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DIVINYL ETHER POLYMERS AND DETERGENT COMPOSITIONS UTILIZING DIVINYL ETHER POLYMERS AS BUILDERS

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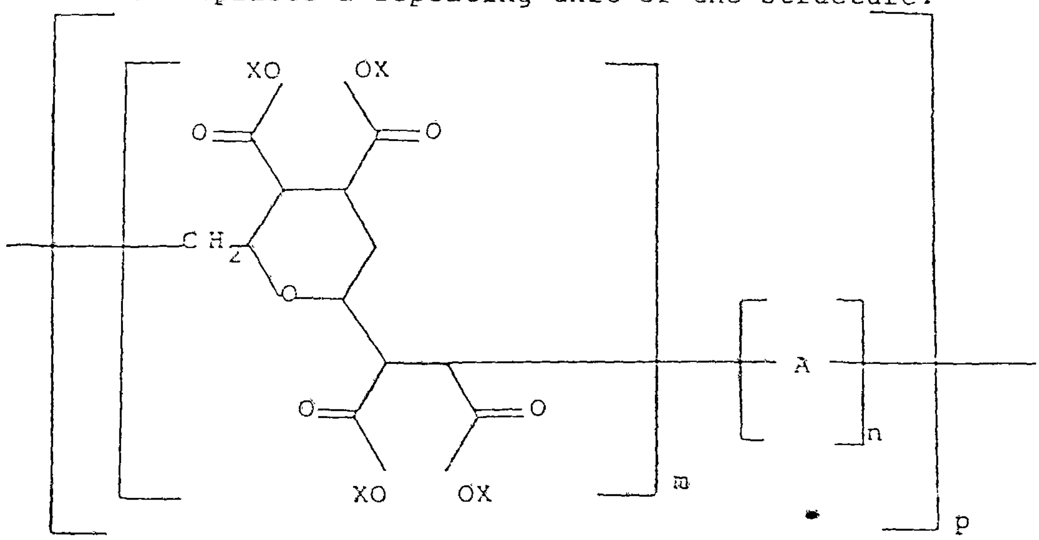
(71) Applicant(s)
INDOPCO INC.

(72) Inventor(s)
CARMINE P. IOVINE; JOHN C. LEIGHTON

(74) Attorney or Agent
GRIFFITH HACK & CO , GPO Box 1285K, MELBOURNE VIC 3001

(57) Claim

1. A polymer of divinyl ether, maleic anhydride and at least one copolymerizable comonomer, selected from the group consisting of alkenyl alkyl ethers, alkyl acrylates, alkenyl carboxyalkyl ethers, vinyl esters of C_1 or C_3 or greater carboxylic acids, unsaturated carboxylic acids, unsaturated dicarboxylic acids and their esters, and olefins, and wherein the polymer further comprises a repeating unit of the structure:



wherein A is the comonomer(s); X is H, alkali metal ion, ammonium ion, hydroxyethylammonium ion, C_1-C_{12} alkyl, or C_5-C_{12} cycloalkyl, or a combination thereof; m and n are greater than 1; and p is from 5 to 4,000.

4. A polymer, according to any one of claims 1 to 3 wherein the comonomer is selected from the group consisting of isobutyl vinyl ether, methyl acrylate, acrylic acid, itaconic acid, styrene, methyl vinyl oxyacetate and ester hydrolysis products of the methyl vinyl oxyacetate.

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Name of Applicant: NATIONAL STARCH AND CHEMICAL CORPORATION

Address of Applicant: 10 FINDERNE AVENUE, BRIDGEWATER, NEW JERSEY UNITED STATES OF AMERICA

Actual Inventor:

Address for Service: GRIFFITH HACK & CO., 601 St. Kilda Road, Melbourne, Victoria 3004, Australia.

Complete Specification for the invention entitled:
DIVINYL ETHER POLYMERS AND DETERGENT COMPOSITIONS UTILIZING DIVINYL ETHER POLYMERS AS BUILDERS

The following statement is a full description of this invention including the best method of performing it known to me:-

DIVINYL ETHER POLYMERS AND DETERGENT COMPOSITIONS UTILIZING DIVINYL ETHER POLYMERS AS BUILDERS

This invention relates to polymers of divinyl ether, maleic anhydride and at least one copolymerizable comonomer.

The DIVEMA copolymer is best known as an experimental antitumor and antiviral drug (Pyran). See Morahan, Page S., et al, Cancer Treat. Rep., 62 (11) 1797-805 (1978). The preparation and the composition of the saturated linear DIVEMA copolymer were disclosed in U.S. -B- 26,407 to Butler, issued June 11, 1968. Use of the DIVEMA copolymer, in a preferred molecular weight range from
about 1,000 to about 10,000, as an aqueous dispersant for fine solids such as pigments, clay and organic polymers was disclosed in U.S. -A- 3,085,077 to Floyd, issued April 9, 1963. Its use as a water loss prevention agent in gas and oil well drilling fluids was disclosed in U.S. -A- 3,157,599 to Gloor, issue November 17, 1964.

The terpolymer of divinyl ether, maleic anhydride and vinyl acetate was disclosed in U.S. -A- 2,640,039 to Williams, issued May 26, 1953. Additionally, this patent discloses the use of this terpolymer to thicken and size aqueous solutions, form gels or films, form protective colloids, disperse agents in aqueous solutions and replace gums.

Detergent compositions are generally a blend of a surfactant(s), builder(s) and, optionally, ion exchangers, fillers, alkalies, anticorrosion materials, antiredeposition materials, bleaches, enzymes, optical brighteners, fragrances and other components selected for particular applications.

Builders are used to improve the effectiveness of detergent compositions and thereby improve their whitening powers. Polyphosphate compounds, such as sodium tripolyphosphate, have long been in use as builders, particularly because of their relatively low cost and their utility in increasing the whitening powers of detergent compositions. It is theorized, however, that the presence of these polyphosphates tends to contribute to the growth of algae in lakes and rivers to a degree sufficient to cause eutrophication of these waters. For many years there has been legislative pressure to lower or discontinue their usage completely in detergent compositions to control phosphate pollution. Thus, detergent manufacturers continue to search for effective, non-phosphate detergent builders.

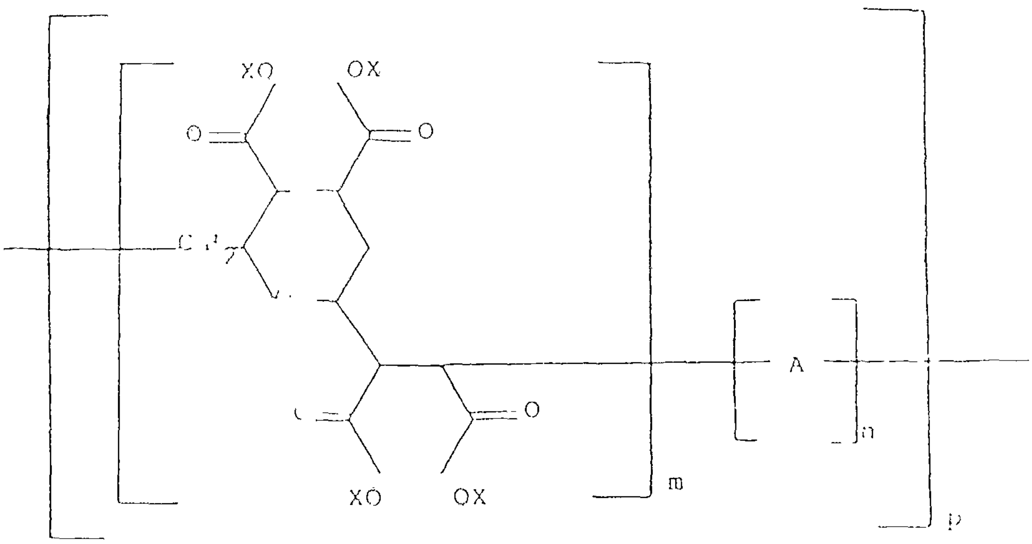
The manner in which detergent builders improve the cleaning powers of detergent compositions is related to a combination of such factors as emulsification of soil particles, solubilization of water insoluble materials, promoting soil suspension in the wash water so as to retard soil redeposition, sequestering of metallic ions, and the like.

Alternatives for sodium tripolyphosphate are widely used by detergent formulators. Many materials are or have been used as builders in detergent formulations. All have one or more drawbacks that offset their value in the formulations. Compositions and materials change frequently as formulators attempt to improve performance of cleaning while offering greater convenience in handling as well as keeping materials cost as low as possible.

Among the materials that have been suggested for use as detergent builders are the ether carboxylates disclosed in U.S. -A- 4,663,071 to Bush, et al., issued May 5, 1987; the copolymers of maleic anhydride and sulfonated styrene or 2-acrylamido-2-methyl propane sulfonic acid disclosed in U.S. -A- 4,711,740 to Carter, et al., issued December 8, 1987; and the carboxylated bicyclic compounds and salts thereof disclosed in U.S. -A- 3,898,034 to Szymanski, et al., issued August 5, 1975.

Notwithstanding the existence of the foregoing types of detergent builders, there remains a continuing need to identify additional non-phosphorus sequestering agents, such as polymers prepared from divinyl ether and maleic anhydride, which can be prepared commercially and utilized as builders in commercial detergent compositions. Accordingly, detergent compositions are disclosed herein which employ effective, non-phosphate builders as a replacement, in whole, or in part, for phosphate builders.

This invention provides a polymer of divinyl ether, maleic anhydride and at least one copolymerizable comonomer, selected from the group consisting of alkenyl alkyl ethers, alkyl acrylates, alkenyl carboxyalkyl ethers, vinyl esters of C_1 or C_3 or greater carboxylic acids, unsaturated carboxylic acids, unsaturated dicarboxylic acids and their esters, and olefins, and wherein the polymer further comprises a repeating unit of the structure:



wherein A is the comonomer(s); X is H, alkali metal ion, ammonium ion, hydroxyethylammonium ion, C_1-C_{12} alkyl, or C_5-C_{12} cycloalkyl, or a combination thereof; m and n are greater than 1; and p is from 5 to 4,000.

Polymers of the invention are exemplified by compositions wherein the comonomer is isobutyl vinyl ether, methyl acrylate, methyl vinyloxyacetate, acrylic acid, itaconic acid, or styrene.

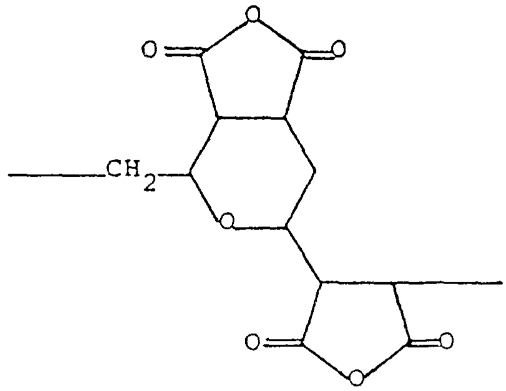
These polymers may be utilized in the salt (e.g., sodium, potassium, ammonium, monoethanolamine, triethanolamine) or the C_1-C_{12} alkyl or C_5-C_{12} cycloalkyl ester form (structure I), or in the anhydride form (structure II). The number average molecular weight of these polymers in the anhydride form may lie in the range from 1,300 to 1,100,000.

Detergent compositions utilizing polymers of this invention comprise any of the compositions which are used for cleaning purposes, wherein at least one builder is selected from the builders disclosed herein. Thus, the compositions include liquid and dry blends useful for household laundry detergents, automatic dishwashing machine detergents, hard surface cleaners, and industrial and specialty cleaning products.

DIVINYL ETHER POLYMERS

The DIVEMA copolymer is described in Butler, G.B., J. Macromol. Sci. - Chem., A5(1), 219-227 (1971). The copolymer may be prepared by the method disclosed in U.S. -B- 26,407 to Butler, issued June 11, 1968. Alternatively, it may be prepared by any method known in the art for cyclocopolymerization of dienes and alkenes to yield a saturated, substantially linear copolymer. In preparing the copolymer, the divinyl ether and maleic anhydride monomers are quantitatively converted to the DIVEMA copolymer in a molar ratio of 1:2.

In the anhydride form, the DIVEMA copolymer comprises from about 5 to 4,000 repeating units of structure II.



II

The anhydride structure II and the salt structure I are shown as the six-member ring DIVEMA isomer. A five-member ring DIVEMA isomer has also been identified. For the purposes of this invention, either or both DIVEMA isomers may be employed. Additionally, either the salt or the ester or the anhydride form may be employed.

The molecular weight corresponding to 5 to 4,000 repeating units of II ranges from about 1,300 to 1,100,000. The ranges of the molecular weight of the copolymer are limited only by the method of preparation, ~~and effectiveness of the polymer as a builder.~~ The corresponding number average molecular weight of the fully neutralized sodium salt of the copolymer ranges from about 2,000 to 1,600,000. In a preferred embodiment the sodium carboxylate salt of the polymer is prepared by dissolving the anhydride in water and neutralizing it with sodium hydroxide in the manner disclosed in Example XVII of U.S. -B- 26,407. The practitioner will recognize that if the anhydride form of the polymer is incorporated into a detergent formulation, hydrolysis to the carboxylic acid form will occur under typical washing or cleaning conditions. The sodium, potassium, ammonium, monoethanolamine or triethanolamine carboxylate salt of the polymer are also preferred. However, with the exception of the polyvalent cations responsible for water hardness, any organic or inorganic base may be utilized in preparing the salt of the polymer.

In a second preferred embodiment, a C_1-C_{12} alkyl or cycloalkyl ester of the polymer is formed by reacting the anhydride with an excess of C_1-C_{12} alcohol. This reaction may be conducted in an aprotic solvent (e.g., toluene). Suitable alkyl esters may be prepared with any alkyl alcohol (e.g., lauryl alcohol); and suitable cycloalkyl esters may be prepared with any cycloalkyl alcohol (e.g., cyclohexanol).

The remaining divinyl ether/maleic anhydride polymers may be prepared by the method disclosed in U.S. -B- 26,407, except that at least one copolymerizable comonomer, selected from the group consisting of alkenyl alkyl ethers, alkyl acrylates, alkenyl carboxyalkyl ethers, vinyl esters of carboxylic acids, unsaturated carboxylic acids, unsaturated dicarboxylic acids and their esters, and olefins, is added to the reaction medium. Like the DIVEMA copolymer, the polymers of the invention are normally saturated, substantially linear polymers whose sodium salts have number average molecular weights in the range between 2,000 and 1,600,000.

esters, and olefins. Structure A may consist of one or more of the selected comonomer(s). Certain of these comonomers (e.g., acrylic acid and maleic acid) are known to form homopolymers and copolymers which have commercial utility as detergent builders (e.g., acrylic acid/maleic acid copolymer and polyacrylic acid).

Structure A is an optional component of the builders, but an essential component of the novel polymers of this invention. Thus, in the novel polymers of this invention, both m and n must be greater than zero and p may range from about 5 to 4,000.

For detergent builder purposes, m must be greater than zero, n may be zero or greater, and p may range from 5 to about 4,000. The practitioner will recognize that as the ratio of n to m increases, the preferred selection of comonomer(s) will shift toward those comonomers with known effectiveness as calcium or magnesium sequestrants or as detergent builders. Likewise, as the ratio of m to n increases, the builder effectiveness of the comonomer(s) becomes less critical and other factors, such as cost and detergent formulation compatibility will guide comonomer(s) selection.

In a preferred embodiment, a novel terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and isobutyl vinyl ether, exemplifying the class of alkenyl alkyl ether monomers. In a second preferred embodiment, a novel terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and methyl acrylate, exemplifying the class of alkyl acrylate monomers. In a third preferred embodiment, a novel terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and acrylic acid, exemplifying the class of unsaturated carboxylic acids. In a fourth preferred embodiment, a novel terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and methyl vinyloxyacetate, exemplifying the class of alkenyl carboxyalkyl ethers. (The methyl vinyloxyacetate may be hydrolyzed after polymerization to yield pendant carboxylic acid groups.) In a fifth preferred embodiment, a novel terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and itaconic acid, exemplifying the class of unsaturated dicarboxylic acids. In a sixth preferred embodiment, a novel terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and styrene, exemplifying the class of olefins.

In a seventh preferred embodiment, a known terpolymer is prepared containing a molar ratio of 1:3:1 of divinyl ether, maleic anhydride and vinyl acetate, exemplifying the class of vinyl esters of carboxylic acids. The novel compounds herein are limited to polymers which do not contain vinyl acetate, and therefore, the copolymerizable comonomers are limited to vinyl esters of C_1 or C_3 or greater carboxylic acids.

It will be recognized by the practitioner that although cyclocopolymerized saturated linear copolymers of divinyl ether and maleic anhydride will not vary from the 1:2 molar ratio, the ~~other~~ divinyl ether/maleic anhydride polymers of this invention are not so limited. Thus, although both divinyl ether and maleic anhydride must be present to form the ~~other~~ cyclocopolymerized polymers, the molar ratio of divinyl ether, maleic anhydride and the comonomer(s) may vary.

Similarly, the practitioner will recognize that although certain comonomers are selected for the preferred embodiments disclosed herein, any monomers within the selected class may be utilized. Furthermore, small quantities of polyfunctional comonomers which are not within the selected classes may be utilized, provided the resulting polymers retain their effectiveness as detergent builders. Examples of such polyfunctional comonomers are acrylates and methacrylates of polyols, allyl and vinyl esters of polycarboxylic acids, divinyl benzene, and the like.

The alkenyl alkyl ether monomers useful herein include vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl i-propyl ether, vinyl n-butyl ether, vinyl sec-butyl ether, vinyl t-butyl ether, vinyl pentyl ether, higher vinyl alkyl ethers, and the like.

The alkyl acrylate monomers useful herein include methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, and higher acrylates and corresponding 2-substituted acrylates where the 2-substitution is C_1-C_6 alkyl and cycloalkyl, and the like.

The alkenyl carboxyalkyl ethers useful herein include methyl vinyloxyacetate, methyl vinyloxypropionate, methyl vinylbutanoate, methyl vinyloxypentanoate, vinyl 3,3-dicarboxymethylpropyl ether, vinyl 3,3,3-tricarboxymethylpropyl ether, and the like.

The polymerizable unsaturated carboxylic and dicarboxylic acid monomers useful herein include acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, and the like.

The olefins useful herein include ethylene, propylene, 1-butene, 1-pentene, higher olefins, and substituted olefins such as styrene and the like.

The vinyl esters useful herein include vinyl formate, vinyl acetate, vinyl propionate, vinyl butanoate, vinyl pentanoate, vinyl neodecanoate, and the like.

Additionally, although only one method of preparation of these polymers was employed in the preferred embodiments disclosed herein, it is intended that the polymers; of this invention may be prepared by any method known in the art. Acceptable methods of preparation are known in the art and include Butler, G., J. Macromol. Sci., Chem, A5(1) 219-227 (1971); Butler, G., J. Macromol., Sci., Chem., A6(8) 1533-68 (1972); and Stackman, Robert W., J. Macromol., Sci., Chem., A5(5) 251-262 (1971).

DETERGENT COMPOSITIONS

The detergent formulations comprise from about 0.5 to 65% by weight of a surfactant, or a blend of surfactants, and 1 to 80% by weight of a polymer builder, or a blend of builders containing at least one polymer according to the invention. In a preferred embodiment, from about 0.5 to 30% by weight; of a surfactant, or a blend of surfactants, and from about 1 to 65% by weight of a polymer builder, or a blend of builders containing at least one polymer according to the invention, are employed. Where a blend of builders is employed, the polymer may be employed at lower percentages, provided that the total builder content is at least 1% of the detergent formulation.

Optional components of the detergent formulations include, but are not limited to, ion exchangers, alkalies, anticorrosion materials, anti-redeposition materials, optical brighteners, fragrances, dyes, fillers, chelating agents, enzymes, fabric whiteners and brighteners, sudsing control agents, solvents, hydrotropes, bleaching agents, bleach precursors, buffering agents, soil removal agents, soil release agents, fabric softening agent and opacifiers.

These optional components may comprise up to about 90% of the detergent formulation. Examples of these optional components, commonly used surfactants and various builders are set forth in detail in U.S. -A- 4,663,071 to Bush, issued May 5, 1987.

Acrylate or isobutyl vinyl ether, are preferred in liquid formulations because their hydrophobicity tends to stablize the detergent and prevent phase separation of the surfactant and the builder.

This invention is illustrated by the following examples.

EXAMPLE 1

This example illustrates the preparation of a DIVEMA copolymer.

A. Preparation of Divinyl Ether Monomer

Divinyl ether was prepared by the dehydrohalogenation of beta-chloroethyl ether with sodium in 2-ethylhexanol. The 2-ethylhexanol (650 ml) was charged to a four-neck 2 liter flask equipped with a coil condensor cooled with ice water, a heating mantle, a thermometer and a glass stirrer, and heated to 100°C. While purging with nitrogen, sodium metal (48.3 g; 2.10 mol) was added at a sufficiently slow rate to maintain the temperature below 130°C. After the sodium had dissolved, the beta-chloroethyl ether (143.0 g; 1.00 mol) was added over one hour at 90°C. The temperature was raised to 170°C and a crude reaction product (b.p. 29-90°C) was recovered by distillation. The product was redistilled twice (b.p. 28-30°C) and 19.0 g divinyl ether (27.1% yield) was obtained.

B. Preparation of DIVEMA Copolymer

Copolymerization of the divinyl either with maleic anhydride was by the method disclosed in Butler, G.B., J. Macromol. Sci. - Chem., A5(1) 219-227 (1971), at page 222-23. 49 g of maleic anhydride, 300 ml of dry xylene, 1 g of benzoyl peroxide and 17.5 g divinyl ether were charged to a cooled 1 litre autoclave. The autoclave was heated to 50°C and held at this temperature for 1 hour, after which the temperature was raised to 70°C for 3 hours. After cooling, the suspended copolymer was removed by filtration and washed thoroughly with hot xylene. The crude product contained 0.64% residual maleic anhydride

The molecular weight of the copolymer in anhydride form was measured by gel permeation chromatography in DMSO against dextran standards. The weight average molecular weight of the anhydride form of the DIVEMA copolymer was 54,700. The number average molecular weight was determined to be 3,570. The intrinsic viscosity was 0.853 in dimethylformamide.

A sodium carboxylate copolymer was obtained upon dissolution of the anhydride copolymer in water, followed by neutralization with sodium hydroxide.

EXAMPLE 2

This example illustrates the preparation of the ~~remaining class of~~ divinyl ether/maleic anhydride polymers of the invention.

The polymers were prepared by the same method as the copolymer in Example 1, except that a third comonomer was added to the reaction vessel.

The following mole ratio terpolymers were prepared:

A. 1:3:1 divinyl ether/maleic anhydride/isobutyl vinyl ether;

B. 1.3:1 divinyl ether/maleic anydride/methyl acrylate;

C. 1:3:1 divinyl ether/maleic anhydride/vinyl acetate;

D. 1:3:1 divinyl ether/maleic anhydride/acrylic acid;

E. 1:3:1 divinyl ether/maleic anhydride/methyl vinyl oxyacetate; and

F. 1:3:1 divinyl ether/maleic anhydride/itaconic acid.

G. 1:3:1 divinyl ether/maleic anhydride/styrene.

Sodium carboxylate salts of these polymers were obtained upon dissolution of the anhydride polymer in water and neutralization with sodium hydroxide.

EXAMPLE 3

This example illustrates the effectiveness of these polymers in calcium sequestration.

Four solutions of calcium chloride in water, containing, respectively, 60, 120, 180 and 240 ppm Ca^{++} ion, were each treated with 0.1, 0.2, 0.3 and 0.4 g/l of the experimental and control builders. A calcium ion selective electrode (Corning Radiometer F2110 Calcium Selective Electrode) was used to measure the free Ca^{++} ion concentration of the treated solutions.

The detergent builders tested for calcium ion sequestration included the DIVEMA copolymer of Example 1, terpolymers A-G of Example 2 and two detergent builders which are commercially used. The commercial builders were Sokalan® CP-7 (a trademark registered to BASF Corporation and used in connection with a 2:1 copolymer of acrylic acid and maleic acid) and A1N (a polyacrylic acid) sold by Rohm & Haas.

Results expressed as p (Ca^{++}) are set forth in Table I. All treatments resulted in higher p (Ca^{++}) (indicating lower concentration of free Ca^{++} ion remained in solution following treatment) as the treatment level was increased. Overall, the DIVEMA copolymer and terpolymers A-G sequestered calcium ions as effectively as the commercially used detergent builders. The Sokalan CP-7 builder was slightly more effective at lower calcium ion concentration levels. Terpolymers C and D (vinyl acetate and acrylic acid) were slightly more effective than Sokalan CP-7 at higher calcium concentration levels.

Thus the polymers of this invention effectively sequester calcium ions in solution.

Table I

Calcium Sequestration at 60 ppm, 120 ppm, 180 ppm and 240 ppm Ca^{++}

Builder	ppm Ca^{++}	Treatment Level (g/l)			
		0.1	0.2	0.3	0.4
Sokalan® CP7	60 ppm	3.81	4.91	5.99	6.41
	120 ppm	3.20	3.44	4.31	4.99
	180 ppm	2.94	3.08	3.48	3.88
	240 ppm	2.77	2.88	3.12	3.32
Rohm & Haas A1N	60 ppm	3.50	3.96	4.38	4.63
	120 ppm	3.06	3.25	3.51	3.77
	180 ppm	2.83	2.95	3.11	3.25
	240 ppm	2.69	2.77	2.88	2.97
DIVEMA Copolymer	60 ppm	3.82	4.73	5.23	5.70
	120 ppm	3.20	3.61	4.07	4.80
	180 ppm	2.91	3.11	3.45	4.01
	240 ppm	2.73	2.86	3.09	3.50
Terpolymer A (Isobutyl vinyl ether)	60 ppm	3.78	4.78	5.37	5.67
	120 ppm	3.13	3.58	4.21	4.75
	180 ppm	2.86	3.11	3.47	3.93
	240 ppm	2.70	2.86	3.08	3.39
Terpolymer B (Methyl Acrylate)	60 ppm	3.68	4.37	4.98	5.55
	120 ppm	3.12	3.44	3.85	4.48
	180 ppm	2.86	3.05	3.29	3.70
	240 ppm	2.70	2.83	2.99	3.25
Terpolymer C (Vinyl Acetate)	60 ppm	3.88	4.66	5.27	5.62
	120 ppm	3.28	3.62	4.11	4.60
	180 ppm	3.04	3.19	3.47	3.84
	240 ppm	2.80	2.96	3.14	3.40
Terpolymer D (Acrylic Acid)	60 ppm	4.03	5.27	5.41	5.82
	120 ppm	3.34	4.11	4.21	4.85
	180 ppm	3.06	3.45	3.53	4.06
	240 ppm	2.89	3.13	3.17	3.53

Table 1 (continued)

Calcium Sequestration at 60 ppm, 120 ppm, 180 ppm and 240 ppm Ca^{++}

Builder	ppm Ca^{++}	Treatment Level (g/l)**			
		0.1	0.2	0.3	0.4
Terpolymer	60 ppm	3.92	4.62	5.34	6.08
E (methyl	120 ppm	3.38	3.65	3.88	4.44
vinyl oxy-	180 ppm	3.12	3.29	3.40	3.77
acetate)*	240 ppm	2.95	3.07	3.14	3.37
Terpolymer	60 ppm	3.64	4.28	4.94	5.41
F (Itaconic	120 ppm	3.13	3.40	3.71	4.13
Acid)	180 ppm	2.89	3.07	3.24	3.45
	240 ppm	2.73	2.87	2.99	3.14
Terpolymer	60 ppm	3.72	4.57	4.77	5.43
G (Styrene)	120 ppm	3.16	3.54	3.81	4.65
	180 ppm	2.90	3.13	3.29	3.84
	240 ppm	2.74	2.89	3.01	3.34

* Methyl ester of the vinyl oxyacetate was not hydrolyzed during preparation of the sodium salt.
** Terpolymer G was in the anhydride form. All other terpolymers were in sodium salt form.

EXAMPLE 4

This example illustrates the preparation and detergency of household laundry detergent compositions employing the builders disclosed herein.

Detergent composition suitable for use as powdered household laundry detergent were prepared according to the following single active anionic formulations:

Anionic Surfactant Formulations

Component	% by Weight in Formulation				
Formula No:	1	2	3	4	5
Sodium Alkylbenzene Sulfonate(C13)	15	15	15	15	15
Sodium Carbonate	18	18	18	18	18
Sodium Silicate	20	20	20	20	20
Sodium Sulfate	47	17	27	27	27
Sodium Tripoly phosphate		30			
Sokalan CP-7			20		
[a]DIVEMA Copolymer				20	
[a]Terpolymer D (Acrylic Acid)					20

[a]Weight percentage of sodium salt of polymer.

Detergency evaluations were conducted in a Terg-o-tometer (U.S. Testing Company) employing detergency monitor cloths which are similar to the widely used detergency monitor cloths sold by Test Fabrics Company. Clay/Particulate type; Fatty/Particulate type; (Vacuum Cleaner Dust); and Fatty/Oily type cloths were used. Water hardness was adjusted to 60, 120 or 180 ppm polyvalent cations (calculated as calcium carbonate; 2:1 ratio of Ca^{++}: Mg^{++}). Water at the appropriate hardness was first added to the Terg-o-tometer beaker. The appropriate amounts of the detergent formulations were then added to make one liter of detergent solution having a total concentration of 1.5 gm/liter. Divinyl ether/maleic anhydride polymers were preneutralized with NaOH. After the test solution reached the desired wash temperature (40°C), the detergency monitor cloths were introduced (4-8 cloths per beaker) and the wash cycle begun (100 rpm). After washing 10 minutes, the cloths were rinsed for 1 minute, dried and their reflectances were recorded using a Gardener reflectometer (Model

Colorgard System 05). Using the reflectances of the clean, soiled and washed cloths, the % detergency was calculated according to the following relationship:

$$\% \text{ Detergency} = \frac{R_{washed} - R_{soiled}}{R_{clean} - R_{soiled}} \times 100$$

As the effectiveness of the detergent formulation improves, the percentage detergency increases.

The detergency results are given in Table II for clay soil cloths at three water hardnesses. It is clear from these results that DIVEMA copolymer and terpolymer provide substantial detergency building across all water hardnesses. They are similar in effectiveness to sodium tripolyphosphate (STP) as well as Sokalan CP-7.

Additionally, the results set forth in Table II demonstrate that the polymers of the present invention are effective when used in formulations containing calcium sensitive anionic surfactants.

Table II

Formula No.	Percentage Detergency 60 ppm[a]	120 ppm[a]	180 ppm[a]
1 Control (0%)	43.6	41.1	34.5
2 Sodium Tripolyphosphate (30%)	74.0	73.7	61.0
3 Sokolan CP-7 (20%)	67.7	64.7	53.7
4 DIVEMA Copolymer (20%)	64.3	59.4	49.7
5 Terpolymer D (Acrylic Acid) (20%)	63.6	59.6	49.3

[a]Polyvalent cations.

EXAMPLE 6

This example illustrates the preparation and detergency of household laundry detergent formulations employing divinyl ether/maleic anhydride polymers as co-builders and sodium citrate or zeolites as the primary builder.

Detergent compositions were prepared according to the following formulations:

Co-Builder Formulations

Component	% by Weight in Formulation					
Formula No:	5-1	5-2	5-3	5-4	5-5	5-6
Na Alkylbenzene Sulfonate (C13)	10	10	10	10	10	10
Na Alcohol Ethoxy (7EO) Sulfate	5	5	5	5	5	5
Sodium Carbonate	18	18	18	18	18	18
Sodium Silicate	3	3	3	3	3	3
Sodium Sulfate	54	49	45	44	39	39
Sodium Citrate	10	10	10			
4A Zeolite				20	20	20
[a] DIVEMA Copolymer		5			5	
[a] Terpolymer-D (Acrylic Acid)			5			5

[a] Weight percentage of sodium salt of polymer.

Detergency evaluations were conducted as in Example 4, except that Fatty/Particulate and Clay/Particulate cloths were employed in 120 ppm water hardness testing. Results are shown in Table IV.

Low levels of divinyl ether/maleic anhydride polymers produce improvements in detergency when employed as co-builders in detergent formulations containing sodium citrate or zeolite builder. Thus, they are useful as co-builders.

Table IV

Percentage Detergency

Formula No.	Clay/Particulate Soil[a]	Fatty/Particulate Soil[a]
5-1 (Sodium Citrate Control)	52.6	37.5
5-2[b]	60.0	40.4
5-3[b]	55.3	39.1
5-4	54.6	42.0
(Zeolite Control)		
5-5[b]	55.0	44.8
5-6[b]	55.3	44.7

[a] Cloths washed in 120 ppm water hardness

[b] Divinyl ether polymer builder.

EXAMPLE 7

This example illustrates the preparation and detergency of household laundry detergent compositions employing the anhydride form of divinyl ether/maleic anhydride polymers as builders.

Detergent compositions were prepared according to the following formulations:

Anhydride and Sodium Salt Formulations

Component	% by Weight in Formulation					
Formula No:	6-1	6-2	6-3	6-4	6-5	6-6
Na Alkyl Benzene Sulfonate (C13)	10	10	10	10	10	10
Sodium Carbonate	30	30	30	30	30	30
Sodium Silicate	20	20	20	20	20	20
Sodium Sulfate	35	30	9.8	9.3	14.5	14.1
Sodium Tripolyphosphate		30				
DIVEMA Copolymer (as Na Salt)					36.5	
(as Anhydride)			25.2			
Terpolymer D (Acrylic Acid)						
(as Na Salt)						36.9
(as Anhydride)				25.7		

Detergency evaluations were conducted by the method of Example 4, except that:

1) In formulations 6-3 and 6-4 the builder was used as a solid anhydride added directly to the wash water;

2) All washes were 14 minutes at 40°C 100 rpm and at a 2:1 ratio of Ca^{++}: Mg^{++} water hardness;

3) Fatty/Particulate and Clay/Particulate cloths were tested; and

4) The pH of the wash water was measured after 2 and 7 minutes.

Results are shown in Table V.

Table V

Percentage Detergency

Formula No.	pH 2 min.	pH 7 min.	Clay/Particulate Soil[a]	Fatty/Particulat Soil[a]
6-1 Control	10.1	10.1	42.8	41.0
6-2 Sodium Tripoly Phosphate	10.1	10.2	71.8	51.0
6-3[b,c]	9.1	9.1	66.2	47.4
6-4[b,c]	9.0	9.1	64.2	45.9
6-5[b]	10.2	10.2	66.5	49.3
6-6[b]	10.1	10.2	66.4	49.4

[a] Cloths washed in 120 ppm water hardners.
[b] Divinyl ether polymer builder.
[c] Anhydride form.

The results show that the anhydride form did not perform as well as the salt on Fatty/Particulate Soil cloth. However, this cloth is particularly sensitive to wash pH. The anhydride form lowers the pH of the wash as shown by pH data in Table V. It is expected that an increase in the alkali content of the detergent formulation would raise wash pH and improve anhydride detergency results on Fatty/Particulate Soil Cloth.

On Clay/Particulate Soil cloth, which is less sensitive to pH, the anhydride form performed as well as the salt. Thus, the divinyl ether/maleic anhydride polymers may be employed as a builder in powdered detergents in the salt or anhydride form.

EXAMPLE 8

This example illustrates the preparation and detergency of household laundry detergent compositions employing various divinyl ether/maleic anhydride terpolymers as builders. Additionally, this example illustrates the use of monoethanolamine, a common organic alkalinity control agent useful in the formulation of liquid detergents.

Detergent compositions were prepared according to the following formulations:

Formulations Containing Divinyl Ether/Maleic Anhydride Terpolymers

Component	% by Weight in Formulation				
Formula No:	7-1	7-2	7-3	7-4	7-5
Na Alkylbenzene Sulfonate (C11)	17	17	17	17	17
Neodol® 25-9	7	7	7	7	7
Monoethanolamine	2	2	2	2	2
Sodium Sulfate	49	49	49	49	74
Sodium Citrate	25				
[a]Terpolymer A (Isobutyl Vinyl Ether)		25			
[a]Terpolymer B (Methyl Acrylate)			25		
[a]Terpolymer C (Vinyl Acetate)				25	

[a] Weight percentage of sodium salt of polymer

Detergency evaluations were conducted as in Example 4, except that Clay/Particulate and Fatty/Particulate Soil cloths were washed at 120 ppm water hardness. Results are shown in Table VI.

Table VI

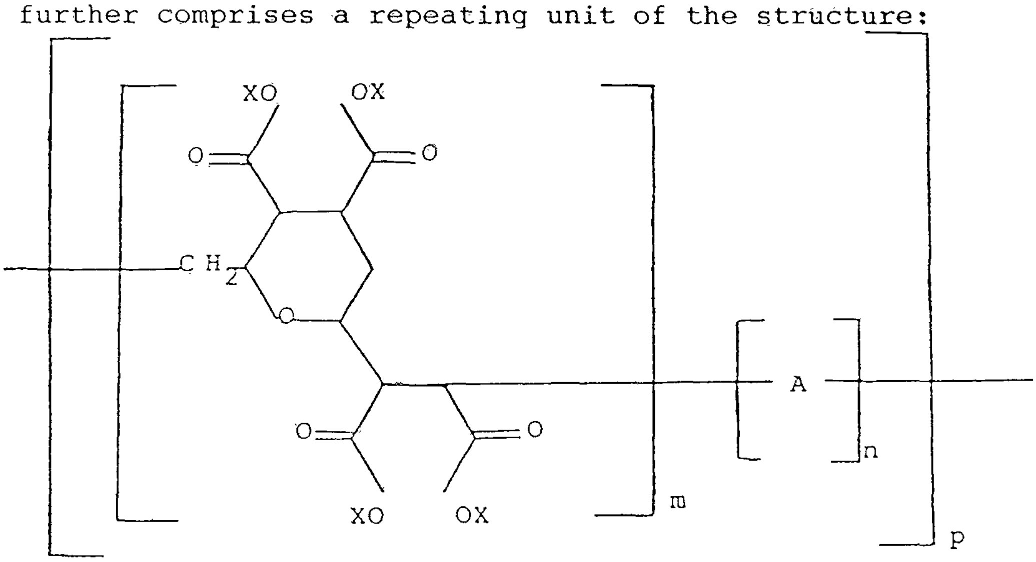
Formula No.	Percentage Detergency	
	Clay/Particulate Soil[a]	Fatty/Particulate Soil[a]
7-1	43.0	36.0
Sodium Citrate		
7-2[b]	58.0	42.1
7-3[b]	53.0	40.1
7-4[b]	52.8	39.5
7-5	37.2	33.5
Sodium Sulfate		

[a] Cloths washed in 120 ppm water hardness.
[b] Divinyl ether/maleic anhydride terpolymer builder.

The results show that divinyl ether/maleic anhydride terpolymers are effective detergent builders in detergent formulations. Furthermore, these builders are significantly more effective than sodium citrate which is a commonly used non-phosphate detergent builders.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A polymer of divinyl ether, maleic anhydride and at least one copolymerizable comonomer, selected from the group consisting of alkenyl alkyl ethers, alkyl acrylates, alkenyl carboxyalkyl ethers, vinyl esters of C_1 or C_3 or greater carboxylic acids, unsaturated carboxylic acids, unsaturated dicarboxylic acids and their esters, and olefins, and wherein the polymer further comprises a repeating unit of the structure:



wherein A is the comonomer(s); X is H, alkali metal ion, ammonium ion, hydroxyethylammonium ion, C_1-C_{12} alkyl, or C_5-C_{12} cycloalkyl, or a combination thereof; m and n are greater than 1; and p is from 5 to 4,000.

2. The polymer of Claim 1, wherein the number average molecular weight of the polymer in anhydride form is between 1,300 and 1,100,000.

3. A polymer, according to claim 1 or claim 2 wherein the polymer further comprises hydrolysis products of the polymer and sodium, potassium, ammonium, monoethanolamine or triethanolamine salts thereof.

4. A polymer, according to any one of claims 1 to 3 wherein the comonomer is selected from the group consisting of isobutyl vinyl ether, methyl acrylate, acrylic acid, itaconic acid, styrene, methyl vinyl oxyacetate and ester hydrolysis products of the methyl vinyl oxyacetate.

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NATIONAL STARCH AND CHEMICAL CORP
By Its Patent Attorneys:

GRIFFITH HACK & CO.
Fellows Institute of Patent
Attorneys of Australia.