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POLYMERS FOR THE TREATMENT OF BOILER WATER

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(71) Applicant(s)
BETZ INTERNATIONAL, INC.

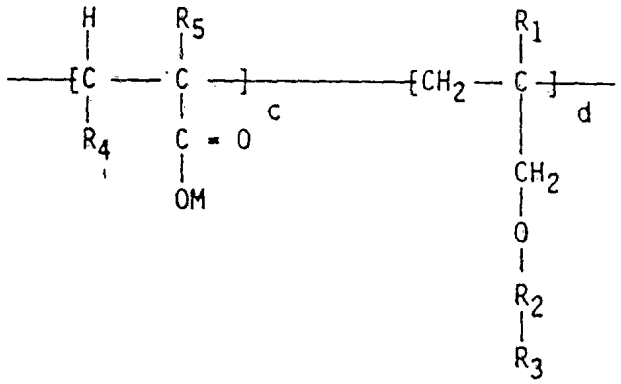
(72) Inventor(s)
FU CHEN; SCOTT M BOYETTE; KEITH A BAIR

(74) Attorney or Agent
GRIFFITH HACK & CO , GPO Box 1285K, MELBOURNE VIC 3001

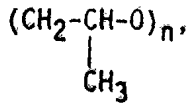
(56) Prior Art Documents
JP 56-155692

(57) Claim

1. A method of controlling the deposition of scale imparting precipitates on the structural parts of a system exposed to an aqueous medium containing scale imparting precipitates under steam generating conditions comprising adding to the aqueous medium an effective amount for the purpose of a water soluble polymer having the structure



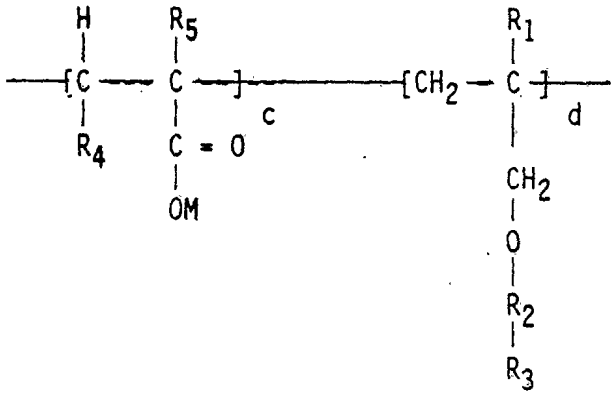
wherein R_1 is H or lower (C_1 - C_4) alkyl, R_2 is $(CH_2 - CH_2 - O)_n$,



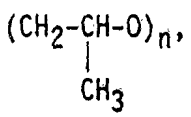
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or a mixture of both, n is an integer of from about 1 to about 40, R_3 is H, lower (C_1 - C_4) alkyl or an acetate, R_4 is H or COOM, R_5 is H or lower (C_1 - C_4) alkyl and M is H or a water soluble cation, the ratio of c:d being from 3:1 to 1:1 and with the water soluble polymer having a chelation value below 200.

16. ~~17.~~ A method of transporting and removing hardness found in an aqueous medium under steam generating conditions comprising adding to the aqueous medium an effective amount for the purpose of a water soluble polymer having the structure



R_1 is H or lower (C_1-C_4) alkyl, R_2 is $(CH_2\text{-}CH_2\text{-}O)_n$,



of a mixture of both, n is an integer of from about 1 to about 40, R_3 is H, lower (C_1 - C_4) alkyl or an acetate, R_4 is H or COOM, R_5 is H or lower (C_1 - C_4) alkyl and M is H or a water soluble cation, the ratio of c:d being from 3:1 to 1:1 and with the water soluble polymer having a chelation value below 200.

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COMPLETE SPECIFICATION

STANDARD PATENT

Applicant(s):

BETZ INTERNATIONAL, INC.

A.R.B.N. 001 775 551

Invention Title:

POLYMERS FOR THE TREATMENT OF BOILER WATER

The following statement is a full description of this invention, including the best method of performing it known to me/us:

1A

POLYMERS FOR THE TREATMENT OF BOILER WATER

FIELD OF THE INVENTION

The present invention pertains to a method of utilizing novel polymers to control the formation and deposition of scale imparting compounds in steam generating systems such as boiler water systems.

BACKGROUND OF THE INVENTION

As detailed in the Betz Handbook of Industrial Water Conditioning, 8th Edition, 1980, Betz Laboratories, Inc., Trevose, PA, Pages 85-96, the formation of scale and sludge deposits on boiler heating surfaces is a serious problem encountered in steam generation. Although current industrial steam producing systems make use of sophisticated external treatments of the boiler feedwater, e.g. coagulation, filtration, softening of water prior to its feed into the boiler system, these 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.

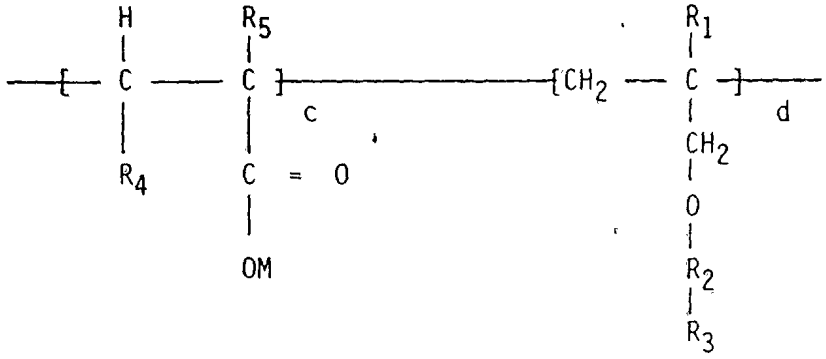
In addition to the problems caused by mud, sludge or silts, the industry has also had to contend with boiler scale. Although external treatment is utilized specifically in an attempt to remove calcium and magnesium from the feedwater, there is always a potential for scale formation due to residual hardness, i.e., calcium and magnesium salts. 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 resultant deposition. The carbonates of magnesium and calcium are not the only problem compounds as regards scale, but also water having high contents of phosphate, 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. As is obvious, the deposition of scale on the structural parts of a steam generating system causes poorer circulation and lower heat transfer capacity, resulting accordingly in an overall loss of efficiency.

SUMMARY OF THE INVENTION

It has been discovered that water soluble copolymers, as shown in Formula I hereinafter, are effective in controlling the formation of mineral deposits and in transporting and removing hardness found in steam generating systems such as boiler water systems.

The water soluble copolymers of the invention have the structure:

FORMULA I



wherein R_1 is H or lower (C_1 - C_4) alkyl, R_2 is $(CH_2 - CH_2 - O)_n$, $(CH_2 - CH(CH_3) - O)_n$ or mixture of both,

n is an integer of from 1 to about 40, R_3 is H, lower (C_1 - C_4) alkyl or an acetate, R_4 is H or COOM, R_5 is H or (C_1 - C_4) alkyl and M is H or a water soluble cation, the ratio c:d is from 3:1 to 1:1. The water soluble polymers have a chelation value below 200. Acrylic acid (R_4 = H, R_5 = H) or methacrylic acid (R_4 = H, R_5 = CH_3) may be replaced with maleic acid (R_4 = COOH, R_5 = H) in Formula I.

RELATED ART

U.S. Patent Nos. 4,326,980 and 4,828,713 disclose the utility of using a polymeric dispersant with a surfactant like molecule in steam generating applications. The combination of these two species provides increased deposit control in chelant/polymer and polymer/phosphate programs. However, experimental data showed that in a coordinated phosphate pH program or an all polymer program, there was no superior performance benefit from a polymer plus surfactant approach.

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U.S. Patent No. 4,457,847 to Lorenc et al discloses a method of treating hardness in boiler waters by using a water-soluble anionic vinyl polymer containing at least 30 weight % of carboxylate functionality and with a chelation value of at least 200. The present invention differs from the '847 patent by using a novel copolymer containing a new comonomer-polyethlene-glycol allyl ether, low carboxylate content and with a chelation value of less than 200. None of these traits is suggested by the '847 patent.

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The use of allyl ether copolymers in non-analogous arts such as dust control, dispersants and detergents is known. Japanese patent publication SH056-~~155569~~ 155692 entitled Method of Collecting Dust discloses the use of acrylic acid/polyethylene glycol monoallyl ether copolymers to treat the recirculating waterin an aqueous dust collection system.

U.S. Patent No. 4,471,100, to Tsubakimoto et. al., discloses a copolymer consisting of maleic acid and polyalkyleneglycol monoallyl ether repeat units useful as a dispersant for cement, paint and as a scale inhibitor for calcium carbonate.

U.S. Patent Nos. 4,872,995 and 4,913,822 to Chen et al., and U.S. Patent Nos. 4,861,429 and 4,895,622 to Barnett et al., disclose methods of using acrylic acid/polyethyleneglycol allyl ether copolymers as felt conditioners or to inhibit calcium oxalate deposition in pulp and paper making systems.

The use of the copolymers of this invention for boiler water treatment is not disclosed in the prior art.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

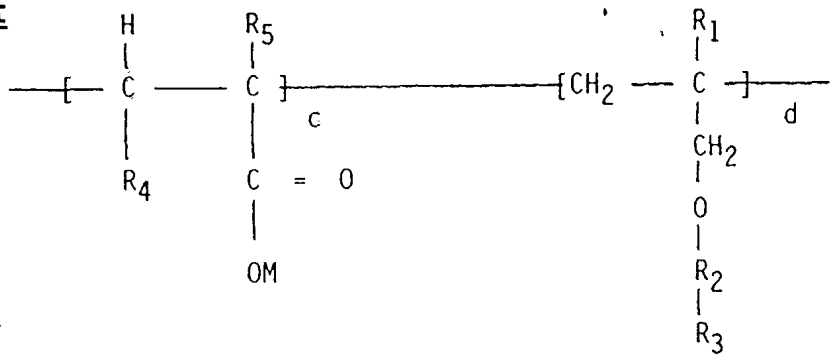
In accordance with the invention, it has been discovered that certain water soluble copolymers, as shown in Formula I hereinafter, are effective in controlling the formation of

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mineral deposits and in transporting and removing hardness found in steam generating systems such as boiler water systems.

The water soluble copolymers of the invention have the structure:

FORMULA I

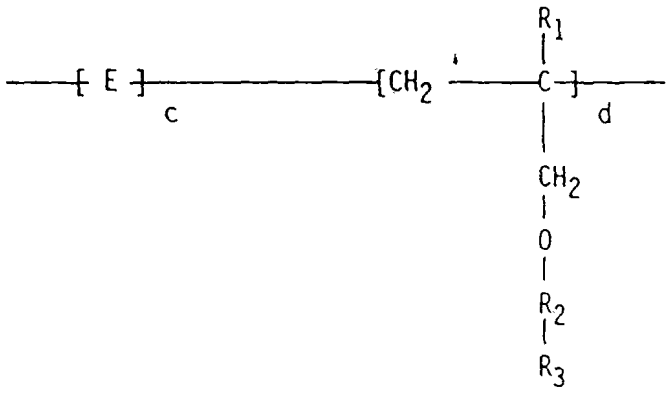


wherein R_1 is H or lower (C_1 - C_4) alkyl, R_2 is $(CH_2 - CH_2 - O)_n$, $(CH_2 - CH(CH_3) - O)_n$ or mixture of both, n is an integer of from 1 to about 40, R_3 is H, lower (C_1 - C_4) alkyl or an acetate, R_4 is H or COOM, R_5 is H or (C_1 - C_4) alkyl and M is H or a water soluble cation, the ratio c:d is from 3:1 to 1:1. The water soluble polymers have a chelation value below 200. Acrylic acid (R_4 = H, R_5 = H) or methacrylic acid (R_4 = H, R_5 = CH_3) may be replaced with maleic acid (R_4 = COOH, R_5 = H) in Formula I.

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Another copolymer of the present invention has the following general formula:

FORMULA II



where E of Formula II comprises the repeat unit obtained after polymerization of an alpha, beta ethylenically unsaturated monomer, preferably a carboxylic acid, amide form thereof, or lower alkyl (C_1 - C_6) ester or hydroxylated lower alkyl (C_1 - C_5) ester of such carboxylic acids. Exemplary compounds encompassed by E include, but are not restricted to, the repeat unit formed by polymerization of acrylic acid, methacrylic acid, acrylamide, maleic acid or anhydride, fumaric acid, itaconic acid, 2-hydroxypropyl acrylate, styrene sulfonic acid, and 2-acrylamido-2-methylpropanesulfonic acid and the like. Water soluble salt forms of these acids are also within the purview of the invention.

R_1 in Formula II is H or lower (C_1 - C_4) alkyl, R_2 is

$(CH_2 - CH_2 - O)_n$,

$(CH_2 - CH(CH_3) - O)_n$,

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or a mixture of both, n is an integer of from about 1 to about 40, R_3 is hydrogen, lower (C_1 - C_4) alkyl, or an acetate formed as a cap on the polyethyleneglycol moiety by reacting an acetylating agent with an allyl ether polyethyleneglycol to produce an acetate capped polyethyleneglycol monoallyl ether which is then reacted with the alpha, beta ethylenically unsaturated compound E to form the copolymer of Formula II. Suitable acetylating agents include acetic acid, acetic anhydride, acetyl chloride, and the like as described in U.S. Patent No. 4,959,156 and 4,847,410 fully incorporated herein by reference. c is the molar percentage being between 0-95 molar %, d is the molar percentage being between 100-5 molar %, c and d should add up to 100%.

Then number average molecular weight of the water soluble or water dispersible copolymers of Formulae I or II is not critical and may fall within the Mn range of about 1,000 to 100,000 desirably, 1,000 to 30,000 and more desirably 1,500 to 10,000.

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The key criteria is that the copolymer be water soluble or water dispersible. Water soluble or water dispersible terpolymers comprising monomer c and d of Formula I may also be effective for use in the present invention. Also, minor amounts of additional monomers may be added to the polymers.

Polyethyleneglycol allyl ether (PEGAE) monomers are prepared by ethoxylation of allyl alcohol, as described in GB Patent No. 1,103,947 and U.S. Patent No. 4,471,100. The monomers are then copolymerized with (meth)acrylic acid or maleic acid to obtain the copolymers of the invention. The polymerization may proceed in accordance with conventional solution, precipitation or emulsion polymerization techniques. Conventional polymerization initiators such as azo compounds, persulfates, peroxides, UV light, etc., may be used. Chain transfer agents such as alcohols (preferably isopropanol), amine or mercapto compounds may be used to regulate the molecular weight of the polymer. The resulting polymer may be isolated by well known techniques including precipitation, etc. If polymerized in water, the polymer may simply be used in its aqueous solution.

The polymers should be added to the boiler aqueous system, for which corrosion inhibiting, and/or deposit control activity is desired, in an amount effective for the purpose. This amount will vary depending upon the particular system for which treatment is desired and will be influenced by factors such as, the area subject to corrosion, pH, temperature, water quantity and the respective concentrations in the water of the

potential scale and deposit forming species. For the most part, the polymers will be effective when used at levels of about 0.1-500 parts per million parts of water. The polymers may be added directly into the desired water system in a fixed quantity and in the state of an aqueous solution, continuously or intermittently.

The polymers of the present invention provide superior performance in several boiler treatment programs including coordinated phosphate/pH, chelant/polymer, and notably, all polymer programs. The polymers also increase iron and hardness transport in the all polymer program.

In addition to superior performance, these polymers provide several application advantages that make them superior additives for steam generating systems. The advantages circum vent problems with formulation difficulties, increased boiler solids, and feedwater train corrosion problems. A description of each of these additional advantages is as follows.

First, although proven viable, the conventional polymer plus surfactant treatment as disclosed in U.S. 4,828,713 has problems with the formulation of concentrated solutions. The high concentrations of polymer and surfactant needed for product storage are also not possible. In contrast the new polymers provide a single water soluble component. In addition, neutralized acrylate and methacrylate polymers present formulatory

problems when adding phosphate salts to the final product. The new polymers eliminate, or greatly reduce this problem.

Second, a current all polymer program using sodium (meth)acrylate as disclosed in U.S. 4,457,847 contains notable concentrations of neutralizing inorganics that can result in increased total boiler solids, affect pH control in high purity systems, and affect conductivity monitoring in the blowdown. There have been several attempts to produce polymers neutralized with amines, but formulatory and expense problems made this impossible. The polymers of the invention eliminate or greatly reduce any additional neutralizing inorganics that can cause increased dissolved solids. They provide the first true all polymer additive and significantly reduce the deleterious effects of additional salts.

Third, it has been shown that compounds having a large lower temperature chelating strength have the potential for corroding feedwater trains prior to reaching the operating pressures of boilers (NACE 1991, Paper #218). Most chelants and commercial anionic polymers have chelation values (the milli grams of hardness sequestered per gram of sequestrant or active polymer) greater than 200 (U.S. Patent 4,457,847).

These same high chelation value compounds are suspected of having corrosion potential in feedwater heaters where the buffering strength is weak compared to cycled steam generating

conditions. Under feedwater conditions the higher chelating species has the opportunity to sequester metals from the metallurgy of the feedwater train. The polymers of the invention have chelation values substantially lower than those anionic polymers cited in U.S. Patent 4,457,847 and have minimal potential for feedwater train corrosion.

The use of the polymers disclosed herein is not limited to steam generating or boiler systems exclusively. For instance, they may be successfully utilized in cooling water systems, gas scrubbing systems and the like where the formation and deposition of scale forming species is a problem.

The water soluble polymers of the present invention can also be used with topping agent components in order to enhance the corrosion inhibition and scale controlling properties thereof. For instance the polymers may be used in combination with one or more kinds of compounds selected from the group consisting of phosphoric acids and phosphonic acids and water soluble salts thereof, oxygen scavengers and metal chelating agents. Such topping agents may be added to the system in an amount of from about 1 to 500 ppm. The weight ratio of the polymer to topping agents may vary from 100:1 to 1:5.

Examples of such phosphoric acids include condensed phosphoric acids and water soluble salts thereof. The phosphoric acids include an orthophosphoric acid, a primary

phosphoric acid and a secondary phosphoric acid. Condensed phosphoric acids include polyphosphoric acids such as pyrophosphoric acid, tripolyphosphoric acid and the like, metaphosphoric acids such as trimetaphosphoric acid, and tetrametaphosphoric acid.

As to the other phosphonic acid derivatives which are to be added in addition to the polymers of the present invention, there may be mentioned aminopolyphosphonic acids such as aminotrimethylene phosphonic acid, ethylenediaminetetramethylene phosphonic acid and the like, methylene diphosphonic acid, hydroxyethylidene diphosphonic acid, 2-phosphonobutane 1,2,4 tricarboxylic acid, etc. The polymers may be used in combination with yet other topping agents including corrosion inhibitors for iron, steel, copper, copper alloys or other metals, conventional scale and contamination inhibitors, metal chelating agents and other conventional water treatment agents. Other corrosion inhibitors comprise tungstate, nitrites, borates, silicates, oxycarboxylic acids, catechols, and aliphatic amino surface active agents. Other scale and contamination inhibitors include lignin derivatives, tannic acids, starch, polyacrylic soda, polyacrylic amide, etc. Metal chelating agents include polyamines, such as ethylenediamine, diethylenetriamine and the like and polyamino carboxylic acids, such as nitrilotriacetic (NTA) acid, ethylenediaminetetraacetic acid (EDTA), diethylenetriamine pentaacetic acid, hydroxyethylethylenediaminetetraacetic acid-(HEDTA), and salt forms of the acids mentioned.

The present polymers can also be used along with chemicals that are capable of reducing dissolved oxygen in boiler water systems. The chemicals referred to as oxygen scavengers, comprise: hydrazine, sulfite, bisulfite, hydroquinone, carbohydrazide, alkyl hydroxylamines, and alkylamine, citric acid, ascorbic acid and its analogs or salt forms, etc. Amines such as morpholine, cyclohexylamine, piperazine, ammonia, various alkylhydroxylamines such as diethylaminoethanol, dimethylisopropanolamine, and diethylhydroxylamine, etc., may be used with the polymers of the invention in steam generating systems.

The water soluble polymers may be added separately to the aqueous system or may be blended with the above topping agents compounds and then added in the state of aqueous solution into the water system either continuously or intermittently.

EXAMPLES

The invention will be further described with reference to a number of specific examples which are to be regarded solely as illustrative, and not as restricting the scope of the invention.

The following examples deal with the preparation of the copolymers which have proven efficacious for boiler water treatment.

Examples 1 - 9
Acrylic Acid/Polyethyleneglycol Allyl Ether (PEGAE) Copolymers

These polymers were all prepared similarly to the procedure given in Examples 9 and 10 of U.S. Patent No. 4,872,995, with the major exceptions being the relative ratios of the reactants used, the moles of ethylene glycol on the PEGAE and the molecular weights of the resulting polymers. The general procedure is outlined hereinbelow.

A suitable flask was equipped with a condenser, addition funnel, mechanical stirrer, thermometer and a nitrogen inlet. PEGAE, deionized water and isopropanol were charged to the flask. The solution was then heated to 85°C under a nitrogen blanket. Acrylic acid and a 25% sodium persulfate initiator solution were co-fed to the flask over 90 minutes. After holding at 85°C for one hour, the isopropanol was removed from the system by azeotropic distillation. The reaction product was cooled to room temperature. Caustic was then added to the solution to adjust to the proper pH.

The copolymer solution, after being diluted with water to the proper solids, was measured for Brookfield viscosity. The resulting polymer was a clear solution. The structure of the copolymer was verified by 13C NMR. The spectrum was characterized by a broad poly(acrylic acid) type backbone, with strong resonances at 60, 69 and 71 ppm corresponding to the polyethyleneglycol moiety and a broad carbonyl region (177-183 ppm). There was no sign of residual monomer.

Examples 10 - 11:
Maleic Acid/Polyethyleneglycol Allyl Ether Copolymers

These copolymers were prepared as described in U.S. Patent 4,471,100 herein incorporated by reference.

Example 12 - 13:
Methacrylic Acid/Polyethyleneglycol Allyl Ether Copolymers

These copolymers were also prepared as described above except that methacrylic acid replaced the acrylic acid.

Table 1 summarizes the structure and physical properties of the copolymers employed in the examples. Commercial Polymers A, B and C are used as standards for comparison. The molecular weight is obtained by a standard GPC analysis.

TABLE I

Polymer	Polymer Composition	Comonomer Ratio	% Solids	Brook-field Visc. (cp.)	Mol.Wt. (GPC) Mn
Example 1	AA/PEGAE 10	3/1	28.9	30.6	3900
Example 2	AA/PEGAE 10	3/1	30.0	25.6	3300
Example 3	AA/PEGAE 10	3/1	29.7	20.2	3300
Example 4	AA/PEGAE 10	3/1	25.3	10.3	2300
Example 5	AA/PEGAE 10	1/1	25.5	8.9	1600
Example 6	AA/PEGAE 15	3/1	30.4	30.7	5200
Example 7	AA/PEGAE 20	4/1	30.4	30.6	4800
Example 8	AA/PEGAE 10	2.5/1	30.1	17.4	2300
Example 9	AA/PEGAE 10	2.5/1	35.0	48.9	3700
Example 10	MA/PEGAE 4	1/1	49.2	237.0	
Example 11	MA/PEGAE 10	1.5/1	39.9	34.6	
Example 12	MAA/PEGAE 4	4.5/1	31.2	100.0	
Example 13	MAA/PEGAE 10	6/1	30.3	105.0	
Polymer A	PMAA		30.0		8000
Polymer B	AA/AM	2.4/1	26.4		
Polymer C	PAA		50.0		3000

AA = acrylic acid
MA = maleic acid
MAA = methacrylic acid
PMAA = polymethacrylic acid, sodium salt
PAA = polyacrylic acid, sodium salt
PEGAE 4 = polyethyleneglycol allyl ether, having an average of 4 moles of ethylene oxide
PEGAE 10 = polyethyleneglycol allyl ether, having an average of 10 moles of ethylene oxide
PEGAE 15 = polyethyleneglycol allyl ether, having an average of 15 moles of ethylene oxide
PEGAE 20 = polyethyleneglycol allyl ether, having an average of 20 moles of ethylene oxide
AA/AM = commercial acrylic acid/acrylamide copolymer
All GPC results are based on polyacrylic acid standards

CHELATION VALUES

Chelation values obtained in this invention are used as a tool to measure a polymer's ability to sequester ions at lower temperatures. These measurements are determined by bench top analysis. The method is similar to that disclosed in U.S. Patent No. 4,457,847.

The system for determining chelation values consisted of the following equipment:

1) An Orion model 701A digital pH/mV meter with an Orion model 93-20 Ca(2+) ion specific electrode and a Ag/AgCl reference electrode.

2) A Markson model 41064 pH meter (battery operated to avoid ground loops) using a Markson pH electrode model 13-620-108.

A calcium calibration curve is established each day. It is prepared with standard solutions of 1, 10, 100, and 1000 ppm Ca (as $CaCO_3$). The electrode potentials (mV) is plotted vs log [Ca] as $CaCO_3$. Only the 10, 100, and 1000 ppm potentials are used for the plot because the lower concentration shows notable deviation from linearity.

The test consists of titrating increments of a known concentration of sequestrant into a known concentration of Ca (as $CaCO_3$) and plotting the mg Ca (as $CaCO_3$) sequestered vs the grams of active sequestrant. The initial slope of the best fitting line which goes through the origin is the chelation value.

Solutions of sequestrant are made using 0.5 grams of active sequestrant per 250 mls. All solutions are prepared so as to maintain constant ionic strength and pH throughout the tests; including the standards and titrating solutions. Ionic strength is fixed using 1 ml of 4 M KCL per 50 mls of solution. The pH of the sequestrant titrating solutions is brought to 10.0 with 1.0 M KOH. During the calibration and titration, the pH was maintained at 10 with 0.1 M KOH. A 100 ppm Ca (as $CaCO_3$) standard solution is used as the test solution for all titrations.

By this methodology, calcium chelation values for the new polymers of this invention were measured. Table II lists these results along with several current boiler treatment polymers as cited in U.S. Patent No. 4,457,847. The values in this test are substantially lower than the prescribed minimum cited for acceptable boiler treatment chemicals. The new boiler treatment polymers do not have chelation values above the 200 threshold level, and many are substantially below this.

TABLE II

Calcium Chelation Values

Polymer/Reagent	Chelation Value
Example 1	174
Example 2	149
Example 3	145
Example 4	108
Example 5	62
Example 6	108
Example 7	76
Example 8	89.6
Example 9	99.9
Polymer A	356
Polymer B	306
Polymer C	351
EDTA	328

EDTA = ethylenediaminetetraacetic acid

The chelation value does not change substantially after the polymer is heat treated at typical boiler pressures of 600 psig for up to 6 hours (Table III). A 2 hour residence time exceeds the residence time in a feedwater train but does not approach the residence time of a typical drum boiler. The 6 hour residence time approaches that of the Research Boiler used in this test. The chelation value of these new polymers remains low at these two extreme conditions, an indication that the polymers have negligible corrosive tendencies in a boiler or boiler feedwater system.

TABLE III

Calcium Chelation Value of Example 5
(Heat treated at 600 psig in 10 ppm phosphate)

Time (Hr.)	Chelation Values
0	62
2	17
6	20

Example 5: Copolymer of acrylic acid/polyethyleneglycol allyl ether (n = 10) having a molar ratio of (1:1).

The characteristics described above show how these polymers of the present invention are novel and a substantial improvement over currently used boiler polymers. The following boiler studies further provide evidence of how these polymers provide superior performance in both a low to medium pressure all polymer program, chelant/polymer program and a medium to high pressure coordinated PO_4/pH program.

BOILER STUDIES

In order to assess the efficacy of the polymers of the present invention in inhibiting scale formation in steam generating systems, research boilers were fitted with two, 4,000 watt electrical heater probes, giving 185,000 BTU/ft^2/hr and about 8 Kg/hr steam. The boiler feedwater contained the contaminants

and treatment agents given herein below. The boilers were operated for 44 hours per run at an average of 15 cycles of concentration. At the conclusion of each run, the deposits were cleaned from the probes with an acid solution and the deposit densities were then calculated based on the known probe surface areas.

During the 44 hour runs, daily blowdown (BD) samples are submitted for calcium, magnesium, and or iron analysis. The average of daily analysis are used to monitor transport of each contaminate in ppm out the boiler.

TABLE IV

Polymer Performance in an "All Polymer" Program
Conditions: 600 psig
4:1:1 Ca: Mg: Fe (ppm)
Polymer actives/hardness 1/1
hydroquinone as oxygen scavenger

Polymer	Ave. Deposit (g/ft^2)	BD Ca (ave. ppm)	BD Mg (ave. ppm)	BD Fe (ave. ppm)
Example 1	0.264	34.0	2.1	1.0
Example 2	0.145	21.5	3.6	2.0
Example 3	0.341	14.1	1.0	0.7
Example 4	0.142	32.9	9.2	1.3
Example 5	0.226	25.9	1.1	0.1
Example 6	0.455	23.9	2.3	1.9
Example 7	0.306	13.7	2.9	0.7
Example 8	0.289	27.4	3.1	0.4
Polymer A	0.297	28.2	4.3	1.4
Polymer B	2.824	5.0	1.6	0.6
Polymer C	4.245	4.8	1.65	0.6
Blank	1.166	2.8	0.8	0.1

BD = boiler blowdown

calcium, magnesium, and iron on the surfaces. In addition to heavy deposition, the blank run shows no evidence of transport of contaminates by boiler blowdown. The blowdown numbers are notably lower than any of the systems with a treatment additive and indicate a need for a boiler treatment program.

Comparative polymers B and C show higher deposit weights than the blank. This increase is due to calcium deposition.

The polymers of the invention are also effective for silica transport. Tables V and VI show the conditions and results of the polymer as compared to the blank and a commercially available polymethacrylic acid. The results demonstrate that the new polymer transports and inhibits the deposition of the contaminant silica.

TABLE V

Polymer Performance in an "All Polymer" Program
Conditions: 300 psig
10:5:1 Ca: Mg: Fe (ppm)
SiO_2 13.3 ppm
Polymer actives/hardness 1/1
hydroquinone as oxygen scavenger
15 cycles

Polymer	Ave. Deposit (g/ft^2)	BD Ca (ave. ppm)	BD Mg (ave. ppm)	BD Fe (ave. ppm)	BD Si (ave. ppm)
Example 9	0.342	39.8	28.7	2.3	189.5
Blank	3.311	2.9	2.3	0.2	89.5
Polymer A	0.415	67.5	35.5	3.5	164.0

Polymer A = polymethacrylic acid

TABLE VI

Polymer Performance in an "All Polymer" Program
Conditions: 600 psig
4:1:1 Ca: Mg: Fe (ppm)
SiO_2 3.33 ppm
Polymer/hardness 1/1
hydroquinone as oxygen scavenger
15 cycles

Polymer	Ave. Deposit (g/ft^2)	BD Ca (ave. ppm)	BD Mg (ave. ppm)	BD Fe (ave. ppm)	BD Si (ave. ppm)
Example 9	0.118	42.5	8.0	4.6	44.0
Blank	4.994	7.9	< 0.6	0.02	7.5
Polymer A	0.284	13.8	2.4	0.51	40.0

Polymer A = polymethacrylic acid

The polymers of the invention listed in Tables IV, V and VI show better performance than the commercial polymers currently used for boiler treatment. The lower deposits are reflected by a notable increase in the transport of the contaminates including calcium, magnesium, iron and silica.

As a class of polymers, these new polymers are superior in an all polymer treatment program.

TABLE VII

Polymer Performance in a Coordinated PO_4/pH program
Conditions: 1450 psig
2.5 ppm Fe feed
20 ppm ortho - PO_4
pH 9.75 - 10.00
hydrazine as oxygen scavenger

Treatment	Ave. Deposit (g/ft^2)	BD Fe (ppm, Day 1)	BD Fe (ppm, Day 2)
Blank	2.109	0.47	0.19
	2.377	0.71	1.16
10 ppm Polymer A	0.963	0.50	0.16
	0.638	0.11	
20 ppm Polymer A	0.729	0.24	0.50
	0.599	0.09	0.28
10 ppm Example 3	0.233	0.24	0.41
10 ppm Example 5	0.776	0.13	0.14

Polymer A: polymethacrylic acid, sodium salt

Table VII lists results for the evaluation of these polymers in a coordinated PO_4/pH program with high iron contaminate concentrations. This test methodology is typical of a higher pressure boiler system with a demineralized pretreatment program, and is very different from the previous test system. Test polymers were fed as 10 ppm PMAA, where the concentration fed was determined using the ratio of equivalent weights of PMAA to the test polymer.

TABLE VIII

Polymer Performance in a Chelant/Polymer Program
Conditions: 600 psig
4:1:1 Ca: Mg: Fe (ppm)
Chelant fed at 0.5:1 stoichiometry
hydroquinone as oxygen scavenger

Polymer	Ave. Deposit (g/ft^2)	BD Fe (ave. ppm)	BD Ca (ave. ppm)	BD Mg (ave. ppm)
Blank	2.873	0.07	8.40	0.81
Polymer A	0.270	3.95	23.60	6.65
Example 4	0.407	1.08	35.00	5.78

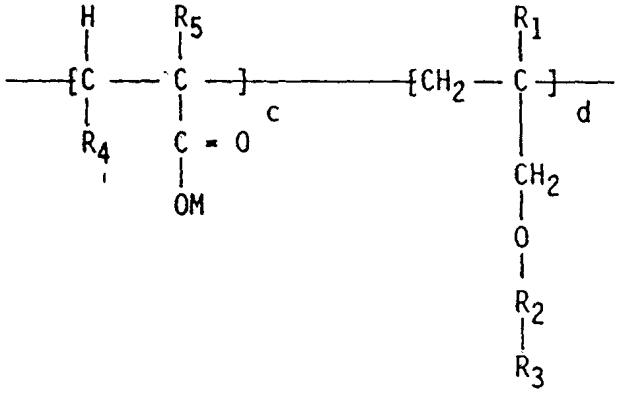
Polymer A: polymethacrylic acid, sodium salt
Chelant: EDTA

Table VIII shows the efficacy of the polymer as compared to polymethacrylic acid in a chelant/polymer program.

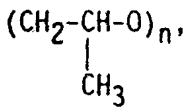
The Research Boiler data (Tables IV through VIII) shows that the polymers of the invention are effective at reducing deposition and increasing transport hardness in three substantially different boiler programs. In addition, these polymers show no potential of being corrosive in the feedwater train, as indicated by chelation values (Table II), and are a substantial improvement over the deleterious effects encountered with currently practiced technology. In addition to the effectiveness of these polymers in boiler treatment programs, the polymers contain much lower concentrations of sodium, thus resulting in less dissolved solids in the boiler. All these traits make the polymers of the invention a novel contribution to boiler water treatment.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of controlling the deposition of scale imparting precipitates on the structural parts of a system exposed to an aqueous medium containing scale imparting precipitates under steam generating conditions comprising adding to the aqueous medium an effective amount for the purpose of a water soluble polymer having the structure



wherein R_1 is H or lower (C_1 - C_4) alkyl, R_2 is $(CH_2 - CH_2 - O)_n$,



or a mixture of both, n is an integer of from about 1 to about 40, R_3 is H, lower (C_1 - C_4) alkyl or an acetate, R_4 is H or COOM, R_5 is H or lower (C_1 - C_4) alkyl and M is H or a water soluble cation, the ratio of c:d being from 3:1 to 1:1 and with the water soluble polymer having a chelation value below 200.

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2. The method of claim 1 wherein c is from 0-95 molar percent and d is from 100-5 molar percent, with the proviso that c and d add up to 100 percent.

2.3. The method of claim 1 wherein the polymer has a molecular weight (Mn) of between about 1,000 and 100,000.

3.4. The method of claim 2 wherein the polymer has a molecular weight (Mn) of between about 1,000 and 30,000.

4.5. The method of claim 3 wherein the polymer has a molecular weight (Mn) of between about 1,500 and 10,000.

5.6. The method of claim 1 wherein water soluble polymer is added to the aqueous medium in an amount of 0.1-500 parts polymer based upon 1 million parts of the aqueous medium.

6.7. The method of claim 1 further comprising adding to the aqueous medium an effective amount for the purpose of a topping agent selected from the group consisting of phosphoric acids and water soluble salts thereof, phosphonic acids and water soluble salts thereof, amines and metal chelating agents.

7.8. The method of claim 6 wherein the phosphoric acid is a member selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, tripolyphosphoric acid, trimetaphosphoric acid, tetrametaphosphoric acid and water soluble salts thereof.

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8. ~~9.~~ The method of claim ~~7~~ 6 wherein the phosphonic acid is a member selected from the group consisting of ethylene diamine-tetramethylene phosphonic acid, methylene diphosphonic acid, hydroxyethylidene diphosphonic acid and 2-phosphonobutane 1,2,4-tri-carboxylic acid.

9. ~~10.~~ The method of claim ~~7~~ 6 wherein the amine is a member selected from the group consisting of morpholine, cyclohexylamine, piperazine, ammonia, diethylaminoethanol, dimethylisopropanolamine, and diethylhydroxylamine.

10. ~~11.~~ The method of claim ~~7~~ 6 wherein the metal chelating agent is selected from the group consisting of ethylenediamine, diethylenetriamine, nitrilotriacetic acid, ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid, hydroxyethyl ethylenediaminetetraacetic acid and water soluble salts thereof.

11. ~~12.~~ The method of claim 1 further comprising adding to the aqueous medium an oxygen scavenger.

12. ~~13.~~ The method of claim ~~12~~ 11 wherein the oxygen scavenger is selected from the group consisting of hydrazine, sulfite, bisulfite, hydroquinone, carbohydrazide, alkylhydroxyamines, and alkylamine, citric acid, ascorbic acid and its analogs or salt forms thereof.

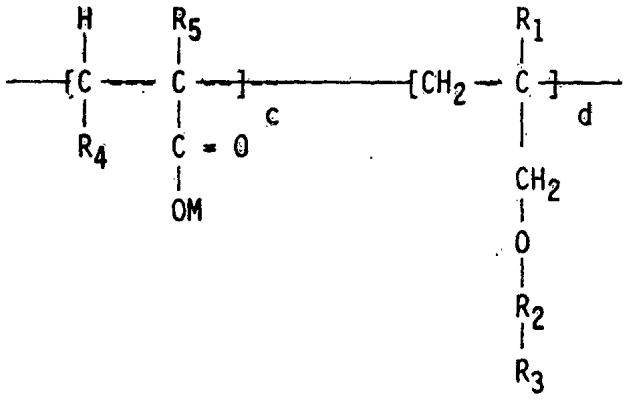
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13. ~~14.~~ The method of claim ~~7~~ 6 wherein the topping agent is added to said system in an amount of 1 to about 500 parts per million parts of the aqueous medium.

14. ~~15.~~ The method of claim 1 wherein the system is a boiler system.

15. ~~16.~~ The method of claim 1 wherein R_4 is H, R_5 is H and M is H or a water soluble cation.

16. ~~17.~~ A method of transporting and removing hardness found in an aqueous medium under steam generating conditions comprising adding to the aqueous medium an effective amount for the purpose of a water soluble polymer having the structure



R_1 is H or lower (C_1-C_4) alkyl, R_2 is $(CH_2\text{-}CH_2\text{-}O)_n$,

$$(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}O)_n,$$

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of a mixture of both, n is an integer of from about 1 to about 40, R_3 is H, lower (C_1 - C_4) alkyl or an acetate, R_4 is H or COOM, R_5 is H or lower (C_1 - C_4) alkyl and M is H or a water soluble cation, the ratio of c:d being from 3:1 to 1:1 and with the water soluble polymer having a chelation value below 200.

17. The method of claim 16 wherein the polymer has a molecular weight (Mn) of between about 1,000 and 100,000.

18. The method of claim 17 wherein the polymer has a molecular weight (Mn) of between about 1,000 and 30,000.

19. The method of claim 18 wherein the polymer has a molecular weight (Mn) of between about 1,500 and 10,000.

20. The method of claim 16 wherein water soluble polymer is added to the aqueous medium in an amount of 0.1-500 parts polymer based upon 1 million parts of the aqueous medium.

21. The method of claim 16 further comprising adding to the aqueous medium an effective amount for the purpose of a topping agent selected from the group consisting of phosphoric acids and water soluble salts thereof, phosphonic acids and water soluble salts thereof, amines and metal chelating agents.

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22. ~~24.~~ The method of claim 21 ~~23~~ wherein the phosphoric acid is a member selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, tripolyphosphoric acid, trimetaphosphoric acid, tetrametaphosphoric acid and water soluble salts thereof.

23. ~~25.~~ The method of claim 21 ~~23~~ wherein the phosphonic acid is a member selected from the group consisting of ethylenediaminetetramethylene phosphonic acid, methylenediphosphonic acid, hydroxyethylidene diphosphonic acid and 2-phosphonobutane 1,2,4-tricarboxylic acid.

24. ~~26.~~ The method of claim 21 ~~23~~ wherein the metal chelating agent is selected from the group consisting of ethylenediamine, diethylenetriamine, nitrilotriacetic acid, ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid, hydroxyethyl ethylenediaminetetraacetic acid and water soluble salts thereof.

25. ~~27.~~ The method of claim 21 ~~23~~ wherein the amine is a member selected from the group consisting of morpholine, cyclohexylamine, ammonia, diethylaminoethanol, dimethylisopropanolamine, and diethylhydroxylamine.

26. ~~28.~~ The method of claim 21 ~~23~~ further comprising adding to the aqueous medium an oxygen scavenger.

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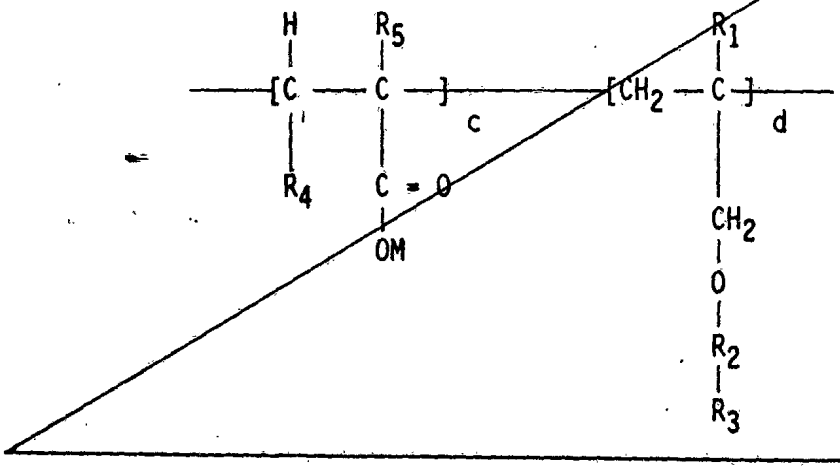
27. ~~29.~~ The method of claim 26 ~~28~~ wherein oxygen scavenger is selected from the group consisting of hydrazine, sulfite, bisulfite, hydroquinone, carbohydrazide, alkylhydroxyamines, and alkylamine, citric acid, ascorbic acid and its analogs or salt forms thereof.

28. ~~30.~~ The method of claim 21 ~~23~~ wherein the topping agent is added to said system in an amount of 1 to about 500 parts per million parts of the aqueous medium.

29. ~~31.~~ The method of claim 16 ~~17~~ wherein the system is a boiler system.

30. ~~32.~~ The method of claim 16 ~~17~~ wherein R_4 is H, R_5 is H and M is H or a water soluble cation.

31. ~~33.~~ A composition comprised of (a) a water soluble polymer having the structure



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35. ~~37.~~ The composition of claim 33 wherein the metal chelating agent is selected from the group consisting of ethylenediamine, diethylenetriamine, nitrilotriacetic acid, ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid, hydroxyethylethylenediaminetetraacetic acid and water soluble salts thereof.

36. ~~38.~~ The composition of claim 33 wherein the amine is a member selected from the group consisting of morpholine, cyclohexylamine, piperazine, ammonia, diethylaminoethanol, dimethylisopropanolamine, and diethylhydroxylamine.

37. ~~39.~~ The composition of claim 33 wherein the oxygen scavenger is selected from the group consisting of hydrazine, sulfite, bisulfite, hydroquinone, carbohydrazide, alkylhydroxyamines, and alkylamine, citric acid, ascorbic acid and its analogs or salt forms thereof.

38. ~~40.~~ The composition of claim 33 wherein R_4 is H, R_5 is H and M is H or a water soluble cation.

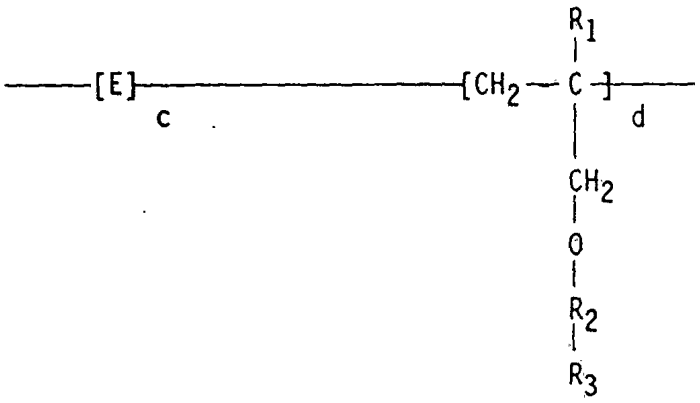
DATED THIS 6TH DAY OF JANUARY 1993
BETZ INTERNATIONAL, INC.
By its Patent Attorneys:
GRIFFITH HACK & CO
Fellows Institute of Patent
Attorneys of Australia

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ABSTRACT

A method for controlling the deposition of scale imparting precipitates on the structural surfaces of steam generating systems comprising the use of a water soluble polymer having the structure

FORMULA I



wherein E is the repeat unit remaining after polymerization of an alpha, beta ethylenically unsaturated compound.

This polymer may also be used in concert with topping agents such as phosphoric acids, phosphonic acids, polyvalent metal salts, metal chelating agents and oxygen scavengers.