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(54) COPOLYMERS CONTAINING HYDROXYL AND CARBOXYL GROUPS AND THEIR USE IN DETERGENT AND CLEANER FORMULATIONS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, 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 copolymers containing hydroxyl and carboxyl groups and based on acrylic acid and/or methacrylic acid as monomer units, and to their salts.

The invention further relates to the use of such copolymers as sequestering agents and as phosphate substitutes in detergent and cleaner formulations.

It is known that in the detergent and cleaner industry, builders are required in addition to surfactants. One of the functions which these builders have to perform is to sequester cations, especially the cations of calcium and magnesium, which form water-insoluble salts. For this reason the builders are also specifically referred to as sequestering agents. Hitherto, phosphates, above all pentasodium triphosphate, have proved most suitable for this purpose. However, the enormous production of phosphate-containing effluents has resulted in waters becoming markedly eutrophic, leading to excessive growth of algae and hence to oxygen deficiency in the waters.

Legislation in most countries tends either to prohibit phosphates entirely or to specify rather low maximum amounts in detergents.

For about the last 15 years, numerous proposals for solving this problem have been put forward, and reference may be made to the summarizing articles in *Angew. Chemie* 87 (1975), 115 et seq. and in *Chemiker-Zeitung* 96 (1972), 685 et seq. According to these publications, numerous low and high molecular weight compounds conventionally used as complexing agents were tested, and it was found that polymers based on acrylic acid and hydroxyl-containing derivatives were fairly suitable as a partial replacement for phosphates.

German Laid-Open Application DOS 2,161,727, for example, discloses a process for sequestering metal ions by means of poly- α -hydroxyalkyl acrylates or their derivatives. According to the publication *Angew. Chemie*, loc. cit., such polymers have a calcium-binding capacity of 228 mg of CaCO_3 per gram at 20°C, and 182 mg at 90°C. Disadvantages of these compounds are that they are relatively difficult to produce and that their calcium-binding capacity is relatively poor.

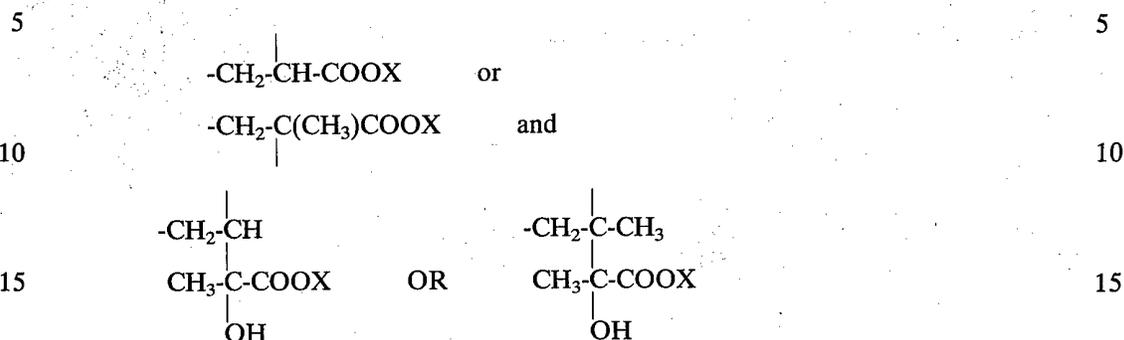
German Published Application DAS 2,025,238 also discloses polymers containing hydroxyl and carboxyl groups, which polymers are obtained by oxidative polymerization of acrolein, with or without acrylic acid or derivatives thereof, followed by a Cannizzaro reaction of the polymer or copolymer. These polymers, again, cannot bind more than 300 mg of CaCO_3 per gram of active ingredient.

The present invention seeks to provide an alternative water-soluble material which is easily manufactured and above all has a very high calcium-binding capacity.

According to the invention there are provided copolymers comprising
a) from 50 to 95 mole % of units of acrylic acid and/or methacrylic acid and/or an alkali metal salt thereof, and

b) from 5 to 50 mole % of units of vinyl-lactic acid and/or isopropenyl-lactic acid and/or an alkali metal salt thereof.

Accordingly, these copolymers are composed of units of the formulae



where X is hydrogen or an alkali metal.

For use as active components in detergents and cleaners, above all dishwashing detergents, the copolymers according to the invention are employed in the form of their alkali metal salts, particularly the sodium salts. The copolymers are distinguished by their high calcium-binding capacity.

The starting compounds a for the copolymers of the invention are acrylic acid and methacrylic acid, singly or together, acrylic acid preferably being employed, preferably in an amount of from 60 to 90 mole % based on the total monomer mixture.

The starting compounds b for the copolymers are vinyl-lactic acid and isopropenyl-lactic acid, singly or together, but preferably vinyl-lactic acid alone, preferably in an amount of from 40 to 10 mole %. These compounds are obtained, for example, in accordance with the method described in German Laid-Open Application DOS 1,795,312, by reacting vinyl methyl ketone or isopropenyl methyl ketone with HCN and then hydrolyzing the cyanohydrins obtained as intermediates; this operation is known to those skilled in the art and does not require specific discussion.

The polymerization is advantageously initiated with a conventional initiator which forms free radicals, for example H_2O_2 , alkali metal peroxydisulfates, ammonium peroxydisulfate, and organic hydroperoxides and peroxides, e.g. caproyl peroxide, benzoyl peroxide, t-butyl perbenzoate, dicumyl peroxide, p-menthane hydroperoxide, cumene hydroperoxide and peroxysuccinic acid, as well as aliphatic azo compounds which decompose into free radicals under the polymerization conditions, e.g. azoisobutyronitrile and other azonitriles, such as are listed, for example, in Jack Hine "Reaktivität und Mechanismus in der organischen Chemie", Verlag Georg Thieme, Stuttgart (1960), page 412, and also redox systems; e.g. potassium peroxydisulfate or ammonium peroxydisulfate and ascorbic acid, sodium bisulfite or iron(II) salts. Chelates of transition metals, e.g. of manganese(III), cobalt(III), copper(II) and cerium(IV), may also be used. In most cases the chelating compound is a 1,3-dicarbonyl compound, e.g. ethyl acetoacetate or acetyl-acetone. For example, Cu acetylacetonate or cobalt(III) ethyl acetoacetate are preferred in such redox systems.

The amount of initiator used is in general from 0.05 to 5% by weight, based on the amount of monomers employed. The optimum amount can be determined by simple tests. The polymerization may be carried out as a mass polymerization, but is advantageously carried out in the presence of a solvent or diluent, such as alcohols of 1 to 5 carbon atoms, eg. methanol, ethanol, isopropanol or n-butanol, ethers, eg. THF or dioxane, ketones, e.g. methyl ethyl ketone or methyl propyl ketone, hydrocarbons, e.g. heptane, cyclohexane or benzene, or aprotic polar solvents, e.g. formamide or dimethylformamide.

The suspension, solution or emulsion polymerization processes conventionally used for a plurality of other monomers or monomer mixtures may also be used for the manufacture of the new copolymers; in respect to any assistants which may be used, e.g. buffers, dispersing agents and protective colloids, the manufacture of the copolymers according to the invention again does not differ from conventional methods.

The polymerization may be carried out over a wide temperature range, from 0 to 150°C, preferably from 50 to 120°C. In general, it is carried out at atmospheric pressure, but may also be carried out under superatmospheric pressure.

Advantageously, the copolymerization of acrylic acid and/or methacrylic acid with the unsaturated lactic acid(s) is carried out in a solvent, eg. isopropanol (50% by weight based on solids), at from 70 to 80°C with, for example, azoisobutyronitrile, after which the mixture is neutralized with an alkali metal hydroxides, e.g. sodium hydroxide solution, and

the solvent is striped off. The copolymer obtained by such a procedure generally has a mean molecular weight of from 2,000 to 20,000 (determined osmometrically).

As stated, the copolymers according to the invention have proved to be excellent sequestering agents, the calcium-binding capacity of which is substantially above that of pentasodium triphosphate and also above that of known copolymers containing hydroxyl and carboxyl groups; furthermore, they have the same whitening power as phosphate alone. Their soil-suspending power is even better than that of phosphate alone. This improvement above all manifests itself if the copolymers are employed as mixtures with phosphate sequestering agents, i.e. if the phosphate is only replaced partially. Preferred weight ratios of pentasodium triphosphate or other phosphate sequestering agent to the copolymer are in that case from 1:4 to 4:1. The sequestering agents, i.e. the copolymers or the above phosphate/copolymer mixtures, are generally present in detergent formulations in amounts of from 10 to 50% by weight, calculated as alkali metal salt and based on the total weight of the detergent formulation.

In addition, such detergent formulations usually contain anionic and/or non-ionic surfactants in an amount corresponding to a weight ratio of surfactant to sequestering agent of from 3:1 to 1:10. Preferably, the detergent formulations contain from 5 to 30% by weight of a surfactant or surfactant mixture. Conventional surfactants may be used. Examples of suitable surfactants are non-ionic compounds, eg. alkylphenoloxethylates (where alkyl is of 8 to 12 carbon atoms) with from 5 to 25 ethylene oxide units, hereinafter referred to as "EO", alcohols (of 8 to 20 carbon atoms) with from 6 to 30 EO, random or block adducts of ethylene oxide and propylene oxide (hereinafter referred to as "PO") with the above materials, the products having from 9 to 15 EO and from 3 to 20 PO, and block copolymers and random copolymers of EO and PO with molecular weights of from about 600 to 4,000, as well as EO/PO adducts of ethylenediamine.

Examples of anionic surfactants are fatty alkyl-sulfates and fatty alkyl-sulfonates, where alkyl is of 8 to 20 carbon atoms, alkylbenzenesulfonates, where alkyl is of 8 to 12 carbon atoms, alkanesulfonates, sulfo-fatty acid esters, fatty alkyl sarcosinates, where alkyl is of 8 to 20 carbon atoms, conventional soaps and, finally, also the ether-sulfates which are obtained by oxyalkylation of alkylphenols (where alkyl is of 8 to 12 carbon atoms) or alcohols of 8 to 20 carbon atoms, followed by sulfation.

These and other suitable surfactants are described, for example, in Schwartz-Perry and Schwartz-Perry-Berch "Surface Active Agents and Detergents" Intesc. Publ. Inc., New York and London, Volumes 1 and 2.

In addition, the detergent formulations may contain neutral salts, e.g. Na_2SO_4 (up to 15% by weight of anhydrous salt), and bleaching agents (up to 30% by weight) as well as brighteners and enzymes. Examples of bleaching agents are peroxide-based compounds, eg. alkali metal or ammonium perborates, peroxydisulfates and percarbonates, or compounds based on chlorine of oxidation level +1, eg. alkali metal hypochlorites or alkali metal dichloroisocyanurates or trichloroisocyanurates.

Cleaning and dishwashing formulations are similar, but since the articles concerned are in general substantially more heavily soiled, they normally contain substantially more alkali, eg. sodium carbonate, potassium carbonate or alkali metal silicates. Dishwashing formulations in general contain from 0 to 50% by weight of sequestering agent, from 0 to 10% by weight of one of the above surfactants, from 0 to 20% by weight of neutral salt and from 0 to 50% by weight of the alkaline compounds.

In addition, detergents and cleanings frequently contain small amounts of disinfectants, eg. based on iodine-containing surfactants or polycarboxylates ("iodophores"), and may also contain scents.

The Examples which follow illustrate the invention.

Examples

I. General manufacturing instructions (parts are by weight).

100 part of monomer were polymerized in a stirred kettle, in the presence of 100 parts of isopropanol and 1 part of azoisobutyronitrile, in the course of 4 hours at 80°C. The solvent was then removed by distillation.

II. The following copolymers were obtained by this method:

Example	mole % acrylic acid	Copolymer of mole % vinyl-lactic acid
1	90	10
2	85	15
3	80	20
4	70	30
5	60	40
6	50	50

10 The average molecular weights were from 8,000 to 12,000. 10

III. Washing tests.

A. Whiteness determination

15 In a simplified detergent formulation, the pentasodium triphosphate component in the 15
sequestering agent was replaced stepwise by one of the copolymers according to Examples 1
to 6 (in the form of its sodium salt) and the whitening action on WFK fabric was determined
(the WFK fabric being a standard soiled fabric from Waschereiforschung Krefeld). The
washing machine used was a Launder-O-meter.

Test conditions:

20 Temperature : 95°C 20

Liquor ratio : 1:25

Fabric : WFK cotton fabric and cotton ballast fabric (1:1)

Washing time: 30 minutes

Water hardness: 10° German hardness

25 pH: 10.5 25

Detergent concentration: 5 g/l

Detergent composition (% by weight) :

10% of Na alkylbenzenesulfonate (where alkyl is of 12 carbon atoms)

5% of a fatty alcohol mixture (of 16 and 18 carbon atoms) + 25 EO

30 5% of sodium stearate 30

10% of Na₂SO₄

20% of sodium perborate

40% of sequestering agent

10% of water

35 35

TABLE 1

40 Weight ratio of pentasodium triphosphate to sodium salt of 40
copolymer
Whiteness, expressed as reflectance (Elrepho instrument) using
copolymers of
Example

	1	2	3	4	5	6
45 3 : 1 45	77.3	78.4	78.5	77.8	77.7	77.5
1 : 1	76.1	76.3	76.5	76.7	76.4	76.4
1 : 3	75.7	75.3	74.6	74.6	73.7	73.5

50 Pentasodium triphosphate alone gives a whiteness of 77.0. 50

B. Determination of the soil suspending power

55 The soil suspending power of sodium salts of copolymers according to the invention as 55
compared to that of pentasodium triphosphate was tested by repeated washing in the
presence of a large amount of soiling pigment (composed of carbon black, yellow iron oxide
and black iron oxide) and determining the resulting whiteness. The soiling pigment was
introduced into the wash liquor in the form of soiled cotton hanks.

The detergent composition was as in A.

Test conditions:

Temperature: 95°C

Liquor ratio: 1 : 12

5 Fabric: 10 g of cotton fabric No. 222
5 g of cotton yarn No. 181
5 g of soiled cotton yarn

Washing time: 30 minutes

Water hardness: 16° German hardness

10 pH : 10.5

Detergent concentration: 5 g/l

The material was washed 5 times, the soiled yarn being replaced after each wash.

15 TABLE 2

20	Sequestering agent composition (% by weight) Sodium salt of copolymer of Example				Pentasodium triphosphate	Whiteness measured as the reflectance (Elrepho instrument) Number of washes					20
	1	3	4	6		1	2	3	4	5	
25	100	-	-	-	-	67.5	63.7	62.5	58.9	58.1	25
	75	-	-	-	25	65.7	61.2	60.2	57.2	56.8	
	50	-	-	-	50	69.5	64.6	62.3	59.5	58.1	
	25	-	-	-	75	65.7	60.0	58.4	56.4	54.5	
	-	100	-	-	-	65.0	60.1	59.7	57.2	56.9	
	-	75	-	-	25	64.9	61.1	60.6	58.9	57.0	
30	-	50	-	-	50	65.4	61.2	59.7	56.6	56.3	30
	-	25	-	-	75	64.0	60.2	58.2	57.3	54.0	
	-	-	100	-	-	63.4	62.6	60.2	59.3	56.3	
	-	-	75	-	25	66.6	61.0	60.0	59.3	58.2	
	-	-	50	-	50	65.3	62.9	62.2	59.4	57.3	
35	-	-	25	-	75	65.7	60.9	59.7	58.4	55.4	35
	-	-	-	100	-	58.9	54.3	52.5	51.5	50.0	
	-	-	-	75	25	61.5	57.8	57.9	54.0	52.1	
	-	-	-	50	50	66.5	62.0	60.7	59.6	56.9	
	-	-	-	25	75	66.2	63.8	60.2	58.4	56.8	
40	-	-	-	-	100	66.5	61.9	58.8	55.8	52.3	40

This shows that the inhibition of graying using the copolymers is better than with pentasodium phosphate.

C. Calcium-binding capacity

45 The calcium-binding capacity was determined by turbidimetric titration with Ca acetate. 1g of the complexing agent to be tested (in free acid form) is dissolved in 100 ml of distilled water and 10 ml of 2% by weight strength Na carbonate solution are then added. The pH of this solution is brought to 11 and is kept constant during the titration. The solution is then titrated with 4.4% by weight strength Ca acetate solution until a distinct and constant turbidity results. The Ca acetate solution is added in portions of 1 ml at intervals of 30 50 seconds. 1 ml of Ca acetate solution consumed corresponds to 25 mg of Ca carbonate. The results are stated in mg of Ca carbonate per gram of complexing agent (calculated as free acid).

TABLE 3

	Complexing agent = sodium salt of copolymer of Example	Ca-binding capacity (mg of CaCO ₃ /g salt)		
		25°C	90°C	
5				5
	1	575	500	
	2	675	525	
10	3	650	475	10
	4	600	475	
	5	550	425	
	6	750	375	
15	= Pentasodium triphosphate	225	150	15

D. Cleaning action in dishwashing agents

The cleaning action of the copolymers (in sodium salt form) in dishwashing agents was determined using plates soiled with starch. 20 g of potato starch are dissolved in 1 liter of boiling water. 4 teaspoons of this solution are spread uniformly over a household plate and are then dried for 45 minutes at 100°C. After cleaning the plates in the dishwasher using a cleaning agent formulation as specified below, the residual starch is determined by staining with 1% by weight strength KI/iodine solution and estimating the blue surface area. Cleaning agent formulation (parts are by weight):

25 9 parts of sequestering agent (calculated as free acid) 25
1 part of Na carbonate
10 parts of Na metasilicate

	Sequestering agent = sodium salt of copolymer of Example	Residual starch, % by weight	
	1	8	
	2	3	
35	3	3	35
	4	3	
	5	2	
	6	4	
40	= pentasodium triphosphate	3	40

All the experiments show clearly that the copolymers can very successfully replace at least part of the phosphates.

WHAT WE CLAIM IS:-

- 45 1. A copolymer comprising 45
a) from 50 to 95 mole % of units of acrylic acid and/or methacrylic acid and/or an alkali metal salt thereof, and
(b) from 5 to 50 mole % of units of vinyl-lactic acid and/or isopropenyl-lactic acid and/or an alkali metal salt thereof.
- 50 2. A copolymer as claimed in claim 1 in which component a) is acrylic acid and component b) is vinyl-lactic acid. 50
3. A copolymer as claimed in claim 1 or 2 in which component a) constitutes 60 to 90 mole % of the copolymer and component b) constitutes 10 to 40 mole % of the copolymer.
- 55 4. A copolymer as claimed in any of claims 1 to 3 in sodium salt form. 55
5. A copolymer as claimed in any of claims 1 to 4 which has a mean molecular weight of from 2,000 to 20,000 (determined osmotically and has been obtained by copolymerization in a solvent with an aliphatic azo compound as initiator, followed by neutralization with alkali metal hydroxide.
- 60 6. A copolymer as claimed in claim 1 and substantially as described in any of the foregoing Examples 1 to 6. 60
7. A detergent or cleaner formulation which contains a copolymer as claimed in any of claims 1 to 6 as sequestering agent in alkali metal salt form.
8. A detergent or cleaner formulation containing as sequestering agent a copolymer as claimed in any of claims 1 to 6 in alkali metal salt form and a phosphate sequestering agent, 65
in a ratio by weight of from 1:4 to 4:1. 65

9. A detergent or cleaner formulation as claimed in claim 7 or 8 containing from 10 to 50% by weight of the sequestering agent based on the total formulation and containing an anionic and/or non-ionic surfactant in a weight ratio of surfactant to sequestering agent of from 3:1 to 1:10.

5 10. A washing or cleaning process in which the material to be washed or cleaned is treated in water with a detergent or cleaner formulation as claimed in any of claims 7 to 9. 5

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