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3,733,280

POLYMERS DERIVED FROM CHLOROMALEIC ANHYDRIDE AS DETERGENT BUILDERS

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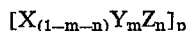
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6 Claims

ABSTRACT OF THE DISCLOSURE

Detergent compositions are described comprising a detergent surfactant and a water-soluble salt of a polymeric builder of the formula



wherein m and n are positive numbers whose sum is less than unity; p is an integer the lower limit of which is 3 and the upper limit of which is determined by the solubility of the salt in an aqueous system; X is derived from the monomer monochloromaleic acid; Y is derived from the monomer maleic acid and Z is 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 aliphatic acyloxy, chloro and lower alkoxy, it being provided that some of the carboxy groups in the polymer can be esterified with a lower aliphatic radical.

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

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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-hydroscopic, 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)nitridiacetate. Alkali metal salts of phytic acid, e.g., sodium phytate, are suitable as organic builders.

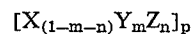
Although the condensed inorganic polyphosphates find the widest commercial acceptance, these exhibit the undesirable property of hydrolyzing into less condensed phosphorus compounds which are essentially devoid of builder properties. Moreover, these hydrolytic derivatives often form undesirable precipitates 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. 3,308,067 to Diehl and U.S. Pat. 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 in the hope of uncovering even more effective members of this class of materials.

SUMMARY OF THE INVENTION

It has now been discovered that excellent builder properties, particularly in mitigating soil redeposition and/or mineral accumulation are exhibited by the water-soluble salts of certain copolymers of chloromaleic acid having the formula



wherein m and n are positive numbers whose sum is less than unity; p is an integer the lower limit of which is 3 and the upper limit of which is determined by the solubility of the salt in an aqueous system; X is derived from the monomer monochloromaleic acid; Y is derived from the monomer maleic acid and Z is 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 aliphatic acyloxy, chloro and lower alkoxy, it being provided that some of the car-

boxy groups in the polymer can be esterified with a lower aliphatic radical, and the provision and use of cleansing compositions containing the builders aforesaid constitutes the principal object and purpose of the invention. Other objects and purposes will become apparent subsequently.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

As can be seen from an inspection of the formula aforesaid, the polymeric builders of the invention some of which have not previously been described, are copolymers of chloromaleic acid and maleic acid with a monoethylenically unsaturated monomer. The copolymers are prepared by copolymerizing a mixture of maleic anhydride, chloromaleic anhydride and the monoethylenically unsaturated monomer and the resulting copolymer treated with water to effect hydrolysis of the anhydride functions to free carboxy acid groups. Water-soluble salts of the polymer are formed by replacing the hydrogen in one or more of the carboxy groups with the appropriate soluble cationic moiety, preferably an alkali metal or ammonium radical.

The polymerization is carried out in the manner of performing ethylenic polymerizations, details of which are provided elsewhere herein. Generally speaking, such polymerization is effected under free radical producing conditions, commonly provided by the use of an organic free radical generating compound, such as benzoyl peroxide, acetyl peroxide, azobis-(isobutyronitrile) etc. The polymerization may be solution polymerization or bulk polymerization.

The copolymer builders of the invention must form water-soluble salts or at least be soluble in the cleansing composition. Accordingly, the copolymer must contain solubilizing groups. These are carboxy groups of the maleic or chloromaleic acid units or from a combination of the latter with a carboxy group attached to one of the ethylenic unit. 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: copolymers of monochloromaleic acid and maleic acid with such ethylenic monomers as itaconic acid, methacrylic acid, acrylic acid, vinyl acetate, vinyl alcohol, methyl vinyl ether, vinyl chloride allyl acetate and the like. Preferred copolymers are those containing units derived from chloromaleic acid and maleic acid with acrylic acid.

The structural features of the operable copolymers have, as a matter of convenience, been defined herein in terms of the carboxylic-acid containing monomers from which such copolymers theoretically can be derived. It is recognized, however, that in many cases it is desirable or even preferable to form the copolymers in practice by employing derivatives or precursors of such carboxylic-acid-containing monomers in the polymerizations leading to the desired 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 poly-

electrolyte builder compounds of this invention has a significant and practical bearing in 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, it can be stated 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% to about 0.50% 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 the solution to act as a builder.

The higher builder concentrations on the order of 0.50% 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% to about 0.06% 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 or 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 62,500.

It is difficult to accurately determine molecular weights of polymeric compounds. Such figures will generally vary 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 manufacturers 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 permeation 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 most 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 coadmixture with other known builders.

In general, in 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 8 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 9 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 of 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 8 to about 12 carbon atoms; the reaction product of fatty acids esterified with isethionic 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 6 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 8 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 8 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 8 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 radicals may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 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)-2-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% 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% to about 55%, 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 invention is illustrated in greater detail by the examples below.

Detergent formulation

The following general detergent formulation was utilized in the examples:

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

The formulation is prepared by merely blending the various ingredients and the novel builders of the invention. In order to determine the performance characteristics of the resulting detergent formulations, they were subjected to the following test procedures.

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 is conducted in a Terg-O-Tometer utilizing swatches of four different fabrics—cotton, cotton-dacron (with durable press finish, cotton-dacron (without durable press finish), and nylon—which had been soiled with a combination of airborne particulate matter and synthetic sebum. Three soil-wash cycles are conducted on each fabric utilizing the following test conditions: water hardness of 150 p.p.m. and 300 p.p.m., respectively, with a Ca/Mg ion ratio of 1.5; detergent formulation concentration of 0.15%; temperature of 120° F.; and a pH level of 9.5; washing time 10 minutes; rinsing time 2 minutes.

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

MINERAL ACCUMULATION

It has come to be recognized that there is a difference between soil redeposition and mineral accumulation. The latter may not appreciably lower the reflectance value of the fabric but may seriously interfere with its "hand" and other properties. As a first approximation one may assume that mineral accumulation will be significant if one or more of the components of the built detergent form an

insoluble precipitate as a result of interaction with the mineral constituents of washing water. Most polyelectrolyte detergent builders described in the Diehl's patent form insoluble complexes when allowed to interact with a certain amount of Ca^{++} and/or Mg^{++} ions. The total amount of precipitate formed by the formulated detergent with hard water under practical washing conditions may, therefore, well represent the degree to which a builder will cause mineral accumulation.

Mineral accumulation was studied by washing cloth swatches with detergent compositions using the builder candidates herein at 300 p.p.m. of water. After 10 washes the swatches are ignited for their ash content which gives a measure of the mineral accumulation on the fabric. The mineral accumulation test procedure is the procedure prescribed in AATCC test method 76-1968 except that only 10 wash cycles using unfinished cotton swatches were used.

In another procedure, the total amount of precipitate formed by interaction of the builder and of the detergent with hard water was determined as a relative measure of mineral accumulation. Two experiments were run with each builder material—one with the builder alone and the other with the builder along with other components of a built detergent. For the first experiment, 0.75 g. of the builder was dissolved in 1 l. of 300 p.p.m. water and 50 ml. of this solution was then diluted to 1 l. with 300 p.p.m. water and filtered through a 0.1μ size millipore cellulose filter. The residue was then weighed and expressed in milligrams. In the second experiment the same procedure was repeated except that in place of 0.75 g. of builder, 1.5 g. of built detergent containing 50% of the builder, 20% of a linear alkyl sulfonate (sulframin-85), 12% sodium metasilicate, 17.5% sodium sulfate and 0.5% sodium carboxymethyl cellulose was used.

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

$$\text{Ca. g./100 g.} = \frac{4.008 \cdot M \cdot V}{W}$$

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

The sequestering capacity of exemplary builders of the invention are presented in the tables.

GENERAL PREPARATIVE PROCEDURES

Solution copolymerization of monochloromaleic anhydride; catalyst added gradually

A mixture of monochloromaleic anhydride (composed of 70% monochloromaleic anhydride and 30% maleic anhydride and abbreviated herein as CMA_n) and the comonomer was dissolved in 2 to 4 times its volume of benzene, xylene, or dioxan, and heated to reflux with stirring in a current of dry nitrogen gas. A solution of the catalyst (usually benzoyl peroxide) in the same solvent was then added dropwise to the reaction mixture. The boiling was continued until the polymer separated as an insoluble material (1 to 5 hours). It was washed repeatedly with the same solvent and dried at 65° C./0.1 mm.

Solution copolymerization of monochloromaleic anhydride; comonomer, catalyst added gradually

Alternatively, both the catalyst and the comonomer can be separately dissolved in the same solvent and both added gradually at similar rates to a solution of the CMAAn. The rest of the procedure was identical to above.

Bulk copolymerization of monochloromaleic anhydride; solid or liquid comonomer

A mixture of CMAAn and the comonomer was heated in a thick walled flask to the desired temperature (55–100° C.) and the catalyst (usually benzoyl peroxide or acetyl peroxide, 2–5% by weight) added all at once. Within a few minutes (2–30 minutes) an exothermic reaction ensued. There was formed a solid mass which was broken into pieces, powdered, washed repeatedly with hot benzene, filtered and dried at 65°/0.1 mm. In some instances, the reaction mixture was initially degassed by repeated freezing (Dry Ice bath), evacuation, and warming. The flask was then filled with dry nitrogen before heating and introducing the catalyst.

Bulk copolymerization of monochloromaleic anhydride; gaseous comonomer

The gaseous comonomer was charged under pressure into a steel bomb containing the catalyst and CMAAn. The bomb was then heated to the desired temperature (60–100° C.). An exothermic reaction usually set in within an hour or so. To ensure that the reaction was complete, heating was continued for about 12 hours. After cooling, the polymer was usually taken out from the reaction bomb by dissolving in acetone. The acetone was then removed in vacuo and the solid polymer broken up first into small pieces and then powdered under ether in a blender, filtered and dried at 65°/0.1 mm.

Hydrolysis

The anhydride function of the copolymers of monochloromaleic anhydride was usually hydrolyzed by treating the polymer at room temperature with water until a clear solution resulted. The free acid was then recovered by either removing the water under reduced pressure or pouring the concentrated aqueous solution into acetone. In the latter case, the polymeric polyacid precipitated out from acetone.

Preparation of sodium salts of the copolymers of monochloromaleic acid

A saturated solution of the copolymeric monochloromaleic acid was first prepared by dissolving the free polyacid in water or by treating the corresponding anhydride directly with water until a clear solution resulted. This solution was then treated with 25% aqueous sodium hydroxide until a pH of 9.5 was achieved or until the equivalence point as determined by a separate titration was reached. The sodium salt was then isolated either by freeze-drying or by pouring into excess acetone. In the latter case, the salt precipitated out; it was filtered and dried at 65°/0.1 mm. before subjecting to builder evaluation test.

SPECIFIC EXAMPLES OF PREPARATIONS

Example 1

A solution of CMAAn (30 g.) in dry benzene (100 ml.) was placed in a three necked flask fitted with a mechanical stirrer, a nitrogen inlet and an addition funnel containing a solution of freshly distilled acrylic acid (18 g.) in dry benzene (50 ml.). The solution in the flask was heated to boiling and 0.75 g. of benzoyl peroxide added. The acrylic acid solution was introduced dropwise and after 15 minutes another 0.5 g. of benzoyl peroxide added. Total addition of the acrylic acid solution took about 30 minutes. The mixture was boiled for another hour and the precipitated white polymer filtered, washed with hot benzene and dried at 65° C./0.1 mm. Yield 35 g. Cl, 75

6.5%; sp. viscosity 0.2148 (in 0.1 M KBr); calcium sequestering capacity 23.6 g./100 g.

PREPARATION OF THE SODIUM SALT

10 g. of the above polymer was stirred in 25 ml. of distilled water until a clear viscous solution was obtained (1 hour). Aqueous sodium hydroxide (25% by weight) was then added dropwise until a test portion of the mixture gave a red coloration with a solution of phenolphthalein. The pH of the solution was then carefully adjusted to 9.5. The solution was poured into 1 l. of acetone. the gummy precipitate separated and washed with fresh quantities of acetone until solid. The solid was powdered and dried at 65° C./0.1 mm. Yield 14 g. Found: calcium sequestering capacity 14.1 g./100 g.; volatile solvents (thermal gravimetric analysis), 8.6%.

Example 2

A solution of benzoyl peroxide (0.3 g.) in dry xylene (25 ml.) was added dropwise to a boiling solution of CMAAn (6 g.) in the same solvent (25 ml.) over a period of three hours with mechanical stirring. Freshly distilled acrylic acid (3.6 g.) was also added to the same solution in 7 portions at regular intervals (0.5 hour) over the same period. Heating was continued for another one-half hour after all the additions were over. The light yellow solid polymer was separated from the solvent, washed first with fresh quantities of hot xylene and then with warm benzene. The material was finally dried at 65° C./0.1 mm. Yield 6 g. Cl, 4.5%; sp. viscosity 0.0562 (in 0.1 M KBr); calcium sequestering capacity 16.8 g./100 g.

Example 3

A mixture of acrylic acid (18 g.) and CMAAn (30 g.) was heated to 60° C. with stirring in a current of nitrogen. Acetyl peroxide (10 ml. of 25% solution in dimethyl phthalate) was then added. A vigorous exothermic reaction set in within 4 minutes and the reaction mixture turned into a solid mass. The solid was broken up, washed thoroughly with benzene and dried. Yield 25 g. Found: Cl, 7.6% sp. viscosity 0.1090 (in 0.1 M KBr); calcium sequestering capacity, 15.8 g./100 g.

Preparation of the sodium salt

A suspension of the above copolymer (17 g.) in distilled water (200 ml.) was stirred until a clear solution was obtained (30 minutes). Aqueous sodium hydroxide (25% w./w.) was then added dropwise with stirring until a drop of the mixture gave a red coloration with a solution of phenolphthalein. The pH of the solution was then adjusted to 9.5. The solution was poured in a thin stream into 2.5 l. of acetone with stirring, the precipitated while solid filtered and dried. Yield 21 g.; of product with calcium sequestering capacity 8.2 g./100 g.; volatile solvents (thermal gravimetric analysis) 10%.

Example 4

To a stirred mixture of CMAAn (12 g.) and acrylic acid (3.6 g.) heated to 60–65° C., was added acetyl peroxide (3.6 ml., 25% solution in dimethylphthalate) in a dropwise manner over a period of 15 minutes. No appreciable reaction occurred during this time. Within 10 minutes after all the catalyst had been added, a vigorous reaction set in and the entire mass set into a solid. The solid was broken up, washed with benzene and dried at 65°/0.1 mm. Yield 7 g. Cl, 8.9%; sp. viscosity 0.1312 (in 0.1 M KBr); calcium sequestering capacity 17.4 g./100 g.

Example 5

To a mixture of CMAAn (18 g.) and acrylic acid (3.6 g.) heated to 55° and in an atmosphere of nitrogen was added in a dropwise manner, acetyl peroxide (4.5 ml. of 25% solution in dimethylphthalate) over a period of 20 minutes. A white polymer gradually separated and after 2 hours at 55–60° C. the solid was filtered after triturating with benzene, washed with fresh quantities of benzene

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and dried. Yield 9 g. Cl, 8.5%; sp. viscosity 0.2032 (in 0.1 M KBr); calcium sequestering capacity 24.5 g./100 g.; volatile solvents (thermal gravimetric analysis) 4.2%.

Example 6

A mixture of CMAN (6 g.), methacrylic acid (4.3 g.) and acetyl peroxide (2 ml. of 25% solution in dimethyl phthalate) was heated to 60–65° C. in an atmosphere of nitrogen. Within 5 minutes a vigorous reaction set in and a solid mass was obtained. The solid was broken up, washed with warm benzene and dried at 65°/0.1 mm. Yield 6 g. Cl, 4.4%; calcium sequestering capacity 13.7 g./100 g.; volatile solvents (thermal gravimetric analysis) 1.7%.

Example 7

A mixture of CMAN (6 g.), vinyl acetate (4.3 g.) and acetyl peroxide (2 ml. of 25% solution in dimethyl phthalate) was heated to 65–70° C. with stirring in an atmosphere of nitrogen. Within 5 minutes a vigorous reaction occurred and a solid mass was obtained. This was ground under benzene and filtered. The residue was washed with fresh benzene and dried. Yield 6 g. Cl, 10.2%; calcium sequestering capacity 9.7 g./100 g.

Example 8

A mixture of CMAN (6 g.), allyl acetate (5 g.) and acetyl peroxide (2 ml. of 25% solution in dimethyl phthalate) was taken in a thick walled glass tube cooled in Dry Ice. The tube was sealed, placed inside a steel sleeve and heated for 16 hours at 55° C. in a bomb furnace. The highly viscous material that resulted was dissolved in acetone (25 ml.) and the solution poured in a thin stream into ether (500 ml.). The precipitated white solid was filtered and dried. Yield 7 g. Cl, 10.6%, calcium sequestering capacity 11.4 g./100 g.; volatile solvents (thermal gravimetric analysis) 2.1%.

Example 9

A 110 ml. capacity steel bomb was charged with CMAN

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(30.8 g.), finely powdered benzoyl peroxide (2.5 g.) and finally with ethylene gas until a pressure of 1000 p.s.i. (calcd. 0.25 mole ethylene) was reached. The bomb was then heated to 100° C. Within an hour an exothermic reaction set in and the temperature shot up to 140° C. The exothermic reaction was soon over and the temperature dropped back to 100° C. After 16 hours at 100° (this time is apparently much longer than what is actually necessary for the reaction) the bomb was cooled to room temperature (pressure 750 p.s.i.). The highly viscous material was taken out by dissolving in acetone (60 ml.) and the polymer precipitated by pouring it into excess ether (1 l.). Yield 29 g. Cl, 16.1%; calcium sequestering capacity 5.7 g./100 g.; volatile solvents (thermal gravimetric analysis) 5.7%.

Example 10

A mixture of CMAN (6 g.), vinyl chloride (3.1 g.) and acetyl peroxide (2 ml. of 25% solution in dimethyl phthalate) was treated exactly in the same way as described under Example 8. The highly viscous product was taken out from the reaction tube, washed with chloroform and the insoluble residue boiled with distilled water for 8 hours. The insoluble solid (2 g.) was filtered and set aside. Upon evaporation to dryness the aqueous filtrate gave 2 g. of amber solid. Calcium sequestering capacity 7.3 g./100 g.; volatile solvents (thermal gravimetric analysis) 7%.

Example 11

A mixture of CMAN (12 g.), itaconic anhydride (11.2 g.) an acetyl peroxide (2.3 ml. of 25% solution in dimethyl phthalate) was heated with stirring at 80–85° C. for 2.5 hours. The reaction product was triturated with dry benzene, the solid polymer filtered, washed with warm benzene and dried at 65°/0.1 mm. Yield 14 g. Cl, 5%; calcium sequestering capacity 20 g./100 g.

Following the procedure of the previous examples, the following preparations were carried out as summarized in Table I below:

TABLE I.—COPOLYMERS OF CMA*

Name and example number	Preparative procedure ^b				Percent Cl	Specific viscosity (in 1 M KBr)	Sequestering capacity, Ca g./100 g.
	Monomers (molar ratio) ^c	Catalyst	Solvent	Temp., °C.			
Copolymer CMA-AA	Anhydride ^e : AA						
12	1:1 Bz ₂ O ₂		Benzene	Reflux	1.5	6.5	23.6 (*15.4)
13	1:1 Bz ₂ O ₂		do.	Reflux	1.5	0.1687	22
14	1:1 Ac ₂ O ₂		do.	60-70	0.5	7.7	12.6 (*8.2)
15	1:1 Bz ₂ O ₂		do.	60-70	1	7.8	12.5
16	1:1 AIBN		do.	60-70	0.75	5.2	12.3
17	1:2 Ac ₂ O ₂		do.	60-70	1	6.6	13.6
18	3:1 Ac ₂ O ₂		do.	50-60	2	8.3	17 (*15.0)
19	4:1 Ac ₂ O ₂		do.	75	6	9.9	17.4
20	4:1 Ac ₂ O ₂		do.	55	1	7.5	24.4
21	4:1 Ac ₂ O ₂		do.	55	1	8.6	17 (*12.0)
Copolymer CMA-IA	Anhydride ^e : IA						
22	1:1 Bz ₂ O ₂		Xylene	Reflux	1.25	0.0182	6.9
23	1:1 Bz ₂ O ₂		do.	Reflux	4.5	1.3	6.5
Copolymer CMA-AlAc	Anhydride ^e : AlAc						
24	1:1 Ac ₂ O ₂		do.	50	15	10.1	11.0 (*8)
25	1:1 Ac ₂ O ₂		do.	50	16	10.4	10.4
Copolymer CMA-VAc	Anhydride ^e : VAc						
26	1:1 Ac ₂ O ₂		do.	60-70	10	9.5	11.1

* Technical grade containing 30% (w./w.) maleic anhydride.

^b For details see examples.

^c Total anhydride (CMA+MA=technical CMA): Comonomer.

^d Very poor yield.

^e Value on sodium salt.

^f Minutes.

NOTE.—CMA=monochloromaleic anhydride; AA=acrylic acid; IA=itaconic acid; VAc=vinyl acetate; AlAc=allyl acetate; Ac₂O₂=acetyl peroxide; Bz₂O₂=benzoyl peroxide; AIBN=azobis(isobutyronitrile).

The results set forth in Table I clearly indicate the ability of the copolymers of monochloromaleic acid to effectively sequester calcium ions. The results are especially noteworthy when compared with 10.9 g. Ca/100 g. sequestering value for the sodium tripolyphosphate, the standard in the builder field.

Tables II and III give the detergency and soil redeposition data for a number of copolymers derived from monochloromaleic anhydride along with known standard samples for comparison. These results clearly indicate the effective laundering characteristics exhibited by detergent formulations containing the sodium salts of the copolymers of monochloromaleic acid.

When reading Tables II and III, no attempt should be made to compare results of one table with those of the other since they have different fabric combinations and as such different fabric interactions, a phenomenon which is very little understood.

TABLE II.—DETERGENCY AND SOIL REDEPOSITION DATA¹

Fabric	Detergency ²				Redeposition ³			
	C	CP ₇	D/C-F	N	C	CP ₇	D/C-F	N
Builder and example no.:								
New candidates:								
Copolymer CMA-AA ⁴ (Example 2)	100	76	82	78				
Sodium salt of copolymer CMA-AA (Example 12)	94	86	90	94	1.3	5.1	4.7	3.0
Sodium salt of copolymer CMA-AA (Example 1)	90	83	87	91	1.0	2.2	2.7	2.5
Sodium salt of copolymer CMA-AA (Example 14)	88	83	86	84	1.1	2.3	1.8	2.7
Sodium salt of copolymer CMA-MAA (Example 6)	81	83	86	86	1.1	1.9	2.1	4.3
Comparable samples:								
NTA	85	85	85	76	0.7	7.4	11.9	16.2
STPP	86	76	76	74	0.5	14.1	19.1	16.4
STPP ⁵	100	83	88	102	1.8-2.4	4.7-8.1	2.4-7.4	2.7-6.4

¹ Unless otherwise mentioned, the data correspond to 300 p.p.m. water and 50% of builder in detergent composition.

² Percent of STPP's standard performance⁵ on cotton.

³ Decrease in reflectance units.

⁴ Measured at 25% builder concentration in 150 p.p.m. water.

⁵ Standard—STPP measured at 50% of detergent formulation in 150 p.p.m. water.

NOTE.—C=100% Indianhead cotton, unfinished (test fabrics); CP₇=50/50 cotton/polyester, finished (carbamate resin 597—American Viscose); D/C-F=65/35 dacron/cotton, finished (Arrow Shirt Co.); N=100% nylon, unfinished (test fabrics). CMA=chloromaleic anhydride (technical grade containing 30% w/w. maleic anhydride); AA=acrylic acid; MAA=methyl acrylic acid; NTA=sodium nitrilotriacetate; STPP=sodium tripolyphosphate.

TABLE III.—DETERGENCY AND SOIL REDUCTION DATA¹

Fabric	Detergency ²				Redeposition ³			
	C	CP ₇	D/C-M	N	C	CP ₇	D/C-M	N
Builder and example number:								
New candidates:								
Sodium salt of copolymer CMA-AA (Example 18)	87	76	73	71	1.6			1.0
Sodium salt of copolymer CMA-AA (Example 21)	85	83	76	78	2.0	5.9	3.6	5.0
Sodium salt of copolymer CMA-ALAc (Example 24)	79	78	71	68	1.3			
Sodium salt of copolymer CMA-IA (Example 11)	86	76	75	79	1.4			
Comparable samples:								
NTA	89	83	78	83	1	8	4	7
STPP	83	75	70	73	2	9	8	11
STPP ⁴	100	83	84	103	2	13	5	10

¹ Unless otherwise mentioned, the data correspond to 300 p.p.m. water and 50% of builder in detergent composition.

² Percent of STPP's standard performance⁴ on cotton.

³ Decrease in reflectance units.

⁴ Standard—STPP measured at 50% of detergent formulation in 150 p.p.m. water.

NOTE.—C=100% Indianhead cotton, unfinished (test fabrics); CP₇=50/50 cotton/polyester, finished (carbamate resin 597—American Viscose); D/C-M=50/50 dacron/cotton, unfinished (test fabrics); N=100% nylon, unfinished (test fabrics); CMA=chloromaleic anhydride (technical grade containing 30% w/w. maleic anhydride); AA=acrylic acid; ALAc=allyl acetate; IA=itaconic acid; NTA=sodium nitrilotriacetate; STPP=sodium tripolyphosphate.

Table IV shows, using the millipore filtration procedure described hereinbefore, the relative amounts of insoluble material formed by different builders, in the presence and absence of other components of a built detergent, when made to interact with 300 p.p.m. water under simulated rinse-cycle conditions.

TABLE IV
Millipore Filtration Results on 0.1 μ Cellulose Filters
Amount of insoluble material formed¹
in mg.

	Builder	STPP	Tide XK	SPM	S(CMA-AA)
Test conditions:					
Builder only		1.8		24.7	0.8
Builder in formulated detergent ²		2.1	³ 5.8	28.9	1.3
¹ From 0.0375 g. of builder and 1 l. of 300 p.p.m. water or from 0.075 g. of built detergent in 1 l. of 300 p.p.m. water.					
² 50% builder, 12% sodium metasilicate, 20% linear alkyl sulfonate (sulfuramin-85), 17.5% sodium sulfate and 0.5% carboxymethyl cellulose.					
³ With distilled water, Tide gives 7.5 mg. insoluble material; in 300 p.p.m. water, the amount becomes 13.2 mg. The difference, 5.8 mg., is assumed to be due to hardness alone.					
NOTE.—STPP=sodium tripolyphosphate; Tide XK=a commercial detergent in the U.S. market containing 50% STPP, 6% sodium silicate salts, 16-20% linear alkyl sulfonate, 15-20% sodium sulfate, 6.5-9% moisture, and small amounts of sodium carboxymethyl cellulose (about 0.5%) enzyme (0.2-0.5%, perfumes etc.; SPM=sodium polymaleate; S(CMA-AA)=sodium salt of copolymer of chloromaleic acid and acrylic acid (Example 2).					

It is clear from the above table that the sodium salt of the copolymer of monochloromaleic acid and acrylic acid gives minimum amount of insoluble material upon interaction with hard water in the presence or absence of the other components of the built detergent.

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A second method for assessing the degree of mineral accumulation is to measure ash content, as described hereinbefore, of the fabric after washing several times with the built detergent. Table V shows these results for a number of builders.

TABLE V

Ash build-up data on cotton¹

Builder in built detergent ² :	Percent ash ³ after 10 washings ⁴
STPP -----	0.08
SPM -----	0.2
S(CMA-AA) -----	0.088

¹ 100% Indianhead cotton, unfinished (test fabrics).² 50% Builder, 12% sodium metasilicate, 20% linear alkylarenesulfonate (sulframin-85), 17.5% sodium sulfate and 0.5% carboxymethyl cellulose.³ Ash content before washing 0.119%.⁴ Washing conditions: 0.15% detergent in 300 p.p.m. water, temp. 120° F., pH 9.5. STPP=sodium tripolyphosphate; SPM=sodium polymaleate; S(CMA-AA)=sodium salt of copoly-(chloromaleic acid and acrylic acid) (Example 2).

The results of Table V shows that the sodium salt of copoly(chloromaleic acid and acrylic acid) is equivalent to STPP and much superior to SPM in preventing mineral accumulation.

What is claimed is:

1. A detergent composition consisting essentially of
 - (1) an organic water-soluble detergent surfactant selected from the group consisting of anionic, nonionic, zwitterionic and amphoteric detergent surfactants and as a builder therefor,
 - (2) a water-soluble salt of a polymeric builder formed by the co-polymerization of an approximately 70:30 mixed chloromaleic anhydride/maleic anhydride with an ethylenically unsaturated monomer selected from the class consisting of acrylic acid, methacrylic acid, vinyl acetate, allyl acetate, ethylene, vinyl chloride and itaconic anhydride followed by the hydrolysis of the anhydride groups to carboxy groups, it being provided that the low limit of the degree

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of polymerization is 3 and the upper limit is determined by the degree of solubility of the salt in an aqueous system.

2. A detergent composition according to claim 1 wherein the ratio of the builder to the detergent surfactant is from about 3:1 to 1:10 by weight.

3. A detergent composition according to claim 1 which provides in solution a pH of from about 8 to about 12.

4. A detergent composition according to claim 1 which provides a pH of from 9.5 to 11.5.

5. A detergent composition according to claim 1 consisting essentially of 20 parts of sodium linear alkylarenesulfonate; 50 parts of the water-soluble salt of the polymeric builder of claim 1; 12.0 parts of sodium metasilicate 5-hydrate; 0.5 part sodium carboxymethylcellulose and 17.5 parts sodium sulfate, all concentrations being on a dry weight basis.

6. A detergent composition according to claim 1 consisting essentially of 20 parts of sodium linear alkylarenesulfonate; 25 parts of the water-soluble salts of the polymeric builder of claim 1; 12 parts of sodium metasilicate 5-hydrate; 0.5 part of sodium carboxymethylcellulose and 42.5 parts of sodium sulfate, all concentrations being on a dry weight basis.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,733,280 Dated May 15, 1973

Inventor(s) Paritosh M. Chakrabarti and Gert P. Volpp

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

Columns 11 & 12, Table I under Time, hr., line 8 "^b6" should read --^f6--.

Columns 13 & 14, Table III Title "Reduction" should read --Redeposition--.

Columns 13 & 14, Table III under Detergency² N "71" should read --72--.

Columns 13 & 14, Table III under Redeposition³ N "1.0" should read --5.0--.

Signed and sealed this 29th day of October 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents