnesium, and any iron or copper present,
react with each and deposit as boiler scale. The problem is compounded by the
deposition of iron oxides and clay with the other scale salts. Iron oxides enter the
systems by escaping the pretreatment procedures and/or are present due to
corrosion of the metal parts in contact with the aqueous medium. As is obvious, the
deposition of scale (including iron oxide) on the structural parts of a steam
generating system causes poorer circulation and lower heat transfer capacity,
resulting accordingly in an overall loss in efficiency.

10 Although the foregoing discussion is directed to boiler water systems, or more
specifically steam generating systems, the same problems occur in pulp and paper
mill systems such as cooling water systems, desalinization systems (calcium sulfate
formation and deposition) and scrubber systems. The problems encountered in
these operations sometimes are more severe since complete external treatments
are not commonly utilized. Any aqueous system having calcium and magnesium
cations and the exemplified anions, in particular phosphate, will experience the
formation and deposition of the scaling salts.

15 Because of the foregoing problems, the water treatment industry is constantly
evaluating new processes, new products and new techniques in an effort to permit
the various process water systems to operate more effectively for longer periods
and at lower costs.

20 Many and different type materials have been used for internal treatment of
water systems, and in particular as sludge conditioning agents. Of the vast number
of such agents may be mentioned alginates, lignins, lignosulfonates, tannins,
carboxymethyl cellulose materials, synthetic polymers such as polyacrylates and in
particular polymethacrylates. United States Patent Specifications Nos. 2,723,956;
3,188,289 and 3,519,538 are merely representative of descriptions of the type
materials used and the functions thereof. United States Patent Specifications Nos.
2,723,956 and 3,519,538 describe boiler treatments utilizing maleic anhydride and
non-sulfonated styrene copolymers wherein the mole ratio of anhydride to styrene
is at least 1:1 and preferably 2:1.

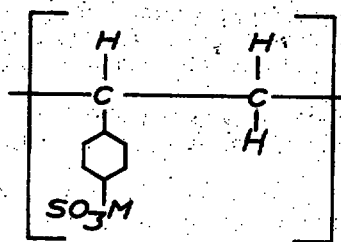
25 It has now been found that if a particular type of polymer composed of
substantially sulfonated styrene moieties and those derived from maleic anhydride
is added or introduced into the water of a process water system, the formation and
deposition of scale, particularly calcium and magnesium phosphates, silicate and
iron oxide scale, on the metallic structures of the equipment can be controlled to a
degree necessary to permit the continual and economical operation of the system.

30 According to the present invention there is provided a method of controlling
the formation and deposition of deposits on the structural parts of a system
containing an aqueous medium which comprises introducing into the aqueous
medium an effective amount of a polymer or a water-soluble salt thereof, the
polymer being comprised of sulfonated styrene moieties and moieties derived from
maleic anhydride, the styrene moieties exceeding the maleic anhydride derived
moieties.

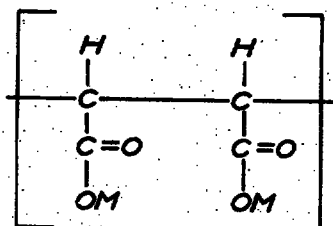
35 According to the present invention there is also provided a method of
controlling the formation and deposition of calcium phosphate on the structural
parts of a system containing an aqueous medium containing calcium and phosphate
ions which comprises introducing into the aqueous medium an effective amount of
a polymer or a water-soluble salt thereof, the polymer being comprised of
sulfonated styrene moieties and moieties derived from maleic anhydride, the
styrene moieties exceeding the maleic anhydride derived moieties.

40 In this specification and the appended claims the term "effective amount"
means the amount necessary to control the formation and deposition of the
indicated deposits or to disperse the indicated materials. When reference is made
in this specification and the appended claims to "sulfonated styrene moieties" it is
normally intended to mean that complete sulfonation of the styrene moieties has
taken place; however the term also covers the situation where sulfonation is less
than complete.

45 When the styrene moieties are completely sulfonated, the polymers which are
used in the present invention are those containing sulfonated styrene moieties, i.e.,
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and moieties derived from maleic anhydride, i.e.,



where the sulfonated styrene moieties exceed the moieties derived from the maleic anhydride and M is a cation.

Preferably the polymers contain a mole ratio of styrene moieties of from 2:1 to 4:1 and preferably 3:1, and possess a molecular weight of from 500 to 100,000. The polymers have been found to be effective when used at levels of from 0.5 to 100 parts per million of water and preferably from 2.5 to 25 parts per million parts of water contained in the steam generating equipment.

The polymers used in the present invention can be produced in different ways. However, their manner of production does not affect in any way their effectiveness as scale, calcium and magnesium phosphate and silicate control agents.

One procedure for producing the polymers is to copolymerize styrene with maleic anhydride in the specified ratios. After the polymer is resolubilized by producing the various water-soluble salts (alkali metal), the polymer is then sulfonated in accordance with well-known techniques for example, as described in United States Patent Specification No. 2,764,576. The degree of sulfonation may vary but substantially complete sulfonation of the styrene moieties is preferred.

Conversion of the polymers into water-soluble salts such as the alkali metal salt forms is accomplished by normal methods. Therefore M represents any one of or a mixture of cations for example one or more of NH_4 , H, Na and K.

As is apparent, the other manner of producing the polymers is to first sulfonate the styrene monomer utilizing a technique such as described in the United States Patent Specification No. 2,764,576 and then copolymerize the resulting sulfonated styrene with the maleic anhydride.

The methods and parameters of copolymerizing the two monomers is well known and is described, for example, in United States Patent Specification No. 2,723,956. Generally the copolymerization may be affected at temperatures from about 80 to 120°C utilizing peroxide catalysts such as cumene hydroperoxide or benzyl peroxide, in an inert medium.

The polymers used in the present invention, which are quite different from the polymers described in the United States Patent Specifications discussed hereinabove are very soluble in water which permits greater protection to be obtained against the potential depositions described earlier.

Commercial polymers suitable for use in the present invention are available from National Starch under the designation NSDP-2509-50 and 2727-18.

The polymers used in the present invention were subjected to steam generating conditions utilizing experimental boiler systems having an electrical heat source. The boilers are equipped with a system permitting circulation of water in a path via natural convection. Two probes are installed in the described path positioned vertically one above the other. These probes permit measurement of deposition, if any, at two different locations in the path through which the water circulated. These probes are referred to in the following Tables as the Upper and Lower probes.

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The tests conducted using the experimental boilers were operated under the conditions specified in the Tables which follow. The respective tests were designed to establish the affects, if any, of variations found in the different steam generating operations.

5 During operation of the boilers, pressure and heat probe amperage were continually monitored and the blowdown volumes and steam generation rates were measured. 5

10 After test completion, the heat transfer probes were removed and visual observations were recorded as to deposit color, quantity, and quality. Chemical analyses were employed to determine total deposit quantity. In certain circumstances, the deposit was dissolved in hydrochloric acid and hydrofluoric acid and the solution was analyzed for calcium, magnesium, phosphate and silica. Deposit weight was calculated from the solution composition in volume and these results have been reported in the Tables which follow. 10

15 In order to establish the scope of the invention, polymers having a 1:1 mole ratio of sulfonated styrene to maleic anhydride were also tested. It was felt that the comparative results provided the necessary evidence to establish the true parameters of the invention. In the following Tables, the "Treatment Concentration" indicates the amount of the respective copolymers added to the boiler water system. For example, under "A" of Table I, Copolymer A was added in an amount of 10 parts per million parts of water in the boiler water system. Conventional boiler water treatment refers to dosages as "ppm". 15

20 "Boiler Balances" refers to the level of alkalinity and silica in the boiler water. Different levels of alkalinity and residual silica (RSiO_2) will directly effect deposit formation on heat transfer surfaces and as such are carefully observed and controlled in boiler water operations. Alkalinity ("P-Alk": alkalinity measured using phenolphthalein as the indicator) is controlled to ensure against corrosion of the parts of the boiler water system. Such corrosion would occur if the water was maintained in the acid range. 20

25 "RSiO₂" refers to residual silica in the boiler water. Efforts are made to remove silica from the boiler feed water to assure against the inherent formation of magnesium silicate which would eventually deposit as scale. RSiO₂ refers in parts per million to that amount remaining in the boiler feed water. Again, these are common control observations and limitations in boiler water or steam generating systems. 25

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TABLE I
Boiler Evaluation of Sulfonated Styrene Maleic Anhydrides

Treatment	Ratio Sulfonated Styrene Maleic Anhydride Moieties	Treatment Conc. (ppm)	Boiler Balance P Alk	Boiler Balance (ppm) RSiO ₂	Upper	Lower	Total
A. Effect of Boiler Balances							
1. Copolymer A	3:1	10	184	26	0.40	0.51	0.91
2. Copolymer A	3:1	10	230	50	0.11	0.17	0.28
3. Copolymer A	3:1	10	242	54	0.20	0.21	0.41
4. Copolymer A	3:1	10	440	49	0.40	0.30	0.70
B. Effect of Dosage							
1. Copolymer A	3:1	2.5	182	16	3.38	3.61	6.99
2. Copolymer A	3:1	3	216	21	0.51	1.07	1.58
3. Copolymer A	3:1	5	186	18	0.42	0.56	0.98
4. Copolymer A	3:1	5	184	19	0.38	0.45	0.83
5. Copolymer A	3:1	10	184	26	0.40	0.51	0.91
6. Polymethacrylate Polymer } (Commercial Product)		5	176	19	2.50	4.61	7.11
7. (Commercial Product)		10	190	25	0.38	0.77	1.15
C. Comparison of Different Monomer Ratios at Different Dosage Levels							
1. Copolymer C	1:1	10	194	17	0.26	1.29	1.55
2. Copolymer B	2:1	10	170	23	0.41	0.50	0.91
3. Copolymer A	3:1	10	184	26	0.40	0.51	0.91
4. Copolymer C	1:1	5	194	18	0.68	3.00	3.68
5. Copolymer B	2:1	5	188	19	0.60	2.27	2.87
6. Copolymer A	3:1	5	186	18	0.42	0.56	0.98

Test Conditions: Pressure: 300 psig

Heat Flux: 185,000 BTU/ft²/hr

Boiler Balances: as indicated above

Treatment concentration: as indicated above

Residual Phosphate: 20 ppm

Steam Rate: 8 lbs/hour

Feedwater Hardness: 15 ppm as CaCO₃ (10 ppm Ca/5 ppm Mg)

Molecular Weight - Copolymers A, B, C - approx. 4,000

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It is evident from the data recorded in the foregoing Table that the copolymers containing less than 2 moles of sulfonated styrene moieties per mole of maleic anhydride moieties were not particularly effective while those having 2 or more were quite effective.

5 Additional comparisons were conducted utilizing various specific tests, the results of which are recorded in Tables IA to IC.

10 In Table IA are recorded specific data derived from a comparison of Copolymer A used at 10 ppm (Item 5 under Table I, Section B) with a Control, i.e., no treatment. The test conditions and boiler balances were those as specified in Table I, Section B, Item 5. The scale was analyzed to establish the effect that treatment had on scale composition.

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TABLE IA

Scale Component	Deposit (g/ft ²) Control	Deposit (g/ft ²) Copolymer A 10 ppm	% Scale Reduction on High Heat Transfer Area
Ca	3.69	0.06	98
PO ₄	5.33	0.10	98
MgO	1.49	0.08	95
SiO ₂	0.26	0.06	77
Insolubles*	4.08	0.61	85
Total	14.85	0.91	94

* Insolubles are composed of magnesium silicate and iron oxide

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In Table IB the results of a deposit comparison are recorded utilizing a Control, the Commercial Polymethacrylate (Item 6, Table I, Section B) and Copolymer A (Item 3, Table I, Section B). The conditions were those as specified in Table I in the respective Section under boiler balances with the Control being conducted at comparable boiler balances.

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TABLE IB

Scale Component	Deposit (g/ft ²)			% Scale Reduction	
	Control	Comm. PMA	Copolymer A	PMA	Copolymer A
Ca	3.69	1.76	0.06	52	98
PO ₄	5.33	3.08	0.12	42	98
MgO	1.49	0.87	0.07	42	95
SiO ₂	0.26	0.36	0.02	--	92
Insolubles	4.08	1.04	0.71	75	83
Total	14.85	7.11	0.98	52	93

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Table IC records data relative to a comparison of Copolymer B (2:1 ratio) and Copolymer A (3:1 ratio) with each other in the conditions specified (Items 5 and 6 respectively in Table I, Section B) and with a Control. The results not only establish the effectiveness of the polymer of the invention but also the relative superiority of the 3:1 ratio polymer to the 2:1 polymer.

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TABLE IC

Scale Component	Deposit (g/ft ²)		% Scale Reduction	
	Control	Copolymer B	Copolymer A	Copolymer B
Ca	3.69	0.42	0.06	89
PO ₄	5.33	0.88	0.12	83
MgO	1.49	0.23	0.07	85
SiO ₂	0.26	0.15	0.02	42
Insolubles	4.08	1.18	0.71	71
Total	14.85	2.86	0.98	81
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TABLE II
Boiler Evaluation of Sulfonated Styrene Maleic Anhydrides

Treatment	Ratio Sulfonated Styrene Maleic Anhydride Moieties		Treatment Conc. (ppm)	Heat Flux BTU/ft ² /hr	Boiler Balance P Alk	Boiler Balance (ppm) RSiO ₂	Deposit (g/ft ²)		
							Upper	Lower	Total
A. The Effect of Heat Flux at 300 psig									
1. Copolymer A	3:1		10	185,000	224	19	0.29	0.31	0.60
2. Copolymer A	3:1		10	240,000	234	19	0.47	0.40	0.87
3. Copolymer A	3:1		10	300,000	220	18	0.34	0.41	0.75
4. Copolymer A	3:1		5	300,000	203	17	0.45	0.33	0.78
B. The Effect of Heat Flux at 900 psig									
1. Copolymer A	3:1		10	185,000	221	32	0.17	0.28	0.45
2. Copolymer A	3:1		10	240,000	198	31	0.38	0.32	0.70
3. Copolymer A	3:1		5	300,000	205	28	0.88	0.85	1.73
4. Polymeracrylate polymer	}		10	185,000	222	24	0.98	1.08	2.06
5. (Commercial Product)			10	300,000	210	19	2.81	2.42	5.23

Test Conditions: Pressure: as noted
Heat Flux: as noted
Feedwater Hardness: 15 ppm as Ca CO₃
(10 ppm Ca/5 ppm Mg)

Boiler Balances: as indicated above
Residual Phosphate: 20 ppm
Treatment Concentration: as indicated above
Steam Rate: 300 psig — 8 lbs/hr
900 psig — 16 lbs/hr

It is apparent from the testing and the data recorded in the foregoing Tables that the copolymers used in the present invention performed quite impressively. This is particularly evident from the comparative results obtained with respect to the commercial product which has been and in some instances is currently being used for deposit control in steam generating systems.

As in Tables IA to IC, Table IIA contains data recorded relative to specific comparisons of the copolymer used in the present invention with the Control and PMA commercial grade. The conditions for the respective tests were those set forth in Table II, Section B, Items 1 and 4, with the Control being conducted at comparable conditions. Even at increased pressures, the polymers used in the present invention are significantly more effective than the PMA.

TABLE IIA

Scale Component	Deposit (g/ft ²)			% Scale Reduction	
	Control	Comm. PMA	Copolymer A	PMA	Copolymer A
Ca	1.93	0.40	0.03	79	98
PO ₄	2.89	0.71	0.07	75	98
MgO	0.36	0.21	0.06	42	83
SiO ₂	0.08	0.10	0.07	--	12
Insolubles	0.60	0.64	0.22	--	63
Total	5.86	2.06	0.45	65	93

In order to establish that the present invention provided overall effectiveness, two different evaluations were conducted which assimilated water conditions found in cooling water systems where the concentration of calcium ions and phosphate ions are such as to provide a calcium phosphate scale prone system.

The evaluations were conducted utilizing solutions respectively containing calcium ion and ortho-phosphate ion. After mixing the two solutions and the specified equilibration time, residual phosphate ion measurements were made after the mixture had been filtered. High residual phosphate ion concentration indicated good inhibition.

The specifics of the test procedure are as follows:

Conditions of Test: Static; T = 70°C; pH = 8.5; equilibration time — 17 hours; Concentration of Ca⁺⁺ as CaCO₃ = 250 ppm; concentration of PO₄⁻³ = 6.0 ppm. Treatment dosage = 10 ppm.

Solutions: (1) prepare solution of 0.4482 g. of Na₂HPO₄ per liter DI water (2) prepare solution of 36.76 g. CaCl₂·2H₂O per liter DI water (3) to 1800 ml DI water, add 20 ml solution (2), followed by 2 drops conc. HCl. Then add 40 ml solution (1) and bring volume to 2000 ml with DI water.

Method: Place 100 ml aliquot of solution (3) in clean 4 oz. glass bottle. Add 1 ml of .1% treatment solution and adjust pH to 8.5 using NaOH. Place bottle in water bath set to 70°C and allow to equilibrate 17 hours.

Analysis: Filtration — remove sample from water bath, filter through 0.2 μ millipore filter. Allow filtrate to cool to room temperature and analyze for PO₄⁻³ using Leitz Photometer.

Treatment was added to phosphate solution before mixing.

TABLE III

Treatment	Ratio sulfonated styrene-maleic anhydride moieties	Dosage ppm ^a	Residual phosphate concentration (ppm PO ₄ -3)
Control	—	0	0
Copolymer A	3:1	5	4.0
Copolymer A	3:1	10	5.9

The effectiveness of the polymer of the invention was apparent. Without treatment all phosphate precipitated while almost 100% inhibition was obtained when 10 ppm of treatment was utilized.

A second evaluation was conducted utilizing the aforescribed procedure. In this evaluation comparisons were made against commercial grade sulfonated polystyrenes and certain maleic anhydride polymers. In this test the percentage inhibition was determined from the measurement of the residual phosphate ion.

TABLE IV

Treatment	% Sulfonated Polystyrene Moieties	% Maleic Anhydride Moieties	% CaPO ₄ Inhibition
Copolymer A	75	25	100
Copolymer B	66.6	33.3	90.2
Copolymer C	50	50	75.4
SPS (MW3400)	100	—	62.3
SPS (MW7000)	100	—	47.6
SPS (MW40,000)	100	—	14.6
SPS (MW70,000)	100	—	4.1
Ethylene maleic anhydride copolymer	—	100	<5
Maleic anhydride telomer	—	100	<5

The data clearly established that the homopolymers of sulfonated polystyrene, maleic anhydride and ethylene maleic anhydride polymers do not control calcium phosphate as well as the polymers used in the present invention. In addition, the data confirmed the importance of having at least a mole ratio of 2 or greater of sulfonated polystyrene to 1 of maleic anhydride.

The present invention is applicable to any aqueous system where calcium phosphate formation and precipitation is a potential problem. For example, the method of the present invention would be effective in gas scrubbing systems where scrubbing mediums such as primary sewage effluents, which contain high phosphate levels are used as the scrubbing or washing medium. These systems would have the prerequisite for the formation and deposition of calcium phosphate

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which is to be avoided. The additional areas of application will be apparent to those operating in the areas of process water systems.

In order to determine the efficacy of the polymers used in the present invention in related areas, certain tests were conducted to

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(ii) establish the dispersive effect of the polymers on suspended matter, more specifically clay and iron oxide, and

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(ii) establish the capability of the polymers to inhibit the formation and thereby the deposition of calcium carbonate in an aqueous system where the effect was likely to occur.

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The protocols followed and the results of the tests were as follows:

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A. Deflocculation and Dispersion of Suspended Matter

A 0.1% iron oxide or clay suspension in deionized water was prepared. The hardness of the slurry was adjusted to 200 ppm CaCO_3 and the resultant medium was mixed for a time required to obtain a uniform suspension. The pH was then adjusted to the testing level.

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Aliquots of the suspension were drawn off, placed in glass bottles and the appropriate amount of treatment added. The samples were then shaken to ensure good mixing of treatment and suspension. Using a turbidimeter or an instrument which measures light transmission, the effect of the treatment compared to a control (suspension to which no treatment was added) was measured. Treatments causing an increase in turbidity or a decrease in light transmitted are considered dispersants.

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TABLE V

Dispersion Properties of SS/MA Polymers

Treatment (10 ppm active)	Mole ratio SS : MA	$\Delta\%T$, Dispersion		$\Delta\%T$, Dispersion	
		* Fe_2O_3 $\frac{1}{2}$ hr.	18 hr.	* Clay $\frac{1}{2}$ hr.	18 hr.
SS/MA Polymers	3:1	14.8	83.2	7.8	86.0
SS/MA Polymers	2:1	18.9	89.8	6.4	84.8
SS/MA Polymers	1:1	12.3	84.8	5.0	86.0

* The higher the $\Delta\%T$ the better the ability of the treatment to disperse.

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As apparent from the results of the studies, the polymers used in the present invention and even the SS/MA polymer having a 1:1 ratio were quite effective in dispersing the suspended matter after an 18 hour duration. The 1/2 hour duration results, although not overwhelming, were acceptable for all practical purposes since the 18 hour test is felt to be the more important result.

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B. Calcium Carbonate Studies

A synthetic environmental was produced containing known quantities of water soluble calcium chloride and sodium carbonate under specific pH and temperature conditions. Treatments were added to various samples of the solution and the amount of calcium remaining in solution after a period of time was measured and compared to a Control. The test measured quite accurately the capacity of the polymers to inhibit the formation and ultimate deposition of calcium carbonate.

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The treatment utilized consisted of 10 ppm of A. a 3:1 SS/MA polymer; B. a 2:1 SS/MA polymer; and C. a 1:1 SS/MA polymer. The results expressed as % CaCO_3 inhibition respectively were 29.6%; 29.3%; and 36.6%. The polymers were considered to be significant since they did establish efficacy. Although the degree of efficacy was perhaps lower than those polymers currently commercially available for calcium carbonate control, this capacity of the polymers when considered together with the results achievable against calcium and magnesium phosphates, magnesium silicates, iron oxides, mud, and clay make the use of these polymers clearly an important advancement in the art.

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Sulfonation Study

The contribution of sulfonation to the efficacy of the copolymers used in the present invention, i.e. sodium salt of sulfonated styrene-maleic anhydride copolymers (SS/MA) was investigated to a certain degree and was only partially resolved. The data determined indicated that sulfonation contributes quite beneficially. The drawback to complete resolution of the question was due to the difficulty in obtaining a 100% solution of the 3:1 mole ratio styrene-maleic anhydride polymer so that a "truly" representative sample could be evaluated.

The following is a synopsis of the work performed in this area:

Styrene-maleic anhydride polymers (SMA) are available in the 1:1, 2:1, and 3:1 styrene to maleic anhydride mole ratios and are reported to have a 1600 molecular weight. However, conversion to a useable soluble form (i.e., ammonium or sodium salts) becomes more difficult as the styrene content increases. Emphasis was directed toward the 3:1 mole ratio because this mole ratio was found to be the most effective copolymer used in the present invention. Although the manufacturer's literature recommended conversion to the ammonium salt, attempts were made to convert the 3:1 SMA polymer to both the ammonium salt and the sodium salt. This manufacturer's procedure was not effective for the 3:1 SMA since some copolymer remained insoluble. Boiler test results indicated the material to be quite ineffective.

Therefore attention was directed toward neutralization as the sodium salt. The SMA (3:1 ratio) was at least partially converted to the sodium salt by a procedure outlined by the manufacturer except the proper amount of sodium hydroxide, rather than ammonium hydroxide, was employed based on the acid numbers provided and higher temperatures were used. The solution which resulted from the 3:1 solubilization still contained some insoluble material and it is not known whether the resultant solution was representative of the dry material although it is estimated that 90 to 95% of the copolymer went into solution.

However, the 3:1 copolymer (SMA) solutions (one the ammonium salt and the other the sodium salt) were evaluated and the results and the testing conditions are set forth in the following table. The comparative test results established quite conclusively that the sulfonated polymers used in the present invention performed quite superiorly.

TABLE VI

Comparison of 3:1 SMA to 3:1 SSMA

Polymer Treatment	Salt	Treatment Conc ppm	Boiler Balances		Deposit (g/ft ²)*
			"P-Alk"	RSiO ₂	
SMA	NH ₄	10	180	14	>8.85**
SMA	NH ₄	10	198	19	14.52
SMA	Na	5	158	19	>11.85**
SMA	Na	5	170	21	15.57
SMA	Na	10	184	33	2.69
SSMA	Na	5	186	18	0.98
SSMA	Na	5	184	19	0.83
SSMA	Na	10	184	26	0.91

* Deposits composed of Ca, PO₄, MgO, SiO₂ and Insolubles (iron oxide and magnesium silicate)

** Heavy deposit, some of which sloughed off

Test conditions:

Pressure: 300 psig
Heat Flux: 185,000 BTU/ft²/hr
Cycles: 15
Feedwater Hardness: 15 ppm as CaCO₃ (10 Ca/5 Mg)
Phosphate Residual: 20 ppm

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WHAT WE CLAIM IS:—

1. A method of controlling the formation and deposition of deposits on the structural parts of a system containing an aqueous medium which comprises introducing into the aqueous medium an effective amount of a polymer or a water-soluble salt thereof, the polymer being comprised of sulfonated styrene moieties and moieties derived from maleic anhydride, the styrene moieties exceeding the maleic anhydride derived moieties.
2. A method as claimed in claim 1, in which the mole ratio of styrene moieties to maleic anhydride derived moieties is from 2:1 to 4:1.
3. A method as claimed in claim 1 or 2, in which the amount of polymer introduced is from 0.5 to 100 parts of polymer per million parts of water in the system.
4. A method as claimed in claim 3, in which the amount of polymer introduced is from 2.5 to 25 parts per million parts of water in the system.
5. A method as claimed in any of claims 1 to 4, in which the polymer possesses a mole ratio of sulfonated styrene moieties to maleic anhydride derived moieties of 3:1.
6. A method as claimed in any of claims 1 to 5, in which the polymer has a molecular weight of from 500 to 100,000.
7. A method as claimed in any of claims 1 to 6, in which the polymer is in the form of its sodium salt.
8. A method as claimed in any of claims 1 to 7, in which the system is a steam generating system.
9. A method as claimed in any of claims 1 to 7, in which the system is a cooling water system.
10. A method as claimed in any of claims 1 to 7, in which the system is a gas scrubbing system.
11. A method of controlling the formation and deposition of deposits on the structural parts of a system containing an aqueous medium substantially as hereinbefore particularly described.
12. A method of controlling the formation and deposition of at least one compound selected from calcium phosphate, magnesium phosphate, calcium carbonate, magnesium silicate, calcium sulfate, iron oxide and clay on the structural parts of a system containing an aqueous medium having the tendency for the formation and deposition of such which comprises introducing into the aqueous medium an effective amount of a polymer or a water-soluble salt thereof, the polymer being comprised of sulfonated styrene moieties and moieties derived from maleic anhydride, the styrene moieties exceeding the maleic anhydride derived moieties.
13. A method as claimed in claim 12 in which the mole ratio of sulfonated styrene moieties to maleic anhydride derived moieties is from 2:1 to 4:1.
14. A method as claimed in claim 12 or 13 in which the amount of polymer introduced is from 0.5 to 100 parts of polymer per million parts of water in the system.
15. A method as claimed in claim 14 in which the amount of polymer introduced is from 2.5 to 25 parts per million parts of water in the system.
16. A method as claimed in any of claims 12 to 15 in which the polymer possesses a mole ratio of sulfonated styrene moieties to maleic anhydride derived moieties of 3:1.
17. A method as claimed in any of claims 12 to 16 in which the polymer has a molecular weight of from 500 to 100,000.
18. A method as claimed in any of claims 12 to 17 in which the polymer is in the form of its sodium salt.
19. A method as claimed in any of claims 12 to 18 in which the system is a steam generating system.
20. A method as claimed in any of claims 12 to 18 in which the system is a cooling water system.
21. A method as claimed in any of claims 12 to 18 in which the system is a gas scrubbing system.
22. A method according to claim 12 substantially as hereinbefore particularly described.
23. A method of controlling the formation and deposition of calcium phosphate on the structural parts of a system containing an aqueous medium containing calcium and phosphate ions which comprises introducing into the aqueous medium an effective amount of a polymer or a water-soluble salt thereof,



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the polymer being comprised of sulfonated styrene moieties and moieties derived from maleic anhydride, the styrene moieties exceeding the maleic anhydride derived moieties.

- 5 24. A method as claimed in claim 23 in which the mole ratio of styrene moieties to maleic anhydride derived moieties is from 2:1 to 4:1. 5
25. A method as claimed in claim 23 or 24 in which the amount of polymer introduced is from 0.5 to 100 parts of polymer per million parts of water in the system.
- 10 26. A method as claimed in claim 25 in which the amount of polymer introduced is from 2.5 to 25 parts per million parts of water in the system. 10
27. A method as claimed in any of claims 23 to 26 in which the polymer possesses a mole ratio of sulfonated styrene moieties to maleic anhydride derived moieties of 3:1.
- 15 28. A method as claimed in any of claims 23 to 27 in which the polymer has a molecular weight of from 500 to 100,000. 15
29. A method as claimed in any of claims 23 to 28 in which the polymer is in the form of its sodium salt.
30. A method as claimed in any of claims 23 to 29 in which the system is a steam generating system.
- 20 31. A method as claimed in any of claims 23 to 29 in which the system is a cooling water system. 20
32. A method as claimed in any of claims 23 to 29 in which the system is a gas scrubbing system.
- 25 33. A method according to claim 23 substantially as hereinbefore particularly described. 25
34. A method of dispersing a compound selected from iron oxide, clay and mixtures thereof contained in an aqueous medium which comprises introducing in the medium an effective amount of a polymer or a water-soluble salt thereof, the polymer being comprised of sulfonated styrene moieties and moieties derived from maleic anhydride, the ratio of sulfonated styrene moieties to maleic anhydride derived moieties being from 1:1 to 4:1.
- 30 35. A method as claimed in claim 34 in which the mole ratio of sulfonated styrene moieties to maleic anhydride derived moieties is from 2:1 to 4:1. 30
36. A method as claimed in claim 34 or 35 in which the amount of polymer introduced is from 0.5 to 100 parts of polymer per million parts of water in the system.
- 35 37. A method as claimed in claim 35 in which the amount of polymer introduced is from 2.5 to 25 parts per million parts of water in the system. 35
38. A method as claimed in any of claims 34 to 37 in which the polymer possesses a mole ratio of sulfonated styrene moieties to maleic anhydride derived moieties of 3:1.
- 40 39. A method as claimed in any of claims 34 to 38 in which the polymer has a molecular weight of from 500 to 100,000. 40
40. A method as claimed in any of claims 34 to 39 in which the polymer is in the form of its sodium salt.
- 45 41. A method as claimed in any of claims 34 to 40 in which the aqueous medium is the cooling medium of a cooling water system. 45
42. A method as claimed in any of claims 34 to 40 in which the aqueous medium is the scrubbing medium for a gaseous system containing iron oxide.
- 50 43. A method as claimed in any of claims 34 to 40 in which the aqueous medium is contained in a steam generating system. 50
44. A method of dispersing a compound selected from iron oxide, clay and mixtures thereof contained in an aqueous medium substantially as hereinbefore particularly described.

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