

[54] **POLYACRYLIC ACID HAVING HIGH CHELATION VALUE AND ITS PRODUCTION**

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[58] **Field of Search**..... **260/526 N, 537 N**

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[57] **ABSTRACT**

Polyacrylic acid having a high chelation value is produced by polymerizing acrylic acid at elevated temperature in the presence of an alkali metal or ammonium persulfate initiator and, in a concentration of about 0.5 to 4% by weight of the acrylic acid, a chain transfer agent selected from the group consisting of alkanethiols, hydroxy alkanethiols, and carboxy alkanethiols. Preferably the chain transfer agent is present in about 1% by weight concentration and is octanethiol, butanethiol, thioglycolic acid, or 2-thioethanol.

7 Claims, No Drawings

POLYACRYLIC ACID HAVING HIGH CHELATION VALUE AND ITS PRODUCTION

BACKGROUND OF THE INVENTION

This invention relates to the production of polyacrylic acid having a high chelation value, e.g., a chelation value which is in excess of 500 milligrams of calcium carbonate per gram of chelant obtained in water with a 200 ppm hardness, pH 9.5 and at the point at which 80% of the hardness has been sequestered. The significance of this 80% chelation level as an index for comparing various chelating agents will be explained later hereinbelow.

Most common detergents, e.g. common household detergents, comprise, in addition to other components, phosphates such as sodium tripolyphosphate. These are inexpensive and effective, but their use is now considered to present a water pollution problem in that the phosphate component has the undesired effect of promoting excessive growth of algae in lakes and streams (eutrophication).

Accordingly, there has been much research aimed at developing detergents which contain little or no phosphate but which will still be safe and effective. In particular, this research has been aimed at developing detergent components which can sequester calcium, magnesium, and like ions found in hard water and which have an economically feasible price/performance ratio. Aside from effectiveness and economic feasibility, it is also important that these detergent components be free from health hazard and that they have no adverse effects on mechanical equipment used in laundering. For example, highly alkaline detergent components such as washing soda have effective detergent action but are hazardous household substances because of their high alkalinity (pH 11 or higher). There is also a question as to whether they may cause mechanical problems in, for example, washing machines. Likewise nitrilotriacetic acid and ethylenediaminetetraacetic acid are very effective in sequestering a large amount of calcium but are relatively expensive and, in addition, have recently been questioned from the health standpoint inasmuch as a question has arisen as to whether they are potentially carcinogenic.

Finally, polyacrylic acid, as such or in the salt form, has also been proposed as a chelant or sequestering agent which does not cause eutrophication, but this material as known heretofore has been of only mediocre effectiveness.

It has now been discovered, however, that polyacrylic acid, when made by a certain procedure which will be described hereinbelow, can be made to have an unexpectedly high chelating value. It is, accordingly, an object of the present invention to provide a method for producing a polyacrylic acid chelating agent which is unexpectedly effective as compared with similar materials known to the prior art and which will be free from the drawbacks which are associated with those alternative detergent components known to the art.

SUMMARY OF THE INVENTION

In accordance with the present invention it has been found that polyacrylic acid having an unexpectedly high chelating value (which will be defined hereinbelow) can be produced by polymerizing acrylic acid at elevated temperature in the presence of an alkali metal or ammonium persulfate initiator and also in the pres-

ence of about 0.5 to 4% (calculated on the basis of the weight of the acrylic acid) of a chain transfer agent selected from the group consisting of alkanethiols, hydroxy alkanethiols, and carboxy alkanethiols. Preferably the chain transfer agent is present in a concentration of about 1% by weight based on the acrylic acid and is a member of the group consisting of octanethiol, butanethiol, thioglycolic acid, and 2-thioethanol. Other thiols which can be employed include methanethiol, ethanethiol, propanethiol, pentanethiol, hexanethiol, heptanethiol, nonanethiol, decanethiol, dodecanethiol, and their branched isomers, e.g. sec.-butanethiol, isopropanethiol, tert.-butanethiol, and the like, as well as their hydroxy and carboxy substitution products, e.g., 3-mercaptopropanol, 3-mercaptopropionic acid, 6-mercaptohexanoic acid and the like.

The initiators may be present in amounts ranging from as little as about 0.5 up to 10% or more by weight of acrylic acid although preferably they are present in about 0.5 to 4%. A concentration of about 1% is especially useful. Preferred initiators include sodium, potassium, or ammonium persulfates or mixtures thereof.

The polymerization can be conducted in bulk but it is preferably conducted in aqueous solution at a concentration of about 5 to 40% and preferably about 10 to 30% acrylic acid by weight. The temperature may be room temperature or lower but, since polymerization rate increases with temperature, the temperature is desirably elevated but below the boiling point so that special equipment will not be required, e.g. about 95°C. The time will typically run about 1 to 2 hours until there is substantially no residual free acrylic acid.

The molecular weight will directly determine the viscosity of the resulting solution, and the viscosity may range from about 25 centipoise or lower up to 200 or more although preferably it is about 50 to 150 centipoise for a 20-25% polyacrylic acid solution by weight.

The solutions may if desired be concentrated to any desired degree, including completely to dryness, optionally after neutralization to form sodium and/or potassium polyacrylate. Alternatively, the solution may be blended with one or more other ingredients of a detergent composition in dry or liquid state and the mixture spray or drum dried.

In assessing the effectiveness of chelating agents it is convenient to employ a term referred to as the "chelating value", the significance and determination of which are explained by J. A. Blay and J. H. Ryland in "Analytical Letters", Vol. 4, No. 10, pp 653-663 (1971). Numerically, the "chelation value" (CV) is expressed as the milligrams of calcium carbonate chelated or sequestered per gram of chelating agent. The chelation reaction is, in effect, a reversible chemical reaction so that the CV depends, numerically, upon the concentration of hardness, e.g. calcium ions, in the solution to which the chelating agent is added, the pH, and also the amount of chelating agent which has been added to that solution. This is particularly noticeable for chelants with a formation constant (log K) smaller than 5 ($K < 10^5$). For these reasons it is desirable, in making practical comparisons of one chelating agent with another, to test them at a constant level of hardness at constant pH and to add each of the several chelants being tested in an amount that the proportion of the hardness which is chelated is the same in each of the several samples being tested.

The polyacrylic acid produced by the present process has a chelation value (CV) which is normally equal to,

or in excess of, about 500 milligrams of calcium carbonate per gram of the polyacrylic acid at an 80% chelation level in an aqueous solution containing a hardness equivalent to 200 ppm of calcium carbonate. This is essentially as good as, if not better than, chelation values characteristic of other chelants known to the prior art which, however, have drawbacks of cost, water-pollution tendency, health hazard, or adverse mechanical effects in washing equipment.

The invention will be further illustrated in the following examples wherein all parts are by weight unless otherwise expressed. It will be understood that these examples are given by way of illustration, rather than limitation, of the invention. The polyacrylic acid (or its salts including especially alkali metal salts) to the production of which this invention is directed will be seen to have very broad applications in combination with surfactants, buffering agents, scouring agents, and other ancillary substances well known in the art, in all end-uses in which a sequestrant or chelant is customarily employed and including specifically such applications as laundry detergents, automatic dishwashing detergents, scouring powders, boiler scale removal, metal degreasing and cleaning, leather and textile treating solutions, ore leaching and beneficiation, and ion-exchange operations to name a few.

EXAMPLE I

250 g of 92% acrylic acid, 3.0 g of potassium persulfate, and 2.3 g octanethiol were reacted in a 1000 g total aqueous solution for 2 hours at 96°–98° C. The resulting aqueous polyacrylic acid solution had a viscosity of 125 cps and contained 20.4 weight percent solids. Only 0.4 g/l of this polyacrylic acid was required to sequester 94% of Ca^{+2} ions present in a pH = 9.5 buffer containing 200 ppm of Ca^{+2} ions. Expressed differently, the polyacrylic acid had the capacity to chelate 560 mg CaCO_3 per gram of polyacrylic acid with 80% of the total calcium present in the medium being sequestered. The chelation power of some known sequestering agents under comparable conditions were as follows: citric acid, 350 mg/g; tripolyphosphoric acid, 370 mg/g; ethylenediaminetetraacetic acid, 330 mg/g.

When evaluated under similar conditions, a typical commercial polyacrylic acid (Versicol E5, from Allied Colloids Co.) required 1.1 g of polyacrylic acid to sequester 95% of the Ca^{+2} ions present in a pH = 9.5 buffer containing 200 ppm Ca^{+2} , corresponding to a chelation capacity of 390 mg CaCO_3 /g chelant when 80% of Ca^{+2} ions have been chelated.

EXAMPLE II

250 g of 92% acrylic acid, 3.0 g of potassium persulfate, and 2.3 g butanethiol were reacted in a 1000 g total aqueous solution for 2 hours at 96°–98° C. The resulting aqueous polyacrylic acid solution had a viscosity of 70 cps and contained 23.9 weight percent solids. Only 0.51 g/l of this polyacrylic acid was required to sequester 95% of the Ca^{+2} ions present in a pH = 9.5 buffer containing 200 ppm of Ca^{+2} ions. Expressed differently, the polyacrylic acid had the capacity to chelate 520 mg CaCO_3 per gram of polyacrylic acid with 80% of the total calcium present in the medium being sequestered.

EXAMPLE III

To evaluate the performance of sodium polyacrylate in detergent compositions, formulations A–F listed below were prepared. Formulation F consists of distilled water and serves as a control only. Formulation E in which no builder is utilized contains the surfactants and the auxiliary components used in a typical heavy-duty laundry formulation. Formulations A–D have the builder added to the basic formulation in E and provide a direct comparison between sodium polyacrylate and other available builders.

Evaluation of the performance of the formulations was by the well established procedure of Spangler, *Journal of the American Oil Chemists Society* 42, 723–727 (1966). Cotton swatches were uniformly soiled in a blend of synthetic sebum and particulate soil and separated into groups with similar aggregate degree of soiling. Measurements of soiling were performed with standard commercial reflectometer (Colormaster Model V, Manufacturers Engineering and Equipment Corporation).

The soiled swatches were washed in a standard laboratory "Terg-O-Tometer" (trade name of U.S. Testing Company, Hoboken, N.J.) operated at 100 rpm. Five swatches were used for each formulation. One and one-half grams of each of the formulations A–F were used in a liter of water containing 160 ppm hardness composed of 85% Ca^{+2} and 15% Mg^{+2} . After washing for ten minutes at 120°F, the swatches were hand squeezed and put through a 5 minute rinse at 100° F. The swatches were next dried in a print dryer, and their reflectance determined again. The operation was repeated three times (3 cycles). The performance of the formulations in terms of changes in reflectance (ΔRd) along with the compositions of formulations A–F are shown in the table below:

COMPOSITION WEIGHT %	A	B	C	D	E	F
Linear alkylbenzene sulfonate	10	10	—	10	10	—
Nonionic surfactant (C_{12} – C_{18} alcohol ethoxylate "60%")	2	2	11	2	2	—
Tallow fatty acids soap	2	2	—	2	2	—
Sodium silicate ($\text{SiO}_2\text{:Na}_2\text{O}$ 2.4:1)	7	7	9	7	7	—
Sodium sulfate	40	40	—	40	40	—
Distilled water	4	4	10	4	39	100
Sodium polyacrylate	35	—	—	—	—	—
Sodium tripolyphosphate	—	35	—	—	—	—
Sodium carbonate	—	—	70	—	—	—
Sodium oxydiacetate	—	—	—	35	—	—
PERFORMANCE (3 cycles)						
Reflectance, Rd, of soiled swatches	61.4	60.6	55.0	58.9	58.6	61.2
Reflectance, Rd, of washed swatched	76.9	76.2	69.6	68.1	64.8	65.8

COMPOSITION WEIGHT %	-continued					
	A	B	C	D	E	F
Δ RD	15.5	15.6	14.6	9.2*	6.2	4.6

*Performed in water of 200 ppm hardness, 60% Ca⁺², 40% Mg⁺²

As the detergency results above clearly indicate, sodium polyacrylate is an excellent performer in heavy-duty laundry composition. Its closest competition, sodium tripolyphosphate, is suspected of contributing to eutrophication of lakes and rivers, and its use in laundry detergents is thought by many to be undesirable. Formulations with sodium carbonate (such as Formulation C) are also disfavored since their high alkalinity makes them hazardous for use in households and can also cause damage to washing instruments. Thus, sodium polyacrylate provides a high performance alternative in laundry detergents.

EXAMPLE IV

The formulation given below is suitable for cleaning metal parts prior to use. It cleanses metal surfaces free of oil and grease and removes surface scale and rust.

Composition	Wt%
Sodium silicate (Na ₂ SiO ₃)	24.0
Sodium silicate (SiO ₂ :Na ₂ O 3.1:1)	48.0
Nonionic surfactant (C ₁₂ -C ₁₈ alcohol ethoxylate, "60%")	1.5
Sodium polyacrylate	25.0
Sodium sulfite	1.5

EXAMPLE V

Formulation below is a low foaming dishwashing powder with excellent grease removal and gentle scouring action.

Composition	Wt%
Soda ash	50

-continued

Composition	Wt%
Sodium meta silicate	10
Trisodium phosphate	15
Sodium polyacrylate	20
Alkylbenzene sulfonate	5

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for producing a polyacrylic acid of high chelation value at 80% chelation which comprises polymerizing acrylic acid in aqueous solution at elevated temperature in the presence of an alkali metal or ammonium persulfate as initiator and about 0.5 to 4% by weight of acrylic acid of a chain transfer agent selected from the group consisting of an alkanethiol, a hydroxy alkanethiol and a carboxy alkanethiol.
2. The process of claim 1, wherein the chain transfer agent is an alkylmercaptan and is present in a concentration of about 1% by weight of the acrylic acid, and wherein the polymerization is conducted at about 95°C for about 1 to 2 hours.
3. The process of claim 2, wherein the chain transfer agent is octanethiol.
4. The process of claim 2, wherein the chain transfer agent is butanethiol.
5. The process of claim 1 wherein the chain transfer agent is thioglycolic acid.
6. The process of claim 1 wherein the chain transfer agent is 2-thioethanol.
7. Polyacrylic acid produced by the process of claim 2 and having a chelation value at 80% chelation in excess of about 500 mg CaCO₃ per gram in an aqueous solution containing calcium ions in a concentration equivalent to 200 ppm of CaCO₃.

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Disclaimer

3,904,685.—*Iraj Khatib Shahidi*, Florham Park, N.J., and *Jorge Alberto Blay*, Corpus Christi, Tex. POLYACRYLIC ACID HAVING HIGH CHELATION VALUE AND ITS PRODUCTION. Patent dated Sept. 9, 1975. Disclaimer filed Apr. 14, 1976, by the assignee, *Celanese Corporation*.

Hereby enters this disclaimer to the remaining term of said patent.
[*Official Gazette June 1, 1976.*]