United States Patent [19]

Hardy et al.

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[54] **NEW POLYMERS AND DETERGENT COMPOSITIONS CONTAINING THEM**

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[21] Appl. No.: **109,657**

[52] **U.S. Cl.**.....**260/86.1 R,** 252/112, 252/523, 252/530, 252/541, 252/549, 260/86.1 N, 260/486 R

[51] **Int. Cl.**.....**C08f 15/14,** C08f 15/16

[58] **Field of Search**.....260/86.1 R, 86.1 N

[56] **References Cited**

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[57] **ABSTRACT**

New copolymers of acrylic and methyl acrylic acid (I) with acrylic and methacrylic acid — ethylene oxide condensates (II). The components have formulas:

I. $CH_2=C(R)COOM$

II. $CH_2=C(R)COO(C_2H_4O)_nH$

wherein R is H or CH_3; M is H, alkali metal, ammonium or amine; and n is at least one. The preferred ratio of (I) to (II) is about 2:1 and n is preferably from 20 to 100.

These compounds are mixed with surface-active agents to form built detergents. They are most effective as whiteness maintenance agents when added to a detergent composition at a 0.1 to 5 percent level by weight of the final product.

8 Claims, No Drawings

NEW POLYMERS AND DETERGENT COMPOSITIONS CONTAINING THEM

BACKGROUND OF THE INVENTION:

The invention relates to new copolymers having useful properties, especially as components of washing compositions. Thus they may be effective for improving "whiteness maintenance," as lime soap dispersants and as detergency builders.

While the primary function of a detergent composition is to remove soil from articles being washed, an important secondary function is to prevent the soil removed from dirtier articles or parts of articles from being redeposited upon cleaner articles or parts of articles which are being treated in the same wash liquor. This activity is known as whiteness maintenance and is measured, in principle, by determining the loss of whiteness of clean white fabrics (or surfaces) when "washed" in standard conditions together with soiled articles, or in a detergent liquor containing soil.

Lime soap dispersants are substances incorporated in soap products, as soap-containing wash liquors which present the formation or the deposition of insoluble soaps formed by reaction of soluble soaps with the constituents of hard water.

Builders are agents, usually alkaline and/or having calcium sequestering properties, which enhance the cleaning power of organic detergents.

The present copolymers are particularly effective as whiteness maintenance improvers when employed in dilute washing liquors containing phosphatic builder salts including pyro-and/or ortho-phosphates, that is in liquors wherein there is not enough sequestrant builder salt present to sequester all the calcium ions strongly enough to prevent calcium pyro- or ortho-phosphates being precipitated. These calcium ions are usually derived primarily from the water hardness, but may also be derived from the soiled articles being washed. Thus, as a typical instance, a conventional tripolyphosphate-built heavy duty granular detergent, prepared by spray drying, normally contains a proportion of pyro- and ortho-phosphates as a result of partial reversion (hydrolysis) of the tripolyphosphate during mixing and spray drying. If, as is not uncommon, such a composition is used in hard water at a concentration such that there is insufficient unreverted tripolyphosphate present to sequester all the calcium etc. in the hard water, the whiteness maintenance is likely to be poor. The copolymers of the invention are particularly valuable in overcoming this fault. While the invention does not depend on any theory of the mechanism whereby these agents act, it appears that the insoluble calcium pyro- or ortho-phosphates encourage or aggravate the redeposition of soil, and that the copolymers of the invention diminish, or affect in some other beneficial way, the effect of said calcium phosphates.

BRIEF DESCRIPTION OF THE INVENTION

The new polymers are copolymers of acrylic or methacrylic acid or their salts having the formula $CH_2{=}C(R)COO\ M$ with one or more acrylic or methacrylic derivatives having the general formula:

$$CH_2{=}C(R)COO\ (C_2H_4O)_nH$$

wherein R is H or CH_3, M is hydrogen or a cation such that the copolymers are water soluble, and n is at least one. Preferred copolymers are those derived from acrylic acid and methacrylic derivatives, i.e., derivatives where R is CH_3. Preferably M represents an alkali metal (especially sodium), ammonium or an amine.

The invention also provides detergent compositions comprising an organic detergent and a copolymer as defined above, and, especially such detergent compositions also comprising a builder salt including pyro- and/or ortho-phosphates.

The invention also provides a laundering process in which fabrics are washed in a solution of a detergent composition according to the invention, especially a process in which there is insufficient sequestering agent present in the wash liquor to sequester all calcium ions present in the wash liquor.

DETAILED DESCRIPTION OF THE INVENTION

The copolymers of the invention may be prepared in any effective way. For instance, a polyethylene glycol of the desired mean molecular weight (i.e. desired average number of polymerized ethylene oxide residues) may be reacted with methacrylic or acrylic acid anhydrides in the presence of a catalyst. The resulting ester may be copolymerized with methacrylic or acrylic acid by methods known in the art for making acrylic-type polymers. It may not be necessary, though it is of course permissible, to separate the copolymers in the reaction product from impurities, such as unreacted monomers, present with them when the material is to be used in detergent compositions. In the acrylic or methacrylic derivative used in the copolymers, n is one or more, generally up to about 150. As agents enhancing whiteness maintenance, the preferred copolymers have n from about 20 to 100, especially at the upper end of this range. As soap scum dispersants, the preferred compounds have n from about 5 to 10, especially about 6. The preferred ranges of values of n stated refer to the mean values when, as is usual, compounds with a range of n values are present together.

In preparing the copolymers in weight ratio of acrylic or methacrylic acid to the acrylic or methacrylic derivative is preferably from about 1:1 to about 5:1 and especially about 2:1.

The degree of copolymerization is usually preferably such as to provide copolymers having molecular weight of the order of 30,000 to 200,000, but reaction mixtures containing copolymers and some unpolymerized or little polymerized materials and having an apparent molecular weight as low as about 3,000 have proved effective.

In detergent compositions, the proportions of the copolymers which can usefully be incorporated varies widely. Thus, especially if they are intended as detergency builders, considerable proportions of the copolymers may be used, for instance up to 50 percent or more by weight of the composition. When they are intended as lime scum dispersants or whiteness maintenance improvers relatively small proportions are usually sufficient, for instance from about 0.1 to about 5 percent, and especially about 1 percent. Larger proportions are, however, effective for these purposes also

and the optimum level will depend upon economic and like considerations.

Apart from their content of the copolymers of the invention, the detergent composition may be conventional, and in any physical form. Thus, they may contain as organic detergent soap or other anionic detergent, or nonionic, semipolar, zwitterionic or cationic detergents, and the usual builder salts such as ortho, pyro or tripolyphosphates, carbonates, silicates, sulfates, borates and the like, or organic sequestrant builder salts such as nitrilotriacetates, ethylene diamine tetra-acetate, ethane-1-hydroxy-1,1-diphosphonates, and the like. These may be present as the sodium, potassium or ammonium or amine salts, more usually the sodium salts. Also present may be bleaching agents such as peroxygen or chlorine bleaches, and the usual minor components of detergent compositions such as coloring matter, perfumes, enzymes, other soil suspending agents, tarnish inhibitors, suds enhancing or depressing agents, preservatives, germicides, stabilizers or activators for the bleaching agents or enzymes, and the like.

The invention is illustrated by the following Examples:

EXAMPLE I

Preparation of Polyoxyethylene Glycol Monomethacrylate

Forty g. of polyoxyethylene glycol, of molecular weight 4,000, in 40 ml. of pyridine were treated with 1.5 g. methacrylic acid and 50 mg. of hydroquinone. The solution was kept at 50°–60° C. for 3 days and then poured into 500 ml. of ether. The precipitated monoester, 40 g., was collected and washed with ether. This was the compound corresponding to the formula $CH_2=C(CH_3)COO\ (C_2H_4O)_nH$ wherein the mean value of n was about 90.

PREPARATION OF COPOLYMER

A solution of acrylic acid (4 g.) and the polyoxyethylene glycol methacrylate prepared above (2 g.) in ethanol (50 ml.) containing α-azoisobutyronitrile (0.005 g.) was heated under reflux for 2 hours. Sodium ethoxide in ethanol (30 ml. from 1.28 g. of sodium) was added, solvent was evaporated under reduced pressure and the residue was triturated with ether and filtered. Yield of copolymer was 7 g.

Copolymers of methacrylate derivatives where n = 20 and n = 50 (mean values) may be prepared similarly.

EXAMPLE II

A detergent composition A was prepared consisting essentially of:

17.5%	Sodium dodecylbenzene sulfonate
46.2%	Sodium tripolyphosphate containing about 20% by weight thereof of pyrophosphate
7.3%	Sodium silicate monethanolamide
1.8%	Coconut monoethanolamine
1.0%	Sodium carboxymethyl cellulose
0.3%	Sodium ethylene diamine tetra-acetate
11.9%	Sodium sulfate
11.0%	Water
1.0%	Copolymer made according to Example I.

A dispersion was made up containing 0.1 percent of this composition, 0.004 percent air born "dirt" (obtained from an airfilter) and 0.04 percent of a 1:1:1 mixture of olive oil, oleic acid and lubricating oil in hard water (258 parts per million as $CaCO_3$). 250 ml. aliquots of this dispersion were placed in containers of a Launderometer, together with six 4½ inches square swatches of cotton long cloth. (Cloth to liquor ratio, by weight 1:25). The swatches were subjected to a 1 hour wash at 38° C. They were then removed, rinsed and dried. This treatment was repeated a further two times. Control tests were carried out in the same conditions using the same detergent composition but with the copolymer omitted (Composition B). The reflectance of the original cotton swatches and of the thrice washed swatches was measured, the variability within the groups of 6 swatches being used to establish 95 percent confidence limits for the results, indicated below as ± figures.

Results were:

Unwashed fabric — reflectance	94.5 percent
Washed in Composition A — reflectance	80 ± 1.7 units
Washed in Composition B — reflectance	74 ± 1.7 units

Having thus described the invention, what is claimed is:

1. A water-soluble copolymer which results from reacting a first compound having the formula

$$CH_2=C(R)COOM$$

with a second compound having the formula

$$CH_2=C(R)COO\ (C_2H_4O)_nH$$

wherein R is selected from the group consisting of H and CH_3, M is selected from the group consisting of H, alkali metal, and ammonium, and n is an integer representing a mean value in the range of from about 5 to about 100, the weight proportion of said first compound to said second compound being in the range of from about 1:1 to 5:1.

2. The copolymers of claim 1 wherein the R of the first compound is H and the R of the second compound is CH_3.

3. The copolymers of claim 1 wherein n is from 20 to 100.

4. The copolymers of claim 1 wherein M is an alkali metal.

5. The copolymers of claim 4 wherein the alkali metal is sodium.

6. The copolymer of claim 1 having a molecular weight of from 30,000 to 200,000.

7. The copolymer of claim 1 wherein the first compound is acrylic acid and the second compound is a polyoxyethylene glycol methacrylate wherein the mean value of n is 90.

8. The copolymer of claim 1 in which the weight proportion of said first compound to said second compound is 2:1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,719,647 Dated March 6, 1973

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 57 delete "proportions" and insert therefor -- proportion --

Column 3, line 59 delete "monethanolamide" and insert therefore --(solids)--

Column 3, line 60 delete "monoethanolamine" and insert therefore -- monethanolamide --

Signed and sealed this 8th day of January 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

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