

[54] **POLYMERS OF 1-BUTENE-2,3,4-TRICARBOXYLIC ACID**

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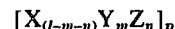
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[57] **ABSTRACT**

A water soluble salt of an aliphatic polycarboxylic acid useful as a detergent builder, and having the formula:



wherein each of m and n can be zero or a positive number, it being provided that the sum of m and n is always less than one; p is an integer the upper limit of which is determined by the solubility of the salts in an aqueous system; X is derived from the monomer 1-butene-2,3,4-tricarboxylic acid and Y and Z are each derived from a monoethylenically unsaturated monomer containing 1 to 3 substituents selected from the class consisting of carboxy, lower carboxyalkyl, lower alkyl, lower chloroalkyl, hydroxy, non-gem. dihydroxy, lower acyloxy, chloro, and lower alkoxy, it being provided that any one of the carboxy groups can be esterified with a lower aliphatic radical. Detergent compositions containing water soluble salts of the aliphatic polycarboxylic acid aforesaid are described.

6 Claims, No Drawings

POLYMERS OF 1-BUTENE-2,3,4-TRICARBOXYLIC ACID

BACKGROUND OF THE INVENTION

A. Field of the Invention

This invention relates to cleansing and laundering compositions. It is particularly concerned with such compositions containing a polyelectrolyte builder material which enhances the cleansing action of detergents.

B. Description of the Prior Art

In the cleansing art, it is known that the detergency level of soaps and synthetic surfactants can be increased by the use of certain materials commonly referred to as builders. Such cleansing fortifiers make possible the attainment of superior cleaning performance and at lower cost than can be realized with the so-called non-built detergent compositions.

The mechanism by which builders enhance the cleansing action of detergents is not fully understood, although, several explanations have been advanced. However, none of the theories thus far advocated enable one to predict accurately which class of compounds possesses usable builder properties and which compounds do not. In short, the built detergent art is still in the empirical stage.

The lack of any satisfactory theory concerning builder behavior may be explained, at least in part, by the complex nature of detergency and the countless factors which contribute to overall performance. It is generally agreed that builder compounds exhibit at least some effect in such areas as stabilization of solid soil suspension, emulsification of soil particles, the surface activity of aqueous detergent solutions, solubilization of water-insoluble materials, foaming or suds-producing characteristics of the washing solution, peptization of soil agglomerates, neutralization of acid soil, and the inactivation of mineral constituents present in the washing solution. Thus, any theoretical discussion of the boosting capacity of a builder compound should give due consideration to all the significant individual actions involved in the detergent process and must apply equally to all the usual conditions of soiling and washing.

Builder materials should exhibit certain ancillary properties in order to be acceptable in current washing processes and consumer marketing techniques. Thus, a builder should preferably be white, inexpensive, non-toxic, stable to oxidizers in the dry state, non-corrosive, non-hygroscopic, stable to hot alkaline detergent solutions and stable during spray drying operations.

Examples of known inorganic builder materials are the water-soluble, inorganic alkaline builder salts which can be used alone or in combination, including alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates.

Examples of known organic builder materials are alkali metal, ammonium or substituted ammonium aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N(2-hydroxyethyl)-ethylenediaminetriacetate, sodium and potassium and triethanolammonium - N - (2-hydroxyethyl) nitrilodiacetate. Alkali metal salts of phytic acid, e.g., sodium phytate, are also suitable as organic builders.

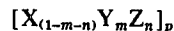
Although the condensed inorganic polyphosphates find the widest commercial acceptance, these exhibit the undesirable property of hydrolyzing into less condensed phosphorus compounds which are essentially devoid of builder properties. Moreover, these hydrolytic derivatives often form undesirable precipitates in aqueous washing solutions. Such lower forms include orthophosphate.

Recently, a great deal of interest has focused on the polyelectrolyte builder materials which are highly polar polymers such as the water-soluble salts of aliphatic polycarboxylic acids. Examples of these classes of builders are disclosed in U.S. Pat. No. 3,308,067 to Diehl and U.S. Pat. No. 3,463,734 to Carter Jr. et al. These new types of builders do not hydrolyze into undesirable by-products.

Manifestly, the detergent and cleansing industry is still actively searching for more effective builder materials and accordingly work is proceeding apace toward uncovering new and more effective classes of these valuable entities.

SUMMARY OF THE INVENTION

It has now been discovered that excellent builder properties are exhibited by a novel class of aliphatic polycarboxylic acids of the formula



wherein each of m and n can be zero or a positive number, it being provided that the sum of m and n is always less than one; p is an integer the upper limit of which is determined by the solubility of the salts in an aqueous system; X is derived from the monomer 1-butene-2,3,4-tricarboxylic acid and Y and Z are each derived from a monoethylenically unsaturated monomer containing 1 to 3 substituents selected from the class consisting of carboxy, lower carboxyalkyl, lower alkyl, lower chloroalkyl, hydroxy, non-gem. dihydroxy, lower acyloxy, chloro, and lower alkoxy, it being provided that any one of the carboxy groups can be esterified with a lower aliphatic radical. The provision of the novel builders, aforesaid including the preparation and their use in cleansing compositions, constitutes the principal objects and purpose of the invention. Other objects and purposes will become apparent.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

As can be seen from an inspection of the formula aforesaid, the polymeric builder compounds of the invention are polymers of 1-butene-2,3,4-tricarboxylic acid or copolymers thereof with 1 or 2 monoethylenically unsaturated monomers. The polymerization is carried out in the manner of preforming ethylenic polymerizations, details of which are given below. Generally speaking, such polymerization is effected under free radical producing conditions, commonly provided by the use of peroxides such as alkali metal persulfates or an organic peroxide such as benzoyl peroxide. The polymerization may be solution polymerization or emulsion polymerization depending on the solubility of the monomer starting materials. In some instances bulk polymerization is preferred.

In the case of copolymers, the ratio of 1-butene-2,3,4-tricarboxylic acid with other ethylenic monomers is governed by the requirement that the copolymer must form water soluble salts or at least be soluble in the cleansing composition. Accordingly, the copolymer must contain solubilizing groups. These are preferably carboxy groups which can come solely from the 1-butene-2,3,4-tricarboxylic acid or from a combination of the latter with at least one of the ethylenic units. There is a tendency toward insolubility when the number of non-carboxy containing units greatly exceeds the carboxy containing units. The minimal percent of carboxy carrying groups needed for water solubility will vary to some extent depending upon the polar character of the substituents attached to the ethylenic units. Thus, where the latter contain other hydrophilic groups, the desired water solubility can be realized with a relatively small percentage of carboxy groups in the copolymer whereas more carboxy groups will be needed if the associated ethylenic groups carry non-polar substituents such as alkyl radicals. Those skilled in the art will generally be able to adjust the ratio of monomer units to achieve the desired solubility.

Typical of the polymeric compounds described herein are the following: homopolymer of 1-butene-2,3,4-tricarboxylic acid; 1:1, 1:2, and 2:1 copolymers of 1-butene-2,3,4-tricarboxylic acid and itaconic acid; 1:1, 1:2, and 2:1 copolymers of 1-butene-2,3,4-tricarboxylic acid and methacrylic acid; 1:1, 1:2, and 2:1 copolymers of 1-butene-2,3,4-tricarboxylic acid and acrylic acid; 1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid and maleic acid; 1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid and vinyl acetate; 1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid and vinyl alcohol; 5:2 copolymer of 1-butene-2,3,4-tricarboxylic acid and methyl vinyl ether; 1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid and vinyl chloride; 1:1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid, itaconic acid and acrylic acid; 1:1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid, maleic acid and acrylic acid; and 1:1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid, itaconic acid and maleic acid; wherein the ratios mentioned are molar ratios.

Preferred compounds are 1:1:1 copolymer of 1-butene-2,3,4-tricarboxylic acid, itaconic acid, and acrylic acid; 1:1, 1:2, and 2:1 copolymers of 1-butene-2,3,4-tricarboxylic acid and itaconic acid; 1:1, 1:2, and 2:1 copolymers of 1-butene-2,3,4-tricarboxylic acid and acrylic acid.

The structural features of the operable and preferred polymers and copolymers have, as a matter of convenience, been defined herein in terms of the carboxylic-acid containing monomers from which such polymers and copolymers theoretically can be derived. It is recognized, however, that in many cases it is desirable or even preferable to form such polymers and copolymers in practice by employing derivatives or precursors of such carboxylic-acid-containing monomers in the polymerizations leading to the desired polymers and copolymers. Thus, the monomeric species employed, can in many cases, be such derivatives or precursors of the designated acids as the anhydrides, the full or partial esters of such acids, amides, nitriles, etc., or mixtures of same, which after polymerization can be converted to the carboxylate salts by appropriate chemical reactions.

The degree of polymerization, p , of the novel polyelectrolyte builder compounds of this invention has a significant and practical bearing on the builder effectiveness of these compounds. The lower limit for p has been established as three resulting in compounds having a molecular weight on the order of not less than about 350. Builder properties of the compounds of this invention drop off substantially as the molecular weight goes below 350.

It is somewhat more difficult to establish an absolute value for an upper limit of the degree of polymerization above which the polyelectrolyte builder compounds no longer function as efficient builders. The fact is that practical considerations appear to be the primary determining factor as the degree of polymerization increases. For instance, as the molecular weight of a polymeric material increases, it is generally acknowledged that the water solubility thereof decreases. In general, the present invention that the polyelectrolyte builder compounds must be adequately soluble in the washing solution under regular usage conditions.

Recommended builder concentrations generally range from about 0.01 percent to about 0.50 percent by weight of the washing solution. The upper operable limit, therefore, so far as the scope of this invention is concerned, is reached when it is no longer possible to get enough of the builder compound into solution to act as a builder.

The higher builder concentrations on the order of 0.50 percent by weight may be found necessary under certain washing conditions such as a water hardness of 21 grains equivalent CaCO_3 per gallon or higher. In such situations, any of the polyelectrolyte builder compounds of this invention could be selected whose solubility characteristics would allow a builder concentration in an aqueous solution to the necessary amount. In more general household situations, builder concentrations of 0.03 percent to about 0.06 percent are found to be adequate.

It can be appreciated, according to the preceding discussion, that the degree of polymerization of these compounds can vary within a very wide range. Generally, however, the degree of polymerization, p , can be within the ranges of 3 to about 5,000. This corresponds to a molecular weight range for the compounds of this invention from 350 to about 1,500,000. A preferred range for the degree of polymerization, p , is from about 4 to about 500. This represents a preferred molecular weight range for the polyelectrolyte builder compounds of this invention of about 500 to about 175,000.

It is difficult to accurately determine molecular weights of polymeric compounds. Such figures will generally very depending upon the method used to determine them. It is widely recognized, for instance, that any molecular weights of polymeric materials which are given by manufactures constitute an average of the molecular weights of the molecules present. Moreover, molecular weight ranges are usually given which vary widely depending again upon the method used to measure the molecular weights. Among the several methods frequently used to measure molecular weights of polymeric compounds are osmometry, molecular weight determination by end-group analysis, cryoscopy, ebullioscopy, light-scattering, gel permea-

tion chromatography, and ultracentrifuge. Each of these methods are presently in varying degrees of development and each one has special types of polymeric compounds to which it is best adapted.

The minimum molecular weight of 350 mentioned above was arrived at empirically and, to a great extent, is based on the knowledge and experience acquired from working with these polyelectrolytic polycarboxylic polymers.

Viscosity is a property more frequently used by polymer chemists than molecular weights in characterizing polymeric compounds. This is no doubt due to the comparatively easier and less complicated methods available for obtaining viscosity data. To make such data meaningful, it is necessary to also give the test conditions under which the measurements were run. Since there is a recognized correlation between the viscosity of polymeric compounds and their molecular weights and since such figures can be more meaningful and can frequently be more available than molecular weights, the polymeric builder compounds used in the examples of this invention are characterized in terms of specific viscosity. In all cases the viscosity characterization corresponds to a molecular weight substantially above 350.

According to this invention extraordinary cleaning results can be obtained by using the above polyelectrolyte builder compounds with a wide range of surface active materials and mixtures thereof. The builder compounds are effective when used alone or in admixture with other known builders.

In general, the detergent compositions of this invention, the essential ingredients are (a) an organic water soluble detergent surface active material as defined and illustrated below and (b) a novel polyelectrolyte builder compound meeting the structural requirements specified and exemplified above. The detergent compositions of this invention, therefore, contain the essential ingredients in a ratio of polyelectrolyte builder to detergent surfactant in the range of about 1:3 to about 10:1 by weight, with such compositions providing in aqueous solution a pH of about 8 to about 12. The preferred ratio of polyelectrolyte builder to detergent surfactant is about 1:2 to about 5:1 and the optimum pH range is 9.5 to about 11.5.

The organic detergent compounds, i.e. surface active agents, which can be utilized in the compositions of this invention are anionic, nonionic, ampholytic and zwitterionic synthetic detergents and mixtures thereof and are exemplified as follows:

A. Anionic synthetic non-soap detergents can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about eight to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of the synthetic detergents are the sodium or potassium alkyl sulfates, sodium or potassium alkylbenzenesulfonates, in which the alkyl group contains from about nine to about 15 carbon atoms (the alkyl radical can be a straight or branched aliphatic chain); alkyl (glycerylsulfate) ether; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts or sulfuric acid esters of the

reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide, sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from eight to about 12 carbon atoms; the reaction product of fatty acids esterified with isothionic acid and neutralized with sodium hydroxide, sodium or potassium salts of fatty acid amide of a methyl tauride, and sulfonated olefins.

b. Nonionic synthetic detergents: One class can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Another class has semi-polar characteristics. Preferred classes of nonionic synthetic detergents are as follows:

1. A class of nonionic synthetic detergents under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol;
2. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about six to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide;
3. Those nonionic synthetic detergents derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine;
4. The condensation product of aliphatic alcohols having from eight to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide;
5. The ammonia, monoethanol and diethanol amides of fatty acids having an acyl moiety of from about eight to about 18 carbon atoms;
6. Long chain tertiary amine oxides such as dimethyldodecylamine oxide; cetyldimethylamine oxide; bis-(2-hydroxyethyl)-dodecylamine oxide; bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide;
7. Long chain tertiary phosphine oxides such as dimethyldodecylphosphine oxide; diethyldodecylphosphine oxide; dimethyl-, (2-hydroxydodecyl) phosphine oxide;
8. Long chain sulfoxides such as dodecyl methyl sulfoxide; 3-hydroxytridecyl methyl sulfoxide; 3-methoxytridecyl methyl sulfoxide; 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

c. Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about eight to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphate, or phosphono. Examples of compounds falling within

this definition are sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropanesulfonate.

d. Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about eight to 18 carbon atoms and one contains an anionic water solubilizing group; e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-1-hydroxy propane-1-sulfonate.

In the novel detergent formulations of this invention, the weight ratio of surface active agent to builder ranges from about 3:1 to 1:10. These two ingredients generally represent at least about 45 percent of the total detergent formulation.

It should be noted that the novel builders herein are used either in the form of their alkali metal salts or in acid-form together with a sufficient quantity of an alkali metal base, such as the carbonate or hydroxide, in order to neutralize the carboxyl group and adjust the pH level of the final detergent solution to within the desired 9.5-11.5 range.

The formulations may also contain minor amounts of optional additives in order to modify certain properties thereof. Among such optional additives are included: foam builders and stabilizers, antiredeposition agents such as sodium carboxymethylcellulose, corrosion inhibitors such as benzotriazole, optical brighteners, bactericides, perfumes, bleaches, enzymes, dyes, blueing agents, inorganic salts, solvents and the like. These total optional ingredients commonly range from about 30 percent to about 55 percent, by weight of the formulation.

Methods for preparing detergent formulations are well known to those skilled in the art, a typical method involving drying the ingredients, forming them into an aqueous slurry and then spray drying. The final detergent formulations may be a mixture of dry ingredients, a concentrated aqueous solution or a solid mix resulting from the drying thereof, or a combination of dry solids and dry ingredients as is common in the art.

The following examples will further illustrate the embodiment of this invention. In these examples, all parts given are by weight unless otherwise noted.

EXAMPLE 1

1-Butene-2,3,4-tricarboxylic Acid-Itaconic Acid-Acrylic Acid (1:1:1) Copolymer

A solution of 1-butene-2,3,4-tricarboxylic acid (4.7 g), itaconic acid (3.25 g), and acrylic acid (1.8 g) in freshly distilled water (20 ml) was placed in 50 ml polymerization bottle fitted with a rubber septum. A solution of potassium persulfate (0.08 g) in water (4 ml) was injected through the rubber septum, and the aqueous mixture degassed by repeated freezing and evacuation. Then a solution of sodium metabisulfite (0.04 g) in water (4 ml) was injected. The bottle was warmed to room temperature, filled with nitrogen and the contents stirred until a clear solution resulted (5 days). The solution was concentrated to half its original volume in vacuo and the polymer precipitated by pour-

ing the concentrated solutions into acetone (1 liter). The white precipitate was filtered and washed five times with 20 ml portions of warm acetone and then dried at 65°/0.1 mm for 2 hr. Yield: 6 g.

EMULSION POLYMERIZATION

This procedure was used for home- and copolymerizing water insoluble oils, i.e., esters of alkenepolycarboxylic acids. An emulsifier solution was first prepared by mixing the following:

Santomerse-3 (65% active, Monsanto)	20 g
Brij-35 (100 % active, Atlas Chemicals)	15 g
Dupanol ME (100 % active, duPont)	25 g
Cellosize WP-4400 (Union Carbide)	2.4 g
Distilled Water	500 ml

The ester of the unsaturated alkenepolycarboxylic acid or a mixture of it with other oily water insoluble vinylic monomer was emulsified in about the same volume of the emulsifier solution. Then about 0.15 times the total volume of emulsion of 2.8 percent aqueous potassium persulfate was added as an initiator along with, if desired, an equal volume of 2.8 percent sodium metabisulfite solution. The pH of the solution was then adjusted to 3-5 by adding 5 percent sodium bicarbonate solution. The mixture was charged into a polymerization bottle fitted with a rubber septum, degassed as described under Example 1 and shaken for 24-150 hr., when a waxy lump of solid had formed. The solid lump was removed, washed successively with water and then dried at 65°/0.1 mm.

The following example is illustrative.

EXAMPLE 2

Homopoly(Trimethyl 1-Butene-2,3,4-tricarboxylate)

Trimethyl 1-butene-2,3,4-tricarboxylate (7.7 g), emulsifier solution (6.5 ml), 2.8 percent potassium persulfate solution (1.9 ml), 2.8 percent sodium metabisulfite solution (1.9 ml), and 5 percent sodium bicarbonate solution (0.4 ml) were charged, in the above order, into a polymerization bottle. The bottle was closed with a rubber septum and the contents degassed by repeating freezing and evacuation as described before. The bottle was mechanically shaken for six days and the white waxy solid that had separated was washed repeatedly with water and dried at 65°/0.1 mm; yield, 6 g.

Solution Polymerization in Organic Solvents

The material or materials to be polymerized along with a chain transfer agent such as lauryl mercaptan, if required, was dissolved in 2-4 times the volume of benzene, toluene, xylene, or dioxan, and heated to reflux in an atmosphere of nitrogen. A solution of the catalyst (usually benzoyl peroxide) in the same solvent was then added dropwise to the reaction medium. The boiling was continued until the polymer separated as an insoluble material (1-5 hr.). It was washed repeatedly with the same solvent and dried at 65°/0.1 mm. The following preparation will serve as an example.

EXAMPLE 3

Copoly(Trimethyl 1-Butene-2,3,4-tricarboxylate-Itaconic Anhydride) (1:1)

A solution of trimethyl 1-butene-2,3,4-tricarboxylate (11.5 g) and itaconic anhydride (5.6 g) in dry benzene

(60 ml) was heated to boiling under reflux in an atmosphere of nitrogen. A solution of benzoyl peroxide (0.8 g) in benzene (30 ml) was added in three equal installments at 1 hr. intervals. After a total of 4 hr. boiling, the polymer that had separated was removed from the solution, washed five times with warm benzene and dried at 65°/0.1 mm; yield, 8 g.

Bulk Polymerization

This procedure was applicable to the esters or anhydrides of the monomeric acids. The material or mixture of materials to be polymerized was intimately mixed with the initiating catalyst and taken in a thick round bottomed flask containing a stirring magnet. The flask was closed with a rubber septum and its charge degassed using similar procedure as described under Example 1. The flask was then heated at the desired temperature with magnetic stirring until a considerable rise in viscosity occurred and the stirrer stopped. The unreacted monomers were then removed under a pressure of 0.1 mm up to a temperature of 180°. In an alternative procedure, used when one of the monomers was highly volatile, instead of a round bottomed flask closed with a rubber septum, a thick walled sealed tube protected with a steel sleeve was used. The latter was heated in a bomb furnace with mechanical shaking. The following examples will serve to illustrate the procedures.

EXAMPLE 4

Homopoly(Trimethyl 1-Butene-2,3,4-Tricarboxylate)

A mixture of trimethyl 1-butene-2,3,4-tricarboxylate (4.6 g) and acetyl peroxide (1 ml of a 25 percent solution in dimethyl phthalate) was placed in a 50 ml round bottomed flask fitted with a rubber septum, degassed as described under Example 1. The flask was heated at 50° until a highly viscous material was obtained (24 hr.). The rubber septum was replaced by an adapted tube and the latter connected through a dry-ice trap to a vacuum pump. The flask was then heated to 180° with stirring and the low boiling fractions removed under a pressure of 0.1 mm. At room temperature residual mass was a tough plastic glass; Yield 3 g.

EXAMPLE 5

Copoly(Trimethyl 1-Butene-2,3,4-Tricarboxylate - Methyl Vinyl Ether)

A mixture of trimethyl 1-butene-2,3,4-tricarboxylate (11.5 g), liquified methyl vinyl ether (1.2 g), and finely powdered benzoyl peroxide (0.2 g) was placed in a thick walled glass tube cooled in dry-ice. The tube was sealed in vacuo, placed inside a steel sleeve and heated for 24 hr. at 100° in a bomb furnace. The highly viscous material that resulted was transferred to a distillation flask with the help of benzene and the low boiling fractions removed at 180°/0.1 mm. The yield was quantitative.

HYDROLYSIS

The esters of the polymeric alkenepolycarboxylic acids were hydrolyzed by boiling their solutions in a minimum quantity of acetone-water-concentrated hydrochloric acid (=2:1:1) mixture under reflux for 2-6 hr. The solvents were then removed under reduced

pressure, the residue dissolved in water, the solution filtered to remove any insoluble material and evaporated to dryness in vacuo. The residue was washed with acetone and dried at 65°/0.1 mm. The following is a typical example.

EXAMPLE 6

Hydrolysis of Copoly(Trimethyl 1-butene-2,3,4-tricarboxylate-Methyl Vinyl Ether)

Copoly(trimethyl 1-butene-2,3,4-tricarboxylate-methyl vinyl ether) (10.5 g) was dissolved in acetone (50 ml), a mixture of concentrated hydrochloric acid (25 ml) and water (25 ml) added and the resulting solution boiled for 6 hr. The solvents were then removed under a current of nitrogen by application of suction at 80°, the residue dissolved in water, filtered after addition of a small amount of filter aid to remove turbidity and dried in vacuo. The copoly(1-butene-2,3,4-tricarboxylic acid-methyl vinyl ether) weighed 7.5 g after a final drying at 65°/0.1 mm.

EXAMPLE 7

1-Butene-2,3,4-tricarboxylic Acid and Itaconic Acid (1:1) Copolymer

Trimethyl 1-butene-2,3,4-tricarboxylate was copolymerized with itaconic anhydride as described in Example 3. A suspension of 1 g of this polymer in 100 ml of 5 percent aqueous hydrochloric acid was stirred at 80° until a clear solution resulted (12 hr.). The solution was evaporated to dryness under reduced pressure and the residual white solid washed with acetone and dried at 65°/0.1 mm. Yield: 0.7 g of the title compound.

EXAMPLE 8

1-Butene-2,3,4-tricarboxylic Acid-Itaconic Acid (1:1) Copolymer

A solution of 1-butene-2,3,4-tricarboxylic acid (9.4 g), itaconic acid (6.5 g), in freshly distilled water (50 ml), was placed together with a solution of potassium persulfate (0.16 g) in water (8 ml) in a 100 ml polymerization bottle fitted with a rubber septum. The aqueous mixture was degassed by repeated freezing and evacuation, and a solution of sodium metabisulfite (0.08 g) in water (8 ml) introduced through a hypodermic syringe. The bottle was warmed to room temperature, filled with nitrogen and the contents stirred until a clear solution resulted (seven days). The solution was concentrated to half its original volume in vacuo and the polymer precipitated by pouring the solution into acetone (1 liter). The white precipitate was filtered and washed several times with acetone and then dried at 65°/0.1 mm for 3 hr. Yield: 11 g.

EXAMPLE 9

Preparation of Sodium Salts of Polymeric Alkenepolycarboxylic Acids

The sodium salts for builder evaluation of the polymeric alkenepolycarboxylic acids were prepared by neutralizing a saturated aqueous solution of the poly-acid with 30 percent aqueous sodium hydroxide until a pH of 9.5 was reached. The solution was then concentrated to half the original volume and poured into a large quantity of acetone to precipitate the sodium salt. The salt was filtered and dried at 65°/0.1 mm.

EXAMPLE 10

Preparation of Methyl Esters of Polymeric Alkenepolycarboxylic Acids

Small quantities of the polymeric alkenepolycarboxylic acids were methylated (for determination of number average molecular weight) by treating either their solutions in tetrahydrofuran or suspensions in benzene with ethereal diazomethane, until the yellow color of the diazomethane persisted for at least 5 hr. The solvents were then removed and the residual solid washed with small amounts of ether and dried at 65°/0.1 mm.

DETERGENT FORMULATION

This example illustrates typical detergent formulations of this invention as well as the excellent laundering properties exhibited by these products.

The general detergent formulation which was utilized in this example is as follows:

Sodium linear alkylarenesulfonate	Parts
	20.0
Builder	50.0 (or 25)
Sodium metasilicate 5-hydrate	12.0
Sodium carboxymethylcellulose	0.5
Sodium sulfate	17.5 (or 42.5)

In each instance the formulation was prepared by merely blending the various ingredients.

A variety of the novel builders were respectively substituted into the detergent formulation. In order to determine the performance characteristics of the resulting detergent formulations, they were subjected to the following test procedures.

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TABLE I

Builder; examples	Percent builder in formulated detergent	Water hardness ^a (in p.p.m.)	Detergency—percent of standard				Redeposition—Δ reflectance units			
			Cotton	Cotton-dacron 50:50	Cotton-dacron 35:65	Nylon	Cotton	Cotton-dacron 50:50	Cotton-dacron 35:65	Nylon
(11) Sodium salt of 1:1:1 copoly BTCA-AA-IA	50	300	101	93	98	104	1.1	4.3	6.3	6.1
(12) Sodium salt of homopoly BTCA	50	300	79	80	78	70	0.7	4.6	6.0	11.6
(13) Sodium salt of 5:2 copoly BTCA-MVE ^b	50	300	78	77	80	70	1.8	4.4	5.0	11.2
(14) Sodium salt of 2:1 copoly BTCA-MAA ^c	50	300	82	84	86	75	1.2	2.3	1.1	3.8
(15) Sodium salt of 1:1 copoly BTCA-MAA ^c	50	300	82	84	84	74	1.1	2.1	2.4	11.6
(16) Sodium salt of 1:1:1 copoly BTCA-MA-AA	50	300	87	85	87	84	0.9	2.2	1.7	2.9
(17) Sodium salt of 2:1 copoly BTCA-AA	25	150	98	82	86	92	1.5	10.0	9.0	7.8
(18) Sodium salt of 1:1 copoly BTCA-IA	50	300	97	93	95	97	0.8	3.1	6.3	3.3
(19) Sodium salt of 1:1 copoly BTCA-IA	25	150	103	74	77	91	1.1	16.7	18.9	8.3
Comparison data:										
STPP	50	300	83	75	70	73	2	14.1	19.1	16.4
STPP	25	150	79	68		50				

^a Hardness of washing water.

^b Not corrected for water (10% w./w.) present in builder.

^c Not corrected for water (17% w./w.) present in builder.

BTCA=1-butene-2,3,4-tricarboxylic acid; AA=acrylic acid; IA=ita conic acid; MAA=methacrylic acid; MVE=methyl vinyl ether; STPP=sodium tripolyphosphate.

DETERGENCY TEST

A full description of this detergency test may be found in the article by Spangler et al., Journal of the American Oil Chemists Society, 42, 723 (1965).

The test was conducted in a Terg-O-Tometer utilizing swatches of four different fabrics — cotton, cotton-dacron (50:50), cotton-dacron (35:65), and nylon — which has been soiled with a combination of airborne particulate matter and synthetic sebum. Three soil-wash cycles were conducted on each fabric utilizing the following test conditions: water hardness of 150 ppm and 300 ppm, respectively, with a Ca/Mg ion ratio of 1.5; detergent formulation concentration of 0.15 percent; temperature of 120°F.; and a pH level of 9.5; washing time 10 minutes; rinsing time 2 minutes.

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Reflectance readings on the washed swatches were then taken from a Hunter Reflectometer, Model D-10. The results were expressed in terms of "percent reflectance" with the arbitrary standard of "100 percent reflectance" being established for the reflectance value obtained on a cotton swatch which had been washed with the standard detergent formulation containing 50 percent sodium tripolyphosphate builder in water of 150 ppm hardness.

REDEPOSITION TEST

The basic functions of a detergent solution may be conveniently divided into two distinct operations. First, removal of soil from the substrate and suspension thereof in the detergent solution, and second, prevention of redeposition of the suspended soil. Redeposited soil is more tenaciously held on the fabric surface and is difficult to remove by subsequent washings. As a result a built detergent formulation which causes considerable redeposition may still wash fabrics brighter in the first few washings but gradually impart a permanent yellow or grey cast on the fabric. The redeposition test is intended to show the ability of the detergent formulation to prevent redeposition of soil during the wash as well as the rinse cycle. The redeposition data are decreases in reflectance (ΔR) of unsoiled swatches when washed with standard soiled swatches. In the test procedure, one unsoiled swatch and three soiled swatches of each fabric type are washed three times in a Terg-O-Tometer using freshly soiled swatches each cycle. Conditions are otherwise the same as those used in the Detergency Test. The detergency test results are summarized in Table I below.

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The results presented in Table I clearly indicate the effective laundering characteristics exhibited by detergent formulations containing our novel builders.

It should be noted that comparable performance results may be obtained by replacing the sodium linear alkylarenesulfonate in the above detergent formulation with any of the other surface active agents previously listed.

SEQUESTERING CAPACITY

Since the ability to sequester calcium ions is a critical feature of an effective detergent builder, the various new builders were subjected to the following test procedures in order to determine their sequestering capacity. Thus, an aqueous solution of the sample was

titrated potentiometrically with a standard calcium nitrate solution at a pH of 10.0 and a temperature of 25°C. using a divalent cation activity electrode (Orion Research, Inc.) as the indicator electrode.

The sequestering capacity was expressed as
Ca g/100 g = (4.008 . M . V)/W

where

M = molarity of the calcium nitrate solution

V = volume of the above solution required to reach the inflexion point, and

W = weight of the sample

Each of the builders tested was prepared according to the procedures set forth in Examples 1 to 9, herein above. The preparative procedures and sequestering capacity of some of these builders are presented in the following table:

TABLE II

Homo- and copolymers of 1-butene-2,3,4-tricarboxylic acid and their calcium sequestering capacities

Example	Name	Prepared from (monomers)	Preparative procedure (solvent, catalyst, temperature and time)	Sequestering capacity Ca, g./100 g.
20	Poly BTCA	TMBTC	Bulk polymerization (—, Ac ₂ O ₂ , 50°, 24 hr.) and hydrolysis	15
21	Copoly BTCA-IA (1:1)	BTCA and IA	Solution polymerization (water, K ₂ S ₂ O ₈ —Na ₂ S ₂ O ₈ , 26°, 7 days)	22.2
22	Copoly BTCA-IA (1:1)	TMBTC and IAn	Solution polymerization (benzene, Bz ₂ O ₂ , reflux, 4 hr.) and hydrolysis	18.0
23	Copoly BTCA-AA (2:1)	BTCA and AA	Solution polymerization (water, K ₂ S ₂ O ₈ , 26°, 7 days)	22.2
24	Copoly BTCA-AA (2:1)	BTCA and AA	Solution polymerization (xylene, Bz ₂ O ₂ , reflux, 5 hr.)	11.7
25	Copoly BTCA-AA (1:1)	BTCA and AA	Solution polymerization (water, K ₂ S ₂ O ₈ , 26°, 5 days)	18.4
26	Copoly BTCA-AA (1:1)	BTCA and AA	Solution polymerization (water, K ₂ S ₂ O ₈ , 70°, 5 days)	12.6
27	Copoly BTCA-MAA (1:1)	BTCA and MAA	Solution polymerization (water, K ₂ S ₂ O ₈ , 26°, 3 days)	†10.6
28	Copoly BTCA-MAA (2:1)	BTCA and MAA	Solution polymerization (water, K ₂ S ₂ O ₈ , 26°, 3 days)	13.5
29	Copoly BTCA-MA (1:1)	BTCA and MAN	Solution polymerization (xylene, Bz ₂ O ₂ , reflux, 3 hr.) and hydrolysis	8.8
30	Copoly BTCA-MVE (6:2)	TMBTC and MVE	Bulk polymerization (—, Bz ₂ O ₂ , 100°, 24 hr.) and hydrolysis	8.0
31	Copoly BTCA-VA	TMBTC and VAe	Bulk polymerization (—, Bz ₂ O ₂ , 60°, 16 hr.) and hydrolysis	7.0
32	Copoly BTCA-AA-IA (1:1:1)	BTCA AA and IA	Solution polymerization (water, K ₂ S ₂ O ₈ , 26°, 5 days)	†23
33	Copoly BTCA-AA-MA (1:1:1)	TMBTC AA and MAN	Solution polymerization (benzene, Bz ₂ O ₂ , reflux, 12 hr.)	13

†Determined on sodium salt.
Bz₂O₂=Benzoyl peroxide; Ac₂O₂=acetyl peroxide; AA=acrylic acid; BTCA=1-butene-2,3,4-tricarboxylic acid; IA=itaconic acid; IAn=ita-

conic anhydride; MA=maleic acid; MAA=methacrylic acid; MAN= maleic anhydride; MVE=methyl vinyl ether; TMBTC=trimethyl 1-butene-2,3,4-tricarboxylate; VAe=vinyl acetate; VAl=vinyl alcohol.

These results clearly indicate the ability of the builders of the invention to effectively sequester calcium ions. The results are especially noteworthy when compared with the 10.90 g. Ca/100 g. sequestering value for the sodium tripolyphosphate, the standard in the builder field.

Summarizing, it is seen that this invention provides effective detergent formulations utilizing the novel builders therein.

Variations may be made in proportions, procedures and materials without departing from the scope of the invention as defined by the following claims.

What is claimed is:

1. A aliphatic polycarboxylic acid polymer exhibiting detergent builder properties selected from the class consisting of: 1-butene-2,3,4-tricarboxylic acid-itaconic acid-acrylic acid (1:1:1) copolymer; copoly(1-butene-2,3,4-tricarboxylic acid - itaconic acid) (1:1) or (2:1) or (1:2); copoly(1-butene-2,3,4-tricarboxylic acid-maleic acid) (1:1); copoly(1-butene-2,3,4-tricarboxylic acid-maleic acid - acrylic acid) (1:1:1) and copoly(1-butene-2,3,4-tricarboxylic acid-itaconic acid - maleic acid) (1:1:1).

2. An aliphatic polycarboxylic acid according to claim 1 having the name, 1-butene-2,3,4-tricarboxylic acid-itaconic acid-acrylic acid (1:1:1) copolymer.

3. An aliphatic polycarboxylic acid according to claim 1 having the name, copoly(1-butene-2,3,4-tricar-

boxylic acid - itaconic acid) (1:1) or (2:1) or (1:2).

4. An aliphatic polycarboxylic acid according to claim 1 having the name, copoly(1-butene-2,3,4-tricarboxylic acid-maleic acid) (1:1).

5. An aliphatic polycarboxylic acid according to claim 1 having the name, copoly(1-butene-2,3,4-tricarboxylic acid-maleic acid - acrylic acid)(1:1:1).

6. An aliphatic polycarboxylic acid according to claim 1 having the name, copoly(1-butene-2,3,4-tricarboxylic acid-itaconic acid - maleic acid) (1:1:1).

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,717,616 Dated February 20, 1973

Inventor(s) Paritosh M. Chakrabarti et al

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

The title "POLYMERS OF 1-BUTENE-2,3,4-TRICARBOXYLIC ACID" should read --POLYMERS OF 1-BUTENE-2,3,4-TRICARBOXYLIC ACID AND THEIR USE AS DETERGENT BUILDERS--.

Column 7, line 2 "sodiumi3" should read --sodium 3--.

Column 7, line 13 "-1-hydroxy" should read -- -2-hydroxy--.

Column 7, line 35 "line" should read --like--.

Column 8, line 6 "home" should read --homo--.

Column 8, line 64 "(Trimethyl" second occurrence should be omitted.

Column 9, line 67 "=/2:1:1)" should read ---=(2:1:1)---.

Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents