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PHOSPHINIC ACID-CONTAINING POLYMERS AND THEIR
USE IN PREVENTING SCALE AND CORROSION

The present invention relates to phosphinic acid-containing polymers for preventing the formation of scale and corrosion on metal surfaces in contact with corrosive and/or scale forming industrial process waters.

The utilization of water which contains certain inorganic impurities, and the production and processing of crude oil water mixtures containing such impurities, is plagued by the precipitation of these impurities with subsequent scale formation. In the case of water which contains these contaminants the harmful effects of scale formation are generally confined to the reduction of the capacity or bore of receptacles and conduits employed to store and convey the contaminated water. In the case of conduits, the impedance of flow is an obvious consequence. However, a number of equally consequential problems are realized in specific utilizations of contaminated water. For example, scale formed upon the surfaces of storage vessels and conveying lines for process water may break loose and these large masses of deposit are entrained in and conveyed by the process water to damage and clog equipment through which the water is passed, e.g., tubes, valves, filters and screens. In addition, these crystalline deposits may appear in, and detract from, the final product which is derived from the process, e.g., paper formed from an



aqueous suspension of pulp. Furthermore, when the contaminated water is involved in a heat exchange process, as either the "hot" or "cold" medium, scale will be formed upon the heat exchange surfaces which are contacted by the water. Such scale formation forms an insulating or thermal opacifying barrier which impairs heat transfer efficiency as well as impeding flow through the system.

While calcium sulfate and calcium carbonate are primary contributors to scale formation, other salts of alkaline-earth metals and the aluminum silicates are also offenders, e.g., magnesium carbonate, barium sulfate, the aluminum silicates provided by silts of the bentonitic, illitic, kaolinitic, etc., types.

Many other industrial waters, while not being scale forming, tend to be corrosive. Such waters, when in contact with a variety of metal surfaces such as ferrous metals, aluminum, copper and its alloys, tend to corrode one or more of such metals or alloys. A variety of compounds have been suggested to alleviate these problems. Such materials are low molecular weight polyacrylic acid polymers. Corrosive waters of this type are usually acidic in pH and are commonly found in closed recirculating systems.

Numerous compounds have been added to these industrial waters in an attempt to prevent or reduce scale and corrosion. One such class of materials are the well known



organophosphonates which are illustrated by the compounds hydroxyethylidene diphosphonic acid (HEDP) and phosphonobutane tricarboxylic acid (PBTC). Another group of active scale and corrosion inhibitors are the monosodium phosphinicobis (succinic acids) which are described in US-A-4,088,678.

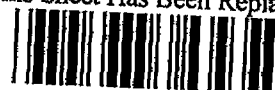
The present invention relates to preventing scale and corrosion of metal surfaces in contact with scale forming or corrosive industrial process waters with low molecular weight acrylamide polymers, acrylic acid polymers and co-polymers of acrylic acid with acrylamide which have been modified to incorporate within their structure pendent C_2-C_6 amidoalkyl-phosphinic acid groups and the alkali metal, ammonia and amine salts thereof.

THE AMINOALKYLPHOSPHINATES USED TO PREPARE

THE PHOSPHINATE POLYMERS

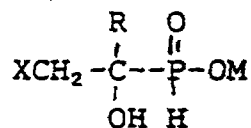
As indicated, these compounds contain C_2-C_6 alkyl groups which may be either straight or branched chain. In a preferred embodiment these compounds contain a hydroxyl group in the alpha position.

Illustrative of such compounds are alpha-hydroxy-beta-aminoethylphosphinic acid, alpha-hydroxy-beta-aminoisopropylphosphinic acid and aminopropylphosphinic acid. Also included are their alkali metal, (e.g., sodium), ammonium and amine salts such as the trimethyl amine salt. They are capable of being used to introduce phosphinic acid and



phosphinic acid salt groups into acrylic acid or acrylamide polymers.

The alpha-hydroxy-beta-aminoalkylphosphinic acids are conveniently prepared by the reaction of a haloalkyl-hydroxyphosphinic acid with ammonia. The starting haloalkyl-hydroxyphosphinic acids are described along with their method of preparation in US-A-4,598,092, the disclosure of which is incorporated herein by reference. This patent teaches that alpha-hydroxy-beta-haloethylphosphinic acid can be produced by reacting a haloacetaldehyde or its dialkyl acetals with aqueous phosphinic acid in the presence of an acid catalyst (e.g., hydrochloric acid, sulfuric acid), usually at a temperature of 10° to 100° C. for 1 to 24 hours. The amount of the phosphinic acid may be 1.0 to 10 equivalents to the haloacetaldehyde or its dialkylacetal. This reaction produces the compound



where M is H, alkali metal, ammonia or amine, X is Cl or Br and R is H or a lower alkyl group such as CH₃, C₂H₅, etc.

These compounds are then reacted with aqueous concentrated solutions of ammonium hydroxide (e.g., about 20%), which are added to a chilled polar solvent solution of alpha-hydroxy-beta-haloalkylphosphinic acids and then heated to about 30-70° C. for about 2-10 hours. To illustrate this preparation the following is given by way of example.

EXAMPLE 1

A solution of $\text{Cl}-\text{CH}_2-\underset{\text{OH}}{\underset{|}{\text{CH}}}-\overset{\text{O}}{\underset{||}{\text{P}}}(\text{OH})_2$ (98.55g theoretical) in water

(165g) was cooled to 0°C and 30% aqueous ammonia (442 ml) was added dropwise over 20 minutes. The mixture was then heated to 55°C for five hours.

Using the above described preparative techniques, the following compounds were prepared: alpha-hydroxy-beta-aminoethylphosphinic acid and alpha-hydroxy-beta-aminoisopropylphosphinic acid. Structures of these compounds were confirmed by NMR.

In the case of aminopropylphosphinic acid, this compound is prepared by reacting allylamine with an alkali metal hypophosphite in the presence of a free radical catalyst. The reaction of olefinic groups with alkali metal hypophosphites to produce alkyl phosphinate salts is well known and is described in US-A-4,590,014, the disclosure of which is incorporated herein by reference. The patent does not disclose the reaction of allylamine with alkali metal hypophosphites to produce aminopropyl(alkali metal)phosphinates. When the acid form of these salts is desired they can be prepared by treatment with dilute mineral acids or by the use of acid form cation exchange resins. The preparation of this compound is shown below in Example 2.



EXAMPLE 2

Allylamine (30g), sodium hypophosphite (50.95g) and azobisisobutyronitrile (AIBN, 2.16g) in 50% aqueous methanol (200ml) were heated to 80°C with vigorous stirring. Additional AIBN (2.16g) was added portionwise over 5 minutes and the reaction was maintained at 80°C for 6 hours.

THE STARTING ACRYLAMIDE AND ACRYLIC ACID POLYMERS

AND CO-POLYMERS OF ACRYLIC ACID WITH ACRYLAMIDE

Homopolymers of acrylamide, acrylic acid and co-polymers of acrylic acid with acrylamide which are modified with the aminoalkylphosphinates should have a weight average molecular weight within the range of 1,000-100,000, preferably 1,000-40,000 or 50,000, and most preferably 1,000-20,000. They are utilized in the reactions described hereafter in the form of aqueous solutions, typically having concentrations between 5%-40% by weight. When the starting polymers are acrylic acid and acrylamide co-polymers, the mole ratios may vary between 5-95 to 95-5 mole percent. Typically, however, these co-polymers will contain between 5-50 mole percent of acrylamide. The polymers may contain up to 15 mole percent of diluent monomers such as acrylonitrile, vinyl acetate, vinyl chloride and styrene.



MODIFICATION OF THE POLYMERS WITH THE
AMINO(C₂-C₆)ALKYL PHOSPHINIC ACID COMPOUNDS

The reaction of the aminoalkylphosphinic acids, or their salts, converts the carboxylic acid groups of the acrylic acid polymer into the corresponding amido groups by means of a simple amidation reaction. When the polymers contain acrylamide groups, the aminoalkylphosphinic acids or their salts undergo a transamidation reaction whereby the amine is substituted for the amide nitrogen in the acrylamide polymer.

The amount of substitution of the amino groups may be as little as 1 mole percent up to about as much as 30 mole percent; typically the substitution will be between 3-20 mole percent. The reaction using the conditions described hereafter results in about a 50% conversion based on the aminoalkylphosphinic acids charged to the amidoalkylphosphinates.

The reaction conditions used to either amidate the carboxylic acid or transamidate the amide groups are described in US-A-4,678,840. This patent is primarily directed to transamidation reactions of aminoalkylphosphonates with acrylamide polymeric moieties contained in acrylic acid copolymers. US-A-4,604,431 discloses reaction conditions for converting acrylic acid groups into amide groups by reacting them with aminosulfonic acid groups. The reaction conditions described in this patent are used to convert a portion of the



acrylic acid groups in the homo- or co-polymers of acrylic acid into amidoalkylphosphinic acid groups or their salts. These patents are incorporated herein by reference.

In conducting the reactions described above, it is beneficial that the pH of the system be within the range of 3 to 11. A pH of 4 to 7 is preferred. Typical reaction temperatures and times are illustrated hereafter in Table 1.

A preferred method for introducing amidopropylphosphinic groups into the acrylic acid polymers or co-polymers thereof with acrylamide is to react these polymers with allylamine to produce the corresponding allylamides. These polymers containing the allylamide groups are then reacted with alkali metal hypophosphites in accordance with U.S. 4,590,014.

The preparation of the phosphinate modified polymers is illustrated in Table 1.

EXAMPLE P1

In Table 1 PAA and AA are polyacrylic acid and acrylic acid, respectively, AAm is acrylamide, MAA is methacrylic acid and VAc is vinyl acetate. RXN means "reaction".

TABLE 1

GENERAL PROCEDURE FOR MODIFICATION: A mixture of the amine and the polymer solution were sealed in a reaction vessel capable of withstanding a pressurized chemical reaction and then heated to the specified temperature for the specified reaction time.

<u>SAMPLE</u>	<u>POLYMER COMPOSITION</u>	<u>MOL. Wt.</u>	<u>AMINOALKYL PHOSPHINIC ACID</u>	<u>MOL% CHARGE AMINE</u>	<u>RXN. TEMP.</u>	<u>RXN. TIME</u>	<u>RXN. pH</u>
A	PAA	4500	$\text{H}_2\text{NCH}_2\text{CH}(\text{OH})(\text{PO}_2\text{H}_2)$	5	150°C	5 HRS.	9.0
B	PAA	4500	$\text{H}_2\text{NCH}_2\text{CH}(\text{OH})(\text{PO}_2\text{H}_2)$	15	150°C	5 HRS.	6.3
C	50/50 AA/AAm	6450	$\text{H}_2\text{NCH}_2\text{CH}(\text{OH})(\text{PO}_2\text{H}_2)$	10	150°C	5 HRS.	6.5
D	50/30/20 AA/AAm/MAA	11,200	$\text{H}_2\text{NCH}_2\text{CH}(\text{OH})(\text{PO}_2\text{H}_2)$	10	150°C	5 HRS.	4.0
E	45/50/5 AA/AAm/VAc	7050	$\text{H}_2\text{NCH}_2\text{CH}(\text{OH})(\text{PO}_2\text{H}_2)$	10	150°C	5 HRS.	3.7
F	PAA	5400	$\text{H}_2\text{NCH}_2\text{C}(\text{CH}_3)(\text{OH})\text{PO}_2\text{H}_2$	10	140°C	8 HRS.	3.7
G	50/50/ AA/AAm	2500	$\text{H}_2\text{NCH}_2\text{C}(\text{CH}_3)(\text{OH})\text{PO}_2\text{H}_2$	25	140°C	8 HRS.	4.8
H	PAA	5400	$\text{H}_2\text{NCH}_2\text{CH}=\text{CH}_2$	10	140°C	12 HRS.	3.8
I	50/50 AA/AAm	2500	$\text{H}_2\text{NCH}_2\text{CH}=\text{CH}_2$	25	140°C	12 HRS.	4.9
J	AAm	-	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{PO}_2\text{H}_2)$	10	140°C	6 HRS.	5.4



USE OF THE AMIDOALKYLPHOSPHINATE POLYMERS TO INHIBIT SCALE AND CORROSION

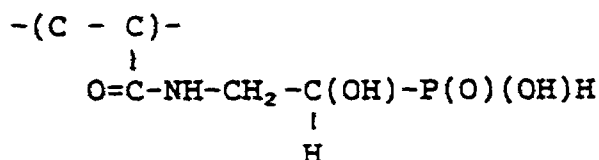
EXAMPLE 2

When modified polymers of the type shown above are used as scale and corrosion inhibitors, the dosage on an active polymer basis may be within the range of one part per million up to as much as several hundred parts per million by weight of polymer. A typical dosage range would be 3-50 ppm. Optimum dosages can be determined by routine experimentation.

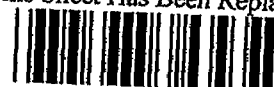
Backbone Polymers

<u>SAMPLE NUMBER</u>	<u>POLYMER COMPOSITION</u>	<u>MW</u>	<u>% POLYMER</u>
001	100% AA	4500	32.5
008	100% AA	5400	35
009	50/50 AA/AAm	2500	35

POLYMERS MODIFIED WITH ALPHA-HYDROXY-BETA-AMINOETHYLPHOSPHINIC-ACID

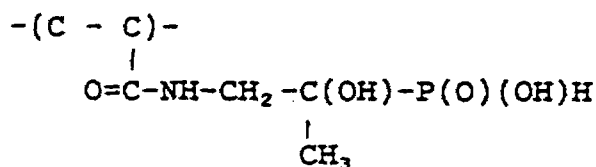


<u>SAMPLE NUMBER</u>	<u>BACKBONE POLYMER</u>	<u>PHOSPHINATE CHARGE (MOLE%)</u>	<u>% POLY</u>	<u>REACTION pH</u>
85	001	5	28.1	9.0
84	001	10	24.9	9.8
93	001	15	22.4	10.0
95	001	15	18.6	6.3



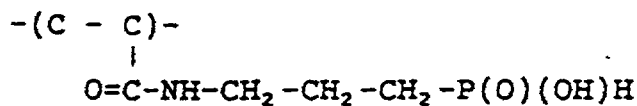
<u>SAMPLE NUMBER</u>	<u>BACKBONE POLYMER</u>	<u>PHOSPHINATE CHARGE (MOLE %)</u>	<u>% POLYMER</u>
027	008	10	33.7
031-A		(OXIDIZED 027)	32.3
031-B	008	25	33.0
033		(OXIDIZED 031-B)	30.4
028	009	10	34.1
032-A		(OXIDIZED 028)	32.7
032-B	009	25	33.1
034		(OXIDIZED 032-B)	30.5

POLYMERS MODIFIED WITH ALPHA-HYDROXY-BETA-AMINOISOPROPYLPHOSPHINIC ACID



<u>SAMPLE NUMBER</u>	<u>BACKBONE POLYMER</u>	<u>PHOSPHINATE CHARGE (MOLE %)</u>	<u>% POLYMER</u>
039	008	10	33.9
035		(OXIDIZED 039)	32.6
045	008	25	33.4
036		(OXIDIZED 045)	30.8
040	009	10	34.3
037		(OXIDIZED 040)	32.9
046	009	25	33.5
038		(OXIDIZED 046)	30.9

POLYMERS MODIFIED WITH ALLYL AMINE, THEN NaH₂PO₂, AIBN



<u>SAMPLE NUMBER</u>	<u>BACKBONE POLYMER</u>	<u>AMINE CHARGE (MOLE %)</u>	<u>% POLYMER</u>
014	008	10	21.9
027		(OXIDIZED 014)	21.3
025	008	25	21.7
029		(OXIDIZED 025)	20.3



015	009	10	21.9
028		(OXIDIZED 015)	21.3
026	009	25	21.6
030		(OXIDIZED 026)	20.2

EXAMPLE 3

Table 2: Benchtop Screening Test for Calcium Carbonate
Scale Inhibition of Several Aminoalkylphosphinic
Acid-Modified Polymers

Water Chemistry/Conditions:

360 ppm Ca/200 ppm Mg/500 ppm HCO_3 (as CaCO_3)

Temperature: 60°C, Stir rate: 300 rpm

Titrant: 0.10 Normal NaOH

Dosage: 5, 10 and 15 ppm actives

Standard Deviation of Saturation Ratio: +/-6.6

Saturation ratio of blank: 3.0

Saturation Ratio

<u>SAMPLE NUMBER</u>	<u>POLYMER DOSAGE</u>		
	<u>5 ppm</u>	<u>10 ppm</u>	<u>15 ppm</u>
<u>alpha-hydroxy-beta-aminoethylphosphinic acid-modified polymers:</u>			
84	74.8	107.5	130.7
85	80.0	107.5	122.9
93	56.6	113.7	114.9
95	56.6	85.4	119.9
Backbone Polymer	88.8	119.9	131.9
027	95.6	121.8	142.6



031-B	93.9	121.8	130.9
028	53.7	46.4	99.5
032-B	53.9	39.8	34.0

alpha-hydroxy-beta-aminoisopropylphosphinic acid modified

polymers:

039	76.8	112.3	130.9
045	62.3	109.2	130.9
040	46.4	53.9	93.9
046	43.0	31.4	50.0

Polymers modified with allylamine, then NaH_2PO_2 :

014	82.3	118.6	142.6
025	39.8	53.9	24.6
015	39.8	36.8	36.8
026	17.5	22.5	19.1



EXAMPLE P4

Table 3: Benchtop Screening Test for Calcium Carbonate Scale
Inhibition of Several Aminoalkylphosphinic Acid
Modified Polymers

Stir and Settle Test

Water Chemistry/Conditions:

360 ppm Ca / 200 ppm Mg / 500 HCO₃ (as CaCO₃)

Temperature: 60°C, Stir Rate: 250 rpm

Titrant: 0.10 Normal NaOH, pH: 9.0 for two hours

Blank: 0.6% inhibition, 1.3% dispersancy

<u>Inhibitor</u>	<u>5 ppm</u>	<u>10 ppm</u>	<u>15 ppm</u>
<u>alpha-hydroxy-beta-aminoethylphosphinic acid modified polymer:</u>			
84: % inhibition:	33.5%	49.5%	52.9%
% dispersancy:	33.5%	47.6%	56.1%
031-B: % inhibition:	46.4%	51.2%	62.0%
% dispersancy:	39.3%	46.5%	74.0%

EXAMPLE P5

Electrochemical Screening Test for Mild Steel Corrosion
Inhibition of Several Aminoalkylphosphinic Acid Modified
Polymers

Water Chemistry/Conditions:

360 ppm Ca / 200 ppm Mg / 440 HCO₃ (as CaCO₃)

Temperature: 120°F, pH: uncontrolled, air agitation,

Unpolished Mild Steel specimen, 30 minute delay time, 500 rpm

Standard deviation of corrosion rate: +/- 0.345 mpy



Table 4

Inhibitor combination:

- (A). 20 ppm inhibitor, 0 ppm PBTC, 15 ppm sulfonated acrylate polymer
- (B). 10 ppm inhibitor, 10 ppm PBTC, 15 ppm sulfonated acrylate polymer
- (C). 10 ppm inhibitor, 10 ppm PBTC, 15 ppm substituted acrylamide, (PBTC - phosphonobutanetricarboxylic acid)

<u>Inhibitor</u>	<u>Corrosion Rate (mpy)</u>		
	<u>(A)</u>	<u>(B)</u>	<u>(C)</u>
Blank	8.63	.975	1.92

alpha-hydroxy-beta-aminoethylphosphinic acid-modified polymers:

84	1.49	.793 (1.14)	2.37
85	3.96	1.40	xxxx
027	xxxx	.961	xxxx
028	xxxx	1.29	xxxx

alpha-hydroxy-beta-aminoisopropylphosphinic acid modified polymers:

039	xxxx	.715	xxxx
040	xxxx	1.65	xxxx



EXAMPLE P6

Polymer modified with allyl amine, then NaH_2PO_2 , AIBN per

Example 2:

014

xxxx

.887

xxxx

The test methods used to generate the above data are set forth below.

Saturation Ratio Test

A test solution was prepared by adding calcium, magnesium, inhibitor and bicarbonate to deionized water. Initial concentrations of the salts should be: 360 ppm Ca^{+2} , 200 ppm Mg^{+2} , 500 ppm HCO_3^- (as CaCO_3) and 5, 10, or 15 ppm of inhibitor as actives/solids. The temperature was maintained at 140°F (60°C), the solution was stirred at all times, and the pH was continuously monitored. The solution was titrated with dilute NaOH at a constant rate. With the addition of NaOH, the pH of the test solution slowly increased, then decreased slightly, and increased again. The maximum pH prior to the slight decrease at supersaturation was the breakpoint pH. A mineral solubility computer program was then used to calculate the calcium carbonate supersaturation ration based on test conditions at the breakpoint pH. This supersaturation ratio is related to the calcium carbonate inhibition performance. The test procedure was repeated for different inhibitor solutions and dosages. All precipitated calcium carbonate must be removed from the test apparatus with dilute HCl prior to the next test run.



Benchtop Calcium Carbonate Inhibition Test

Calcium, magnesium, inhibitor and bicarbonate were added to deionized water to prepare a test solution with 360 ppm Ca^{+2} , 200 ppm Mg^{+2} , 500 ppm HCO_3^- (as CaCO_3) and 5, 10 or 15 ppm inhibitor as actives/solids. An initial sample of the test water was collected for calcium analysis by atomic absorption. The test temperature was maintained at 140°F (60°C). Using dilute NaOH, the pH of the solution was slowly increased to 9.0, and maintained during the two hour duration of the test. At the conclusion of the test, a small sample of the solution was filtered (0.45 μm) and the calcium concentration was determine by atomic absorption. The remainder of the unfiltered sample was allowed to settle, undisturbed for 24 hours, at room temperature. Water was then collected from the top of the flask after 24 hours and analyzed for calcium. The % inhibition and % dispersancy are calculated in the following manner:

$$\% \text{ inhibition} = \frac{\text{ppm Ca}^{+2} \text{ filtered}}{\text{ppm Ca}^{+2} \text{ initial}} \times 100$$

$$\% \text{ dispersancy} = \frac{\text{ppm Ca}^{+2} \text{ unfiltered, settled}}{\text{ppm Ca}^{+2} \text{ initial}} \times 100$$

Electrochemical Test

Both the Tafel plots and linear polarization resistance tests were conducted in the same water chemistry and



conditions. The test solution for the electrochemical corrosion cell was prepared by adding calcium, magnesium, various inhibitors and bicarbonate to deionized water to obtain 360 ppm Ca^{+2} , 200 ppm Mg^{+2} , 400 ppm HCO_3^- (as CaCO_3). Temperature was maintained at 120°F and the solution was aerated throughout the test period. pH was uncontrolled. A standard three electrode cell was assembled for the polarization studies. Pre-polished mild steel specimens were used as the rotating working electrode, at a speed of 500 rpm. All potential measurements were made against a saturated calomel reference electrode. Two graphite rods were used as the counter electrode. Polarization resistance measurements were conducted within +/- 20 mV of the corrosion potential at a scan rate of 0.1 mV/sec. Tafel plots were performed by polarizing the mild steel specimen at 250 mV cathodically and anodically from the corrosion potential.

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CLAIMS

1. A method of inhibiting scale and corrosion of metal surfaces in contact with scale forming and/or corrosive industrial process waters which comprises treating such waters with at least one part per million of an acrylamide homopolymer and acrylic acid homopolymer or co-polymer of acrylic acid with acrylamide having a molecular weight within the range of 1,000-100,000 which have been modified to contain up to about 30 mole percent of amido(C_2-C_6 alkyl)phosphinic acid groups or the alkali metal, ammonium and amine salts thereof.
2. The method of inhibiting scale and corrosion of metal surfaces in contact with scale forming and corrosive industrial process waters of Claim 1 where the amido (C_2-C_6 alkyl) phosphinic acid groups are alpha-hydroxy-beta-amidoethylphosphinic acid, alpha-hydroxy-beta-amidoisopropylphosphinic acid or amidopropylphosphinic acid.
3. The method of Claim 2 where the amido (C_2-C_6 alkyl) phosphinic acid group is alpha-hydroxy-beta-amidoethylphosphinic acid.



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4. The method of claim 2 where the amido (C_2-C_6 alkyl) phosphinic acid group is alpha-hydroxy-beta-amidoisopropylphosphinic acid.

5. The method of claim 2 where the amido (C_2-C_6 alkyl) phosphinic acid group is amidopropyl-phosphinic acid.

6. A polymer which is an acrylamide or acrylic acid homopolymer or a copolymer of acrylic acid with acrylamide, the homopolymer or copolymer having up to 30 mole percent of pendent amido (C_2-C_6 alkyl) phosphinic acid groups or an alkali metal, ammonium or amine salt thereof.

7. A polymer according to claim 6 wherein the phosphinic acid group is alpha-hydroxy-beta-amidoethylphosphinic acid, alpha-hydroxy-beta-amidoisopropylphosphinic acid or amidopropylphosphinic acid.

8. A polymer according to claim 6 or claim 7 having 3 to 20 mole percent of the said groups.

9. A polymer according to any one of claims 6 to 8 having a weight average molecular weight of 1,000 to 40,000.

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10. A polymer according to claim 9 wherein the weight average molecular weight is 1,000 to 20,000.