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POLYELECTROLYTE BUILDER AND DETERGENT COMPOSITIONS

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Int. Cl. C11d *1/08, 1/14*

U.S. Cl. 252—550 3 Claims

ABSTRACT OF THE DISCLOSURE

A novel class of polyelectrolytes having the form of poly-β-ketoacids and their salts is described, as in the use of these polyelectrolytes as builders in detergent formulations.

This application is a divisional application of U.S. Ser. No. 33,914.

BACKGROUND OF THE INVENTION

(A) Field of the invention

The invention relates to the preparation of novel poly-β-ketoacids and their salts and to the use of these polymer compounds in certain detergent formulations to impart improved cleansing power to such formulations.

(B) Description of the prior art

It is known that certain materials have the ability to improve the cleansing power and detergency levels of detergent formulations. These materials, which are termed "builders," are widely used in the detergent industry and the resulting formulations are termed "built" detergents. These "built" detergents are advantageous in that at a given detergent level they give better cleaning and are less expensive than the non-built detergent formulations.

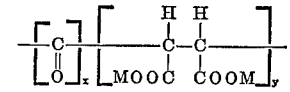
The most widely known builder materials are the water-soluble inorganic alkaline builder salt such as the alkali metal polyphosphates, e.g. sodium tripolyphosphate or sodium pyrophosphate and others such as alkali metal carbonates, bicarbonates and silicates. Often these builder materials are used in combination.

There has been increased interest in expanding the number of builder materials which are available, particularly organic builders. Among the presently 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, and sodium and potassium triethanolammonium-N-(2-hydroxyethyl)-nitrilodiacetate. Alkali metal salts of phytic acid, e.g. sodium phytate, are also suitable as organic builders. Other organic builders include those set forth in U.S. Pat. 3,308,067, issued on Mar. 7, 1967 to Francis L. Diehl, covering polyelectrolyte builders made up of water-soluble salts of polymeric aliphatic polycarboxylic acids, alone or as copolymers of said salts with alkylenes or specified monocarboxylic acids.

While many of these organic builders are satisfactory from the point of view of detergency enhancement, they do not meet important requirements satisfied by the inorganic builders, e.g. the ability to avoid mineral accumulations on laundered textiles after repeated launderings, and an organic builder that has all the advantages of the inorganic builders is desired.

SUMMARY OF THE INVENTION

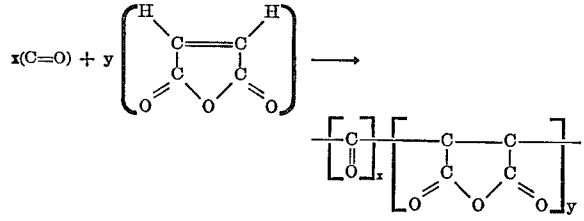
We have now found a new class of effective detergent builders which are poly-β-ketoacids and their water-soluble salts, and which have the formula



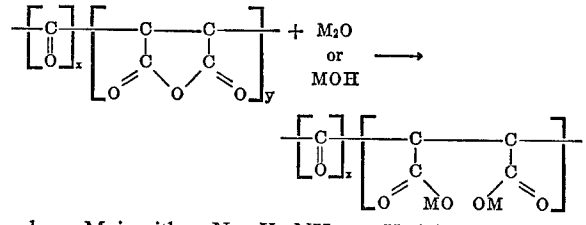
wherein M is either hydrogen, sodium, potassium or ammonium, the mole ratio of $x:y$ is not greater than 1, and the molecular weight of the resulting copolymer is at least 400; these polymers when mixed with an organic water-soluble detergent surfactant in weight ratios of 1:20 to 100:1, and preferably 1:3 to 10:1, respectively, form new and useful cleaning and laundering compositions in which the polymer functions as a builder.

DESCRIPTION OF THE INVENTION AND THE PREFERRED EMBODIMENTS

Preparation of the builders of the present invention is commenced by reacting maleic anhydride and carbon monoxide gas in a solvent at an elevated temperature and under pressure in the presence of an initiator to form a copolymer. The reaction is carried out by dissolving maleic anhydride in a suitable solvent, placing the solvent and dissolved maleic anhydride in a suitable reactor and then supplying carbon monoxide gas to the sealed container under superatmospheric pressure. The reaction is carried out at elevated temperatures by heating the reactor and a polymerization reaction occurs as follows:



This resulting product is a poly-β-ketoanhydride in which the mole ratio of carbon monoxide to maleic anhydride ($x:y$) is not greater than 1:1 and preferably is not less than about 0.05:1. The poly-β-ketoanhydride is then hydrolyzed under neutral or alkaline conditions to form the corresponding poly-β-ketoacid acid salt. The reaction that occurs is as follows:



where M is either Na, K, NH_4 or H. The poly-β-ketoacid and its water-soluble salts serve as the builders of the present detergent formulations.

In carrying out the above reaction to produce the product of the present invention, the polymerization must suitably is conducted in a solvent. A requirement of the solvent is that it should not interfere with the polymerization procedure in the course of the free radical chain process. That is, it should not function, for example, as a chain-transfer agent, i.e. a compound that terminates the chains of the polymeric reaction products or one which tends to commence new chains and which results in generally low molecular weight polymers. The solvent preferably is chosen so that under the conditions of the polymerization, the monomeric maleic anhydride is very soluble while the polymer which results is essentially insoluble. Further, the solvent must be one in which carbon monoxide has some degree of solubility. Suitable solvents include perchlorinated aliphatic hydrocarbons,

such as carbon tetrachloride, perchloroethylene and the like, aromatic hydrocarbons such as benzene, and chlorinated hydrocarbons such as monochlorobenzene and o-dichlorobenzene.

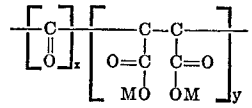
In carrying out the polymerization the solvent is placed in a pressure-tight container and the desired amount of maleic anhydride is dissolved in the solvent. Carbon monoxide gas is then pumped into the chamber under superatmospheric pressure. The function of the superatmospheric pressure is to facilitate dissolving carbon monoxide gas in the solvent. The ratio of carbon monoxide to maleic anhydride in the resulting polymer is a function of the relative concentration of these reagents dissolved in the solvent. The carbon monoxide gas pressure is maintained most conveniently at from 400 to 800 p.s.i.g., with most desirable operating pressures being in the range of 600 to 750 p.s.i.g. The carbon monoxide pressure often drops during the polymerization due to the consumption of carbon monoxide during the course of a successful copolymerization. It is desirable to maintain the pressure in the chamber at a steady value to assure maintaining carbon monoxide gas dissolved in the solvent in which the reaction is taking place.

In order for polymerization of the maleic anhydride and carbon monoxide to occur, an initiator must be present. The initiator may be a free-radical initiator, ionic initiator or radiation initiator such as ^{60}Co. We have found that organic peroxides are especially effective initiators. Peroxides which have been found suitable include benzoyl peroxide, acetyl peroxide and the like. An important requirement of the initiator, e.g. the organic peroxide, is that it should be one which does not significantly initiate homopolymerzation of maleic anhydride under the reaction conditions. For example, when operating at a temperature of about 100° C. benzoyl peroxide is more suitable than acetyl peroxide because the benzoyl peroxide has little tendency to homopolymerize maleic anhydride under these reaction conditions.

The initiator is added in an amount sufficient to effect and promote the polymerization reaction; this normally requires 1 to 5% by weight of the initiator. The initiator can be added all at once to the reaction mixture, or it can be introduced in portions during the course of the polymerization reaction. Portion-wise addition of the initiator has certain advantages. It prevents premature decomposition of the initiator during the course of the reaction. It also limits the extent of the polymerization reaction that occurs as a result of injecting only a portion of the initiator.

The polymerization reaction is run at an elevated temperature and most desirably at a temperature between 80° to 120° C. The temperature to be utilized is determined on the basis of the initiator selected, and is chosen so that the initiator preferentially promotes the production of the copolymer instead of homopolymerization of the maleic anhydride. For example, when benzoyl peroxide is used as the initiator, the reaction temperature is preferably maintained in the range of 105° to 110° C. In contrast, when acetyl peroxide is utilized as the initiator, the preferred temperature is 90° to 95° C.

The reaction of the maleic anhydride and carbon monoxide at elevated temperatures and pressures and in the presence of an initiator is carried out over several hours, until substantial reaction of the monomers has occurred. At the end of this period, where a solvent is used in which the polymer is insoluble, the polymer is found as a precipitate in the solvent and can be separated readily, for example by filtration or centrifugation. Where a solvent is used in which the polymer is soluble, other normal means of separating the polymer obviously must be employed. Desirably, the precipitated polymer after separation from the reaction solvent is washed with a suitable solvent, for example the solvent utilized in the reaction mixture, and then is suspended in 4 to 9 parts by weight of water per part of polymer. Stirring of the polymer in its water suspension at room temperature causes the poly-β-ketoanhydride to be hydrolyzed to its acidic form, which readily dissolves in water. The acidic solution may then be treated with an aqueous sodium hydroxide, potassium hydroxide or ammonium hydroxide solution to a pH of 9.5 to 10.5. When enough of the base material has been added to obtain a final pH of the solution at 9.5 to 10.5, the solution is vacuum stripped to dryness, yielding a solid amorphous salt product having the following configuration:



The most desirable water-soluble salts of the above product are those where M is sodium, potassium or ammonium. These salts can be prepared initially for use in a detergent formulation, or they can be prepared in situ by introducing the poly-β-ketoacid (where M is H) and an alkali, e.g. NaOH separately into the detergent formulation for reaction in an aqueous washing medium.

While the degree of polymerization of the above compounds can vary within wide ranges, it normally is within the range corresponding to a molecular weight of 400 to 1,000,000. A preferred range for the molecular weight is from about 3,000 to 50,000.

The resulting poly-β-ketoacid and its water-soluble salts have been found to have calcium sequestering capacities of on the order of 15 to about 17 grams of calcium ion per hundred grams of builder. The calcium sequestering capacity measures the ability of the builder to sequester calcium ions. Normally the greater the sequestering capacity, the better the building property of the material.

The calcium sequestering capacity is determined by titrating the builder sample with an aqueous calcium nitrate or other water-soluble calcium salt solution using a calcium ion-sensitive electrode to determine an end point. The end point is reached when the sample no longer sequesters calcium ions and free calcium ions are detected by means of the electrode.

These novel builders have also been found to have kaolin dispersing efficiencies of 90 to 110% that of sodium tripolyphosphate. The kaolin dispersing efficiency is a measure of the ability of the sample to keep a soil-like material, i.e. kaolin, suspended in water as compared with sodium tripolyphosphate. Normally the greater the kaolin dispersing efficiency, the better builder properties it has.

The kaolin dispersing efficiency is determined by making up a solution containing 700 parts per millon of the sample builder and 300 parts per million of a surfactant, namely Sulframin-85, an 85% aqueous solution of sodium linear dodecyl benzene sulfonate, and mixing this solution with an aqueous solution of distilled water containing 100 parts per million of kaolin. The mixture is vigorously agitated and then permitted to stand for 17.5 hours to permit any settling to take place. Thereafter, the sample is analyzed by means of a Brice-Phoenix universal light scattering photometer and a reading determined. An identical procedure is repeated on a control sample containing exactly the same solutions except that 700 p.p.m. of sodium tripolyphosphate are utilized in place of the sample builder. At the end of the 17.5 hours a reading is taken on the same photometer of the control sample. The kaolin dispersing efficiency is then calculated by dividing the meter reading of the sample over the meter reading of the sodium tripolyphosphate control and multiplying by 100. For example, if the meter reading for the standard sodium tripolyphosphate solution is 85 on the photometer and the meter reading of the sample is 80, the kaolin dispersing efficiency of the sample is

$$\frac{80}{85} \times 100 = 94\%$$

The inermediate poly-β-ketoanhydride which is the initial product of the polymerization also has utility as a reactant in certain polymerizations, particularly where cross-linkages are desired. For example, poly-β-ketoanhydrides are useful as polyesterification agents, resin-formers and the like.

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

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 1:20 to about 100:1 by weight, with such compositions providing in aqueous solution a pH of about 9 to about 12. The preferred ratio of polyelectrolyte builder to detergent surfactant is about 1:3 to about 10:1 and the optimum pH range is 9.5 to about 11.5.

The detergent surface active compounds which can be used within the compositions of this invention include anionic, nonionic, zwitterionic, ampholytic detergent compounds and mixtures thereof. These suitable substances are outlined at length below.

(a) Anionic detergent compositions which can be used in the compositions of this invention include both soap and non-soap detergent compounds. Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids (C_{10}–C_{20}). Particularly useful are the sodium or potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Examples anionic organic non-soap detergent compounds are the water-soluble salts, 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. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the synthetic detergents which form a part of the compositions of the present invention are the sodium or potassium alkyl sulfates especially those obtained by sulfating the higher alcohols (C_8–C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzenesulfonates, such as are described in U.S. Letters Patents No. 2,220,009 and No. 2,477,383 in which the alkyl group contains from about 9 to about 15 carbon atoms; other examples of alkali metal alkylbenzene sulfonates are those in which the alkyl radical is a straight chain aliphatic radical containing from about 10 to about 20 carbon atoms for instance, 2-phenyl-dodecanesulfonate and 3-phenyl-dodecanesulfonate; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; 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 alkylphenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to about 12 carbon atoms; the reaction product or fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyl tauride in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in United States Letters Patents Nos. 2,486,921, 2,486,922 and 2,396,278.

(b) Nonionic synthetic detergents may be broadly defined as compounds aliphatic or alkylaromatic in nature which do not ionize in water solution. For example, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1,500 to 1,800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecules as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) 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, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said hydrophobic base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 24 carbon atoms.

(4) Long chain tertiary amine oxides corresponding to the following general formula, $R_1R_2R_3N\rightarrow O$, wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms, and R_2 and R_3 are each methyl or ethyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, dimethylhexadecylamine oxide.

(5) Long chain tertiary phosphine oxides corresponding to the following formula $RR'R''P\rightarrow O$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R′ and R″ are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxide are:

dimethyldodecylphosphine oxide,
dimethyltetradecylphosphine oxide,
ethylmethyltetradecylphosphine oxide
cetyldimethylphosphine oxide,
dimethylstearylphosphine oxide,
cetylethylpropylphosphine oxide,
diethyldodecylphosphine oxide,
diethyltetradecylphosphine oxide,
bis(hydroxymethyl)dodecylphosphine oxide,
bis(2-hydroxyethyl)dodecylphosphine oxide,

2-hydroxypropylmethyltetradecylphosphine oxide,
dimethyloleylphosphine oxide, and
dimethyl-2-hydroxydodecylphosphine oxide.

(6) Dialkyl sulfoxides corresponding to the following formula, RR'S→O, wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxylalkyl radical containing one or two other oxygen atoms in the chain, the R groups ranging from 10 to 18 carbon atoms in chain length, and wherein R' is methyl or ethyl. Examples of suitable sulfoxide compounds are:

dodecyl methyl sulfoxide
tetradecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
2-hydroxydodecyl methyl sulfoxide
3-hydroxy-4-decoxybutyl methyl sulfoxide
3-hydroxy-4-dodecoxybutyl ethyl sulfoxide
2-hydroxy-3-decoxypropyl methyl sulfoxide
2-hydroxy-3-dodecoxypropyl methyl sulfoxide
dodecyl ethyl sulfoxide
2-hydroxydodecyl ethyl sulfoxide

The 3-hydroxy-4-decoxybutyl methyl sulfoxide has been found to be an especially effective detergent surfactant. An outstanding detergent composition contains this sulfoxide compound in combination with the polymaleate builder compound of this invention.

(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. Examples of compounds falling within this definition are sodium-3-dodecylaminepropionate and sodium-3-dodecylaminopropanesulfonate.

(d) Zwitterionic synthetic detergents can be broadly described as derivatives of alpihatic quaternary ammonium compounds 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. 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-hydroxypropane-1-sulfonate which are especially preferred for their excellent cool water detergency characteristics.

The anionic, nonionic, ampholytic and zwitterionic detergent surfactants mentioned above can be used singly or in combination in the practice of the present invention. The above examples are merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

The foregoing organic detergent surfactant compounds can be formulated into any of the several commercially desirable composition forms for example, granular, flake, liquid and tablet forms.

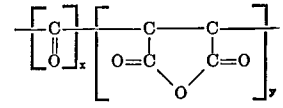
In a finished detergent formulation of this invention there will often be added in minor amounts materials which make the product more effective or more attractive. The following are mentioned by way of example. Soluble sodium carboxymethylcellulose can be added in minor amounts to inhibit soil redeposition. A tarnish inhibitor such as benzotriazole or ethylenethiourea can also be added in amounts up to about 2%. Fluorescers, perfume and color, while not essential in the compositions of the invention, can be added in amounts up to about 1%. An alkaline material or alkali such as sodium hydroxide or potassium hydroxide can be added in minor amounts as supplementary pH adjusters. There might also be mentioned as suitable additives, water, brightening agents, bleaching agents, sodium sulfate, and sodium carbonate.

Corrosion inhibitors generally are also added. Soluble silicates are highly effective inhibitors and can be added to certain formulas of this invention at levels of from about 3% to about 8%. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of $SiO_2:M_2O$ of from 1:1 to 2.8:1 can be used. M in this ratio refers to sodium or potassium. A sodium silicate having a ratio of $SiO_2:Na_2O$ of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

The following examples are given to illustrate the present invention and are not deemed to be limiting thereof.

EXAMPLE 1

A stainless steel autoclave, equipped with an automatic stirrer and heating mantle, was charged with 1.5 liters of a benzene solution containing 400 grams of maleic anhydride. To the solution in the autoclave was added a 20% by weight solution of benzoyl peroxide dissolved in benzene until 20 grams of benzoyl peroxide had been added to the autoclave. The autoclave was then closed, flushed three times with nitrogen and charged with carbon monoxide until a pressure of between 600 and 700 p.s.i.g. was obtained. The heating mantle surrounding the autoclave was activated and the temperature of the reaction mixture within the autoclave was adjusted to between 100° and 110° C. The resulting mixture was maintained at this temperature with constant stirring for a period of four hours. Thereafter, the reactor was cooled and vented and a slurry was removed. The slurry was filtered from the benzene reaction medium and the insolubles were washed three times with hot benzene and then with a light petroleum distillate and finally dried. 70 grams of a polymer were recovered, which was identified as a poly-β-ketoanhydride having the following formula:



The molecular weight of the polymer was 15,000. A sample of the above polymer was added to water in amounts sufficient to make up a 10% aqueous solution of the copolymer. This was then neutralized by adding a 20% aqueous sodium hydroxide solution until a pH of 10 was maintained. A clear pale yellow solution resulted which, upon evaporation of the solution, yielded a solid salt, the corresponding sodium poly-β-ketoacid salt of the above poly-β-ketoanhydride. The sodium salt was readily soluble in water in amounts over 20 weight percent and on further testing had a calcium sequestering capacity of 16 grams of calcium per 100 grams of the sodium salt. The calcium sequestering capacity was determined by titrating 100 grams of the salt with an aqueous calcium acetate solution using a calcium ion-sensitive electrode. The end point was determined when free calcium ions were detected in the solution.

The salt solution remained clear during the calcium sequestering testing and continued to be clear after the end point was reached. In fact, the addition of from four to six grams of calcium ions beyond the end point still did not result in the formation of insolubles by reaction with the polymer. This is desirable in a builder to prevent mineral buildups by calcium precipitation of the polymer during repeated washings with the polymer builder.

The kaolin dispersing efficiency of the salt, as previously defined, was also determined and was found to be 108 to 110% of the kaolin dispersing efficiency of sodium tripolyphosphate.

The builder efficiency of the sample relative to sodium tripolyphosphate was also determined by the following test:

Swatches of various materials were equally soiled using an aqueous emulsion of dust and then washed in a Terg-o-tometer laboratory washer with solutions of the detergents being evaluated. Soil removal is measured by a re-

flectometer. An arbitrary standard which is used is the reflectance value obtained when the following formulation, in which sodium tripolyphsphate is the builder, is utilized for washing the soiled swatches in water contained 150 p.p.m. total of Ca^{++} and Mg^{++} ions:

	Percent by weight
Sulframin 85 (sodium linear dodecyl benzene sulfonate)	20
Sodium metasilicate 5-hydrate	12
Carboxy methyl cellulose	0.5
Sodium sulfate	17.5
Builder	50

Tests are performed in 300 p.p.m. total of Ca^{++} and Mg^{++} ions to more clearly show comparative levels in detergency. The results are reported as percent detergency and are obtained by dividing the reflectance values for the samples by the reflectance values for the standard and multiplying by 100. The percent detergency results are set forth in Table I.

EXAMPLE 2

A second polymerization was carried out in the same manner as set forth in Example 1 except that the benzene solution of benzoyl peroxide which functions as the catalyst or initiator was added in four equal portions, one at the beginning of each hour, each portion of which contained 10 grams of benzoyl peroxide. The catalyst solution was forced into the reactor from a stainless steel bomb under excess carbon monoxide pressure. During the course of the polymerization, the carbon monoxide pressure in the reactor was maintained between 500 and 700 p.s.i.g. A carbon monoxide pressure drop of about 200 p.s.i.g. was observed during the period the catalyst was fed to the reactor; to compensate for the pressure drop, additional carbon monoxide was fed. A solid polymer weighing 160 grams was isolated and washed and dried as set forth in Example 1. The polymer was found to have the same structural configuration as in claim 1, except that the molecular weight of the polymer was found to be 5,000.

A sample of the polymer was placed in water sufficient to form a 10% aqueous solution thereof. This was then neutralized with 20% aqueous sodium hydroxide to a pH of 10. A sodium salt of the polymer was then recovered as set forth in Example 1 which had calcium sequestering capacities and kaolin dispersing efficiencies similar to those of the polymer salt of Example 1. The polymer was then tested for builder efficiency as set forth in Example 1. The results are set forth in Table I.

EXAMPLE 3

A polymerization reaction was carried out by the procedure set forth in Example 2, except that the charge of benzene solution to the autoclave contained 800 grams of maleic anhydride. The solution of benzoyl peroxide in benzene was added in 4 equal increments sufficient to supply 1.25% by weight of benzoyl peroxide based on the weight of the maleic anhydride. The reaction was run at a temperature of 105° to 110° C. and the carbon monoxide pressure was maintained at between 940 to 1,000 p.s.i.g.; to compensate for the pressure drop, additional carbon monoxide was fed. During the reaction, the pressure of the carbon monoxide decreased 200 p.s.i.g. The resulting polymer was worked up and purified as set forth in Example 2, and then converted to its sodium salt by hydrolysis and neutralization with an aqueous sodium hydroxide solution. The resulting polymer salt was found to have the same structural configuration as the polymer salt in Example 1, except that the molecular weight of the polymer was found to be 8,000. The sodium salt was found to have a calcium sequestering capacity of 17 grams of calcium ion per 100 grams of polymer.

The detergency building properties of the material is set forth in Table I.

EXAMPLE 4

A polymerization reaction was carried out by the procedure set forth in Example 2, except that the initiator solution employed was a 25% acetyl peroxide in dimethyl phthalate. This solution was added in 4 portions each containing 2.5% of acetyl peroxide based on the weight of maleic anhydride. The temperature during the run was maintained at 90° to 95° C. and the carbon monoxide pressure was maintained at 1,000 p.s.i.g. The resulting precipitated polymer yielded 230 grams of product. Upon hydrolysis and neutralization by the procedure set forth in Example 2, a sodium salt of the polymer having a molecular weight of 18,000 was obtained.

TABLE I

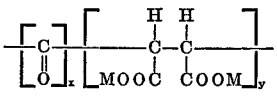
[Percent detergency in water having 300 p.p.m. total of Ca^{++} and Mg^{++} ions]

Fabric	Builder (percent)			
	STPP [1]	Example 1 salt	Example 2 salt	Example 3 salt
Cotton	86	94	95	90
Polyester cotton	76	84	77	69
Nylon	74	85	91	83

[1] Sodium tripolyphosphate.

What is claimed is:

1. A cleaning and laundering composition consisting essentially of (1) an organic, water-soluble detergent surfactant selected from the group consisting of anionic, non-ionic, zwitterionic, and ampholytic detergent surfactants, and mixtures thereof, and (2) a polyelectrolyte builder material having the following formula:



where M is hydrogen, sodium, potassium or ammonium, the mole ratio of $x:y$ is about 0.05:1 to about 1:1 and the molecular weight of the polyelectrolyte builder material is from about 3,000 to about 50,000 and the ratio of said polyelectrolyte builder to said detergent surfactant is in the range of from about 1:20 to about 100:1 by weight.

2. The cleansing and laundering composition of claim 1 wherein the ratio of polyelectrolyte builder to the detergent surfactant is from about 1:3 to about 10:1 by weight.

3. The cleansing and laundering composition of claim 1 comprising as the detergent surfactant an anionic, water-soluble alkali metal salt of an organic sulfuric reaction product having in its molecular structure an alkyl radical having 8 to 22 carbon atoms and a radical from the group consisting of sulfonic acid and sulfuric acid ester radicals, and in which the ratio of said polyelectrolyte builder to said detergent surfactant is from about 1:3 to about 10:1 by weight and said composition provides in aqueous solution a pH of about 9 to 12.

References Cited

UNITED STATES PATENTS

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P. E. WILLIS, Assistant Examiner

U.S. Cl. X.R.

252—89, 135, 545,546, 554, 555, 558, Dig 11

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,761,412

DATED : September 25, 1973

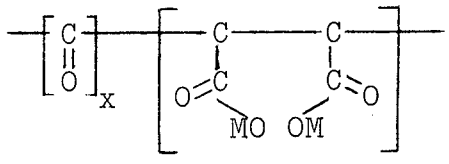
INVENTOR(S) : Charles J. Lancelot and Donald G. MacKellar

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

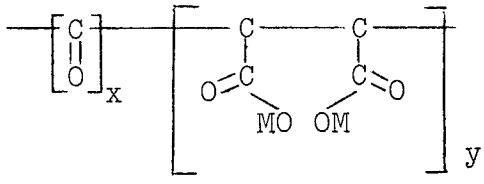
Column 1, line 44, "bicarbonates and" should read --bicarbonates, borates and--.

Column 2, line 43, "acid salt" should read --or acid salt--.

Column 2, lines 50 to 53,



should read



Column 2, line 57, "reaction" should read --reactions--.

Column 2, line 58, "must" should read --most--.

Column 6, line 46, "10 to 24" should read --10 to 14--.

Continued...

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,761,412

DATED : September 25, 1973

INVENTOR(S) : Charles J. Lancelot and Donald G. MacKellar

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

Column 7, line 17, "ethyl" should read --methyl--.

Signed and Sealed this

sixteenth Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks