

PATENT SPECIFICATION

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(54) TREATMENT OF WATER TO PREVENT THE DEPOSITION OF SCALE

- (71) We, CIBA - GEIGY, (UK) LIMITED, a British Company, of 30 Buckingham Gate, London SW1E 6LH, 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 treating water in order to prevent the formation of calcium and magnesium salt deposits on the surfaces of pipes, boilers, evaporators, steam ejectors and the like as well as providing protection of metal surfaces against corrosion at ambient temperatures.
- Various proposals have been made for the use of polymaleic anhydride and copolymers thereof in water treatment processes. For example, U.S. Patent Specification No. 3,617,577 describes the use of copolymers of maleic anhydride and ethylene with molecular weights of from about 1000 to 5000, and states that with polymers of lower molecular weight no substantial inhibition of scale deposition is achieved at threshold concentrations.
- U.S. Patent Specification No. 2,723,956 describes the use of copolymers of maleic anhydride and another monoethylenic compound in a molar ratio of 1:2 to 2:1 for the reduction and prevention of scale formation but the molecular weights are not disclosed. U.K. Patent Specification No. 772,775 describes a process for treating hard water with water soluble copolymers of maleic anhydride and other monomers, having molecular weights of from 1000 to 40000.
- We have now surprisingly found that water-soluble, hydrolysed copolymers of maleic anhydride and other monomers having an average molecular weight of below 1000, as determined by vapour phase osmometry using methyl ethyl ketone as solvent, and a molar ratio of maleic anhydride to mono-olefinic compound of from 2.5:1 to 100:1, exhibit a threshold activity towards calcium carbonate and in certain cases also towards calcium sulphate.
- According to the present invention, therefore, there is provided a process for treating water to prevent the deposition of scale caused by scale-forming impurities in the water which comprises adding thereto a hydrolysed copolymer of maleic anhydride with a mono-ethylenically unsaturated monomer or a mixture of monomers, the molar ratio of maleic anhydride to the total of other monomers being from 2.5:1 to 100:1 preferably from 2.5:1 to 30:1, more preferably 2.5:1 to 7:1 and most preferably 2.5:1 to 5:1, the molecular weight of the copolymer being up to 1,000, preferably in the range 300—1000. They may also be used in conjunction with other water treatment compounds well known in the art. Dispersing and/or threshold agents may be used, such as for example polyacrylic acid and its salts, hydrolysed polyacrylonitrile, polymethacrylic acid and its salts, polyacrylamide and co-polymers thereof from acrylic and methacrylic acids, lignin sulphonic acid and its salts, tannin, naphthalene sulphonic acid/formaldehyde condensation products, starch and its derivatives, and cellulose derivatives, e.g. carboxymethyl cellulose. Specific threshold agents such as for example, polymaleic acid and its salts, alkyl phosphonic acids, 1-aminoalkyl 1,1-diphosphonic acids and their salts and alkali metal phosphates, may also be used.
- The copolymers may also be used in combination with precipitating agents such as alkali metal orthophosphates, carbonates and hydroxides, oxygen scavengers such as alkali metal sulphites and hydrazine and sequestering agents such as nitrilotriacetic acid and their salts and ethylene diamine tetraacetic acid and its salts. They may also be used in conjunction with corrosion inhibitors such as cyclohexylamine, morpholine, distearylamine/

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5	ethylene oxide condensation products, stearylamine, sodium sulphate, magnesium sulphate and also in conjunction with antifoaming agents such as distearyl sebacamide, distearyl adipamide and related products derived from ethylene oxide condensations, in addition to fatty alcohols, such as capryl alcohols and their ethylene oxide condensates.	30	
10	The ethylenically unsaturated monomers can be selected from a wide range of compounds, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, aconitic acid (and their esters), itaconic anhydride, ethyl acrylate, methyl methacrylate, acrylonitrile, acrylamide, vinyl acetate, styrene, α -methyl styrene, methyl vinyl ketone, acrolein ethylene, propylene or mixtures thereof.	35	
20	When mixtures of monomers are used, the resulting polymer may be, e.g. a terpolymer derived from maleic anhydride and two other monomers. Such terpolymers are, for example, those derived from maleic anhydride, vinyl acetate and ethyl acrylate. Other suitable combinations may also be used as shown in the Table below.	40	
25		45	
		50	

Particularly preferred copolymers are those derived from hydrolysed copolymers of maleic anhydride and acrylic acid, its amide and its esters, methacrylic acid, its amide and its esters and vinyl esters.

The copolymers may be prepared by polymerisation in a reactive solvent using a free radical initiator such as benzoyl peroxide, di-tertiary butyl peroxide or monobutyl hydroperoxide. The polymer then precipitates out of solution.

Examples of the reactive solvents that can be employed include xylene, toluene, ethylbenzene, carbon tetrachloride and acetonitrile. Particularly preferred are xylene and toluene.

When a reactive solvent is used it functions as a chain terminator, particularly for the short chain copolymers and forms a minor portion of the polymer molecule. Such end-stopped copolymers may also be termed cotelomers. Examples of copolymers which may be used in the present invention, and suitable reactive solvents which may be used in their preparation are given in the following Table.

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TABLE

Moles of maleic anhydride	Moles of First monomer	Moles of second monomer	Solvent	Example No.
2.5	0.5 ethyl acrylate	0.5 vinyl acetate	toluene	13
9.0	1.0 ethyl acrylate	2.0 vinyl acetate	xylene	
10.0	1.0 ethyl acrylate	—	toluene	
3.0	1.0 vinyl acetate	—	ethyl benzene	12
6.0	1.0 vinyl acetate	1.0 ethyl acrylate	xylene	14
29.0	1.0 vinyl acetate	—	toluene	9
2.5	1.0 ethylene	—	toluene	50
2.5	1.0 propylene	—	xylene	
3.0	0.5 methyl vinyl ketone	0.5 vinyl acetate	toluene	
14.0	1.0 methyl vinyl ketone	—	toluene	7
3.0	1.0 methyl methacrylate	—	toluene	8
6.0	1.0 methyl methacrylate	1.0 ethyl acrylate	xylene	10
3.0	0.5 acrylonitrile	0.5 vinyl acetate	ethyl benzene	
10.0	1.0 acrylonitrile	—	ethyl benzene	
14.0	1.0 acrolein	—	toluene	6
3.0	1.0 acrylamide	—	toluene	
9.0	1.0 acrylamide	2.0 vinyl acetate	xylene	
3.0	0.5 crotonic acid	0.5 vinyl acetate	carbon tetrachloride	3
7.0	1.0 crotonic acid	—	toluene	
29.0	1.0 styrene	—	toluene	

The amount of initiator used can be varied over a wide range but depends to some extent on the ratio of monomers. All the copolymers may be made using 20% or more by weight of initiator based on the weight of monomers, this amount being necessary for those copolymers containing high ratios of maleic anhydride to other monomers, e.g. 14:1 upwards, such as 29:1, if a high yield is desired. As the proportion of maleic anhydride is reduced, the amount of initiator

may also be reduced without affecting the yield.

The reactants may be mixed in different ways, for example, the initiator may be added to a solution of the monomers, or else a solution of monomers and initiator may be added to a heated solvent.

The final copolymer may be hydrolysed before it is used to treat water. The hydrolysis may be carried out by means of water, an alkali or a mineral acid.

General Procedure for Preparation of Copolymers

A general method which was used to pre-

pare the homopolymer of the comparative example and the copolymers of Examples 1 to 11 is as follows:—

Two solutions were made up:—

Monomer solution	Maleic Anhydride	30 parts by weight
	Comonomer(s)	
	Toluene	70 parts by weight
Initiator suspension	Benzoyl peroxide	8.6 parts by weight
	70% paste in dimethyl phthalate	
	Toluene	35 parts by weight

The monomer solution was stirred and heated to 70° C. and the initiator solution added over 5 minutes. The solution was then refluxed at 110° C.—113° C. for 6 hours. After cooling, the precipitated resin was separated from the toluene solution and dried under vacuum. Yields were generally 70—90% based on weight of monomers.

The polymer was ground to a powder and boiled with water for an hour to hydrolyse the anhydride to the acid. In most cases, this rendered the polymer water soluble, but occasionally (e.g. with styrene/maleic anhydride 1:3) it was found necessary to add sodium hydroxide to dissolve the polymer.

The copolymers containing hydrolysable comonomers e.g. vinyl acetate, acrylonitrile, or ethyl acrylate, were hydrolysed further by taking a quantity of water-hydrolysed polymer solution containing 1 gram of polymer and adding 25 mls of M NaOH. This was gently boiled in a beaker for 6 hours at the end of which time it was neutralised to pH10 with M HCl.

The amount of hydrolysed copolymer added to the water to be treated can vary over a wide range and may be from 0.1 to 100 parts per million by weight. Preferably the amount added is from 2 to 10 ppm, most preferably from 5 to 10 ppm.

As well as being useful for the prevention of scale and as corrosion inhibitors the copolymers may also be used as detergent builders.

Procedures for testing the copolymers

The high activities of the preferred copolymers and terpolymers towards scale forming salts were demonstrated in an experimental boiler and in a sea water evaporator rig. These test methods are described in examples: 12 and 14. Both are, however, lengthy procedures and in order to test the large number of polymers described in the examples, a simpler test was devised. The threshold ac-

tivity tests described below can be completed in 2 hours and give very good indications of the activity of the compound under test towards boiler scale forming salts.

Threshold activity towards CaCO_3 (Test 1).

2 cm³ of a 1000 ppm solution of the scale inhibitor compound which is being tested, is mixed in a beaker with 100 cm³ of an aqueous solution containing 1.47 gm/litre $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. 100 cm³ of an aqueous solution containing 0.646 gm/litre Na_2CO_3 are added and the beaker placed on a hot plate so adjusted that the solution is heated to 90° C in 10 minutes. The solution is pumped through the colorimeter cell of an Auto Analyser and its optical density measured and continuously recorded on a chart.

From the chart of optical density vs. time two measurements are noted, a) the initiation time (I.T.) defined as the time after mixing the two solutions at which precipitation occurs (as judged by an increase in optical density), and b) the rate of precipitation defined as the maximum positive slope of the recorded track of optical density vs. time, disregarding any rapid short term increases from the base line, of less than 15% of the optical density shown by a fully precipitated blank solution.

Threshold activity towards CaSO_4

The test is the same as that described above except that 1 cm³ of a 1000 ppm solution of the scale inhibitor compound is added to 50 cm³ of an aqueous solution containing 20 gm/litre $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and after mixing, 50 cm³ of an aqueous solution containing 17 gm/litre Na_2SO_4 are added.

In both the above tests only 10 ppm of scale inhibitor in the final test solutions is used.

The initiation times and rates for CaCO_3 and CaSO_4 precipitation in the absence of any additive are given in the tables in Examples 1—11.

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An increase in initiation time or a decrease in the rate of precipitation in the presence of a test additive indicates that the additive has a retarding effect on the precipitation of the scale forming salts.
The procedures described above and in examples 12 and 14 assess the activities of test compounds against scale forming salts at high temperatures. However, in some applications it is required to retard the deposition of scale, in particular of calcium sulphate, at ambient temperatures i.e. 15—30° C. A test procedure is described in example 15 which demonstrates the effectiveness of the co-

polymers of the invention in delaying precipitation of CaSO₄.2H₂O at 20° C.
The invention is illustrated with reference to the following examples.

Comparative Example.
Maleic anhydride homopolymer
Three polymers were prepared for comparison purposes by the general method outlined above. The number average molecular weight of the first resin prepared was found to be 450. After hydrolysis with water they were found to have the following threshold activities.

	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins)	Rate	I.T. (mins)	Rate
1st Preparation	7	0.4	3	> 30
2nd ..	5	0.6	3	> 30
3rd ..	5	0.6	3	> 30
Blank (no polymer)	1	8	3	> 30

Thus homopolymaleic acid has high activity towards CaCO₃ but no activity towards CaSO₄.

Example 1.
Maleic anhydride/acrylic acid copolymers
These were prepared as in the general method outlined above and hydrolysed with water. The yields and number average molecular weights obtained are given below:—

Molar Ratio MA/Acrylic Acid	Yield %	M.wt.
3 : 1	86	490
8 : 1	85	380
14 : 1	85	—
29 : 1	88	—

On threshold testing they were found to have the following activity:

Molar Ratio MA/AAC	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins)	Rate	I.T. (mins)	Rate
3:1	5	1.3	6	>30
8:1	5	0.5	6	>30
14:1	6	0.2	—	—
29:1	5	0.3	—	—
Blank	1	8	3	>30

The maleic anhydride/acrylic acid copolymer, thus, has high CaCO₃ activity and slight activity towards CaSO₄.

Example 2.

5 *Maleic anhydride/methacrylic acid copolymers*

These were made according to the general method in yields of 80—90% and hydro-

lysed with water. The 3:1 MA/MAAc copolymer had a molecular weight of 440. They had the following activities towards CaCO₃ and CaSO₄:—

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Molar Ratio MA/MAAc	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins)	Rate	I.T. (mins)	Rate
3:1	4	0.4	5	>30
7:1	7	0.3	5	>30
14:1	5	0.3	5	>30
29:1	8	0.4	5	>30
Blank	1	8	3	>30

Example 3.

15 *Maleic anhydride/crotonic acid copolymers*

These were made according to the general

method in yields of 70—80%. They had the following activities towards CaCO₃ and CaSO₄ after hydrolysis with water:—

10

Molar Ratio MA/Crotonic Acid	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins)	Rate	I.T. (mins)	Rate
7:1	6	0.2	4½	>30
14:1	6	0.3	4	>30
29:1	7	0.2	4	>30
Blank	1	8	3	>30

The maleic acid copolymer thus has a high activity towards CaCO₃ and only a marginal activity towards CaSO₄.

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Example 4.

Maleic anhydride/ethylacrylate copolymers
These were prepared by the general method in yields of 75—90%. The 3:1 copolymer

had a molecular weight of 560. Following aqueous hydrolysis, they had the following activities towards CaCO_3 and CaSO_4 :-

Hydrolysed with water

Molar Ratio MA/EAc	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	4	0.4	3	>30
7:1	3	0.15	3	>30
14:1	5	0.3	3	>30
29:1	6½	0.3	3	>30
Blank	1	8	3	>30

and following sodium hydroxide hydrolysis, these activities were as shown below:-

Hydrolysed with sodium hydroxide

Molar Ratio MA/EAc	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	3	0.3	9	>30
7:1	4	0.3	12	>30
14:1	3	0.2	11	4
29:1	4	0.4	10	9
Blank	1	8	3	>30

10 Thus, maleic anhydride ethylacrylate copolymers which have been hydrolysed with sodium hydroxide have good activity towards CaSO_4 .

Example 5.

Maleic anhydride/styrene copolymers
These were prepared by the general method in yields of 75—80%. They were hydrolysed

with water and neutralised with sodium hydroxide prior to testing. The molecular weight of the 3:1 co-polymer was 738.

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Molar Ratio of MA/Styrene	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	1	4.0	4	>30
7:1	5	0.8	3	>30
14:1	5	0.8	3	>30
29:1	5	0.5	3	>30
Blank	1	8	3	>30

These copolymers have high threshold activity towards CaCO₃, but are inactive towards CaSO₄.

5 Example 5.
Maleic anhydride/styrene copolymers
These were prepared by the general method in yields of 75—80%. The copolymers of

this series were soluble in hot water. They were neutralised with sodium hydroxide prior to testing.

Molar Ratio of MA/Styrene	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
7:1	5	0.8	3	>30
14:1	5	0.8	3	>30
29:1	5	0.5	3	>30
Blank	1	8	3	>30

These copolymers have high threshold activity towards CaCO₃, but are inactive towards CaSO₄.

15 Example 6.
Maleic anhydride/acrylamide copolymer
These were prepared by the general method in yields of 75—85%. The 29:1 copolymer

precipitated as a resin whereas the other copolymers precipitated as powders. After hydrolysis with sodium hydroxide they had the following threshold activities:—

Molar Ratio MA/Acrylamide	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	5	0.5	8	>30
7:1	5	0.3	11	>30
14:1	5	0.4	11	>30
29:1	6	0.3	10	>30
Blank	1	8	3	>30

Thus, sodium hydroxide hydrolysed maleic anhydride acrylamide copolymers have higher activity towards CaSO₄ than homopolymaleic acid and equivalent activity towards CaCO₃.

Example 7.
Maleic anhydride/methyl vinyl ketone
copolymers
These were prepared by the general method

outlined above in yields of 70—80%. The 3:1 copolymer had a molecular weight of 440. Following hydrolysis with water, they had the following threshold activities:—

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Molar Ratio MA/Methyl Vinyl Ketone	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	4	0.6	5	>30
7:1	6	0.6	4	>30
14:1	8	0.6	3	>30
29:1	5	0.6	5	>30
Blank	1	8	3	>30

10 Hence, only a slight activity towards calcium sulphate was demonstrated by certain maleic anhydride methyl vinyl ketone copolymers. They all, however, exhibited a similar activity towards CaCO₃ as polymaleic acid.

Example 8.
Maleic anhydride/methyl methacrylate *co-*
polymers
15 These were prepared by the general method

outlined above in yields of 75—80%. The 3:1 copolymer had a molecular weight of 510. After hydrolysis with water they had the following activities:—

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Molar Ratio MA/Methyl methacrylate	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	3½	0.3	3	>30
7:1	5	0.2	3	>30
14:1	6	0.6	3	>30
29:1	5	0.3	3	>30
Blank	1	8	3	>30

and after sodium hydroxide hydrolysis, they had the following activities:—

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Molar Ratio M/A Methyl methacrylate	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	3	0.5	7	>30
7:1	3	0.6	8	6
14:1	5	0.4	9	6
29:1	3½	0.3	10	4
Blank	1	8	3	>30

Thus, the sodium hydroxide hydrolysed copolymers show good activity towards CaSO₄. All the copolymers exhibit activity towards calcium carbonate.

- 5 Example 9.
Maleic anhydride/vinyl acetate copolymer
These were prepared by the general method outlined above and the 3:1 co-polymer had

a molecular weight of 657. After hydrolysis with water they exhibited the following threshold properties:—

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Molar Ratio MA/Vinyl acetate	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	5	0.7	8	6
7:1	5	0.4	5	>30
14:1	5	0.7	5	>30
29:1	7	0.6	5	>30
Blank	1	8	3	>30

After sodium hydroxide hydrolysis the copolymers showed an improved activity towards CaSO₄ as shown below:

Molar Ratio MA/Vinyl acetate	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins.)	Rate	I.T. (mins.)	Rate
3:1	5	2	8	2
7:1	6½	0.5	13	9
14:1	7	0.6	13	>30
29:1	5	0.6	10	>30
Blank	1	8	3	>30

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	CaCO ₃		CaSO ₄	
	IT (mins)	Rate	IT (mins)	Rate
After aqueous hydrolysis	7	0.3	3	>30
After sodium hydroxide	5	1.6	9	5
Blank (no polymer addition)	1	8	3	>30

The water hydrolysed resin was tested for activity against alkaline scale in a laboratory experimental boiler, steaming at 150 p.s.i.g. Four mild steel sheaths, three of which contain 1 Kw electric cartridge heaters permanently switched on, are screwed through the boiler base plate, so that they are in the vertical position. Thermocouples are brazed into the surface of each of the four sheaths, the unheated sheath acting as a reference, to monitor any temperature changes of the surface due to scale formation.

The boiler was fed with a natural water with 300 ppm total hardness (expressed as CaCO₃). It was run continuously at 150

p.s.i.g. for a period of 500 hours, during which time the water was allowed to concentrate by a factor of 30 and thereafter maintained constant by removing concentrate in the form of a blowdown. Routine water analyses were carried out daily. At the end of a test the heater sheaths were removed and the weight and thickness of scale recorded; the average temperature increase of the heater sheath surfaces during steaming was recorded.

The following results reveal the advantageous effect of the product of the invention. They also show that it may safely be used with other conventional water treatment chemicals.

Treatment	Conc. in feed water in (ppm)	Scaling rate	Wt. of scale (grams)	Thickness of scale (inches)	Temperature rise
Na ₂ CO ₃	230	0.9	5.3	0.010	57°F
Condensation product of Naphthalene sulphonic acid and formaldehyde	35				
Na ₂ CO ₃	230	<0.1	0.1	0	<10°F
Condensation product of Naphthalene sulphonic acid and formaldehyde	10				
Hydrolysed homopolymaleic anhydride	3				
Na ₂ CO ₃	230	0	0	0	<10°F
Condensation product of Naphthalene sulphonic acid and formaldehyde	10				
Product of Example 12 after aqueous hydrolysis	3				
None	—		14.7	0.030	110°F

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10°F

10°F

0°F

Example 13.

Preparation of a 9:2:1 molar ratio terpolymer of maleic anhydride, vinyl acetate and ethyl acrylate

- 5 117.6 Parts by weight maleic anhydride, dissolved in 320 parts by volume of xylene, were heated to 143° C. A solution comprising 13.2 parts by weight ethyl acrylate, 22.8 parts by weight vinyl acetate and 5.2 parts by weight ditertiary butyl peroxide in 160 parts by volume xylene was maintained at 20° C. and added to the stirred maleic anhydride solution at 140—145° C. over 1½ hours. Heating and stirring were continued for a further 1½ hours prior to cooling, pour-
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ing off the xylene solution from the solid resin, and superficially drying the latter in a vacuum oven at 50° C. A yield of 160 grams of resin was obtained.

100 Parts by weight of this resin was boiled with 300 parts of distilled water for 1 hour under reflux and the solution then distilled to remove traces of xylene. A solution of 100 parts by weight of sodium hydroxide in 200 parts of water was added and refluxing continued for 2 hours. The excess of sodium hydroxide was neutralised by adding concentrated hydrochloric acid solution until a pH value of 10 was attained. The following threshold values were recorded:—

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	CaCO ₃ activity		CaSO ₄ activity	
	I.T. (mins)	Rate	I.T. (mins)	Rate
Resin of Example 13	5	0.5	13	5.4
Blank	1	8	3	>30

Thus, the hydrolysed polymer has good threshold activity for calcium sulphate.

Example 14.

- 35 *Preparation of a 6:1:1 molar ratio terpolymer of maleic anhydride, vinyl acetate and ethyl acrylate.*

294 parts by weight of maleic anhydride dissolved in 300 parts by weight of xylene were heated to reflux temperature with stirring. A solution comprising:

- 43 parts by weight of vinyl acetate
50 " " " " ethyl acrylate
5 " " " " ditertiary butyl peroxide
45 and 150 " " " " xylene

was maintained at 20° C and added over a 2 hour period to the refluxing maleic anhydride solution. Stirring and refluxing were continued for a further 4 hours. The temperature was reduced to 120° C and the lower resin layer transferred to a separate vessel containing water at 80° C. The resin and water were stirred and residual xylene removed by distillation. During this part of the process the resin dissolved. Depending upon the type of hydrolysis required, the resin solution was treated in three different ways.

- 60 *Polymer 14A—Water hydrolysed*
After boiling with water the solids content was adjusted to 50% w/w. yield of 50% solution=798 parts by weight.

Polymer 14B—Alkali hydrolysed

Sufficient 50% sodium hydroxide solution was added to raise the pH of the resin solution to 10. The temperature was maintained at 80—90° C for 2 hours. During this time more sodium hydroxide solution was added to maintain the pH at 10. After cooling to 20° C the solids content was adjusted to 50% w/w. Yield of 50% solution = 1000 parts by weight.

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Polymer 14C—Acid hydrolysed

The water was removed by distillation. 800 parts by weight of 47% w/w hydrobromic acid solution were added and the ensuing solution distilled slowly for two hours. At the end of this time the remaining hydrobromic acid was removed by distillation under reduced pressure. The resin was taken up in water, neutralised to pH 10 with sodium hydroxide solution and the solids content adjusted to 50% w/w.

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Yield of 50% solution=1000 parts by weight.

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The excellent scale inhibiting activities of the maleic anhydride/vinyl acetate/ethyl acrylate terpolymer are demonstrated by means of:

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- Threshold test
- Laboratory boiler test
- Sea water evaporator rig test

a. Threshold Test Values

The following test results were obtained at a solid polymer concentration of 10 ppm

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Additive	CaCO ₃		CaSO ₄	
	I.T. (mins)	Rate	I.T. (mins)	Rate
Polymer 14A	5	0.5	8	4
Polymer 14B	3	1.9	8	3
Polymer 14C	3	1.0	10	2
Blank (No Polymer)	1	8	3	>30

b. *Laboratory boiler test*

The antiscaling activity was measured in the experimental boiler described in Example

12 using the same procedure described therein. The results obtained were as follows:—

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Treatment	Conc. in feed water (ppm)	Scaling rate	Wt. of scale (grams)	Thickness of scale (ins.)	Temperature rise
Na ₂ CO ₃	230	0	0.5	0.002	<10°F
Condensation product of Naphthalene sulphuric acid and formaldehyde	10				
Polymer 14A	1				
None	—	—	14.7	0.03	110°F

c. *Antiscaling activity in sea water evaporator rig*

The antiscaling activity of the polymers in sea water evaporators was assessed in the following way:

Sea water containing the additive was passed at a rate of 10 litres/day through a test cell. Steam was passed into the cell through an aluminium/brass U-tube to maintain the temperature at 220° F. and air was

blown in to the cell to agitate its contents and facilitate decomposition of the bicarbonate ion in the sea water. After 14 days, the cell was stripped and any scale deposited on the U-tube and cell walls scraped off and weighed.

The tube scale rate and total scale rate were then assessed. These values are derived from the following relationships:—

$$\text{Tube scale rate} = \frac{\text{Weight of material deposited on U tube}}{\text{Total volume of water passing through cell}}$$

$$\text{Total scale rate} = \frac{\text{Total wt. of solids deposited in cell}}{\text{Total volume of water passing through cell}}$$

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The following results were obtained with a concentration of 5 ppm (solid) polymer in the feed water.

Additive	Scaling Rate in mgms./litre	
	Tube	Total
Polymer 14A	1.2	34.0
Polymer 14B	1.4	34.1
None	16.6	46.0

Example 15.

The excellent threshold activity of the maleic anhydride/vinyl acetate/ethyl acrylate terpolymer towards calcium sulphate at room temperature is illustrated by the following test.

The aluminium stub is immersed in a super-saturated solution of calcium sulphate,

containing 1750 ppm Ca²⁺, at 20° C. Crystallisation occurs on the stub and on the walls and base of the vessel. At the end of the test period the stub is removed for examination of the crystal structure. An aliquot from the test solution is titrated with EDTA to determine residual calcium content.

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The following results were obtained:

Additive	Additive Concn. (p.p.m.)	Duration of Test (days)	Residual Ca ²⁺ (p.p.m.)
Polymer 14A	5	4	1640
Polymer 14B	5	14	1720
Polymer 14C	5	30	1720
Homopolymer of maleic anhydride	5	4	1640
" "	5	14	800
" "	10	14	800
None	Nil	4	680

Thus after 30 days the alkali hydrolysed terpolymer of maleic anhydride, vinyl acetate and ethyl acrylate at 5 ppm concentration has superior activity to the homopolymer at 10 ppm concentration.

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WHAT WE CLAIM IS:—

1. A process for treating water to prevent the deposition of scale caused by scale-forming impurities in the water which comprises adding thereto a hydrolysed copolymer of maleic anhydride with a mono-ethylenically unsaturated monomer or a mixture of mono-

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mers, the molar ratio of maleic anhydride to the total of other monomers being from 2.5:1 to 100:1, and the molecular weight of the copolymer being up to 1,000.

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2. A process as claimed in Claim 1 in which the molar ratio of maleic anhydride to other monomers is from 2.5:1 to 30:1.

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3. A process as claimed in Claim 1 or 2 in which the molar ratio of maleic anhydride to other monomers is from 2.5:1 to 7:1.

4. A process as claimed in any preceding claims in which the amount of copolymer added to the water to be treated is from 0.1

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The following results were obtained with a concentration of 5 ppm (solid) polymer in the feed water.

Additive	Scaling Rate in mgms./litre	
	Tube	Total
Polymer 14A	1.2	34.0
Polymer 14B	1.4	34.1
None	16.6	46.0

Example 15.

The excellent threshold activity of the maleic anhydride/vinyl acetate/ethyl acrylate terpolymer towards calcium sulphate at room temperature is illustrated by the following test.

The aluminium stub is immersed in a super-saturated solution of calcium sulphate,

containing 1750 ppm Ca^{2+} , at 20° C. Crystallisation occurs on the stub and on the walls and base of the vessel. At the end of the test period the stub is removed for examination of the crystal structure. An aliquot from the test solution is titrated with EDTA to determine residual calcium content.

The following results were obtained:

Additive	Additive Concn. (p.p.m.)	Duration of Test (days)	Residual Ca^{2+} (p.p.m.)
Polymer 14A	5	4	1640
Polymer 14B	5	14	1720
Polymer 14C	5	30	1720
Homopolymer of maleic anhydride	5	4	1640
" "	5	14	800
" "	10	14	800
None	Nil	4	680

Thus after 30 days the alkali hydrolysed terpolymer of maleic anhydride, vinyl acetate and ethyl acrylate at 5 ppm concentration has superior activity to the homopolymer at 10 ppm concentration.

WHAT WE CLAIM IS:—

1. A process for treating water to prevent the deposition of scale caused by scale-forming impurities in the water which comprises adding thereto a hydrolysed copolymer of maleic anhydride with a mono-ethylenically unsaturated monomer or a mixture of mono-

mers, the molar ratio of maleic anhydride to the total of other monomers being from 2.5:1 to 100:1, and the molecular weight of the copolymer being up to 1,000.

2. A process as claimed in Claim 1 in which the molar ratio of maleic anhydride to other monomers is from 2.5:1 to 30:1.

3. A process as claimed in Claim 1 or 2 in which the molar ratio of maleic anhydride to other monomers is from 2.5:1 to 7:1.

4. A process as claimed in any preceding claims in which the amount of copolymer added to the water to be treated is from 0.1





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to 100 parts per million (ppm) by weight.

5. A process as claimed in Claim 4 in which the amount of copolymer added to the water to be treated is from 2 to 10 p.p.m. by weight.

6. A process as claimed in Claim 5 in which the amount of copolymer added to the water to be treated is from 5 to 10 p.p.m. by weight.

7. A process as claimed in any preceding claim in which a reactive solvent is used in the preparation of the copolymer which is toluene or xylene.

8. A process as claimed in any preceding claim in which the other monomer is selected from acrylic acid, methacrylic acid, crotonic acid, acrylonitrile, acrylamide, vinyl acetate, styrene, α -methyl styrene, methyl vinyl ketone, acrolein or mixtures thereof.

9. A process as claimed in any of Claims 1 to 7 in which the other monomer is selected from vinyl acetate, ethyl acrylate, acrylamide and methyl methacrylate.

10. A process as claimed in any of Claims 1 to 7 in which the copolymer is derived from maleic anhydride, vinyl acetate and ethyl acrylate.

11. A process as claimed in any of Claims 1 to 7 in which the other monomer is selected from itaconic acid, itaconic anhydride, esters of acrylic, methacrylic, itaconic or cro-

tonic acid, ethylene, propylene or mixtures thereof or a mixture of one or more of these monomers with one or more of the monomers listed in Claim 8.

12. A process as claimed in any preceding claim in which the molecular weight of the copolymer is in the range 300 to 1000.

13. A process as claimed in any preceding claim in which the molar ratio of maleic anhydride to the other monomers is from 2.5:1 to 5:1.

14. A process as claimed in any preceding claim in which the copolymer is finally hydrolysed with water.

15. A process as claimed in any of Claims 1—12 in which the copolymer is hydrolysed with alkali.

16. A process as claimed in any of Claims 1—12 in which the copolymer is hydrolysed with a mineral acid.

17. A process as claimed in Claim 1, substantially as hereinbefore described with reference to any of Examples 1 to 13.

18. A process as claimed in Claim 1, substantially as hereinbefore described with reference to Example 14 or 15.

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