

[54] **DETERGENT POLYELECTROLYTE BUILDERS**

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252/142, 152, 161, 156

[56] **References Cited**

**UNITED STATES PATENTS**

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3,308,067	3/1967	Diehl .....	252/161
3,332,880	7/1967	Kessler et al. ....	252/161
3,535,258	10/1970	Sabatelli et al. ....	252/105
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**FOREIGN PATENTS OR APPLICATIONS**

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"Surface Active Agents" Schwartz & Perry, Vol. I  
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[57] **ABSTRACT**

Synthetic detergents are prepared having improved cleaning power using polyacrylic acid salts. For example, sodium polyacrylate of controlled molecular weight is an excellent substitute for the "suspect" phosphate builder-sequestrant presently used in household detergent compositions. Regardless of the merit of the charge that detergent phosphates are the primary cause of eutrophication in our lakes and rivers, the search for phosphate-free detergents intensifies daily. The polyacrylates described herein provide a very effective and attractive answer to the controversy.

**9 Claims, No Drawings**

# DETERGENT POLYELECTROLYTE BUILDERS

## BACKGROUND OF THE INVENTION

The word "affluent" has several meanings, one of them being: a tributary stream; the word "effluent" likewise has several meanings, one of them being: sewage after purification treatment. In our modern, affluent (opulent) society there are those who contend that the worst enemy of the "affluent" is the "effluent."

Whether or not this contention is proved or disproved, it has had a profound influence on the manufacturers of detergent compositions and their suppliers of inorganic phosphates. The phosphate which receives the greatest criticism is sodium tripolyphosphate STPP, a builder-sequestrant which improves the cleaning power of heavy duty detergents and is used, generally, in concentrations of better than 2:1, builder to detergent. The most commonly used detergent is sodium dodecylbenzene sulfonate.

According to those who would ban phosphates (annual use about 2.0 billion pounds at present), effluent containing these phosphates pollutes our rivers, streams and lakes by causing eutrophication, i.e., excessive growth of algae.

Attempts to substitute the phosphate builder-sequestrants have met with questionable success. For instance, the trisodium salt of nitrilotriacetic acid SNTA has been used in partial replacement of STPP but there is great hesitancy to use it unrestrainedly. Why? There is insufficient evidence that it will be safe for humans and the environment, particularly when used in large quantities. Assurance is being sought with respect to its physiological effects, its decomposition products, and the possibility that its chelating properties might give rise to usually high concentrations of lead and other metals in receiving waters.

Even if the putrefaction argument were proven false, sodium tripolyphosphate has the disadvantage of losing its sequestering power when formulated as a solution, i.e., it degenerates into the orthophosphate.

It should be understood that any material which is selected for use as a builder must exhibit good cleaning power under actual washing conditions. It pays, however, in selecting a candidate, to look for properties such as: ability to sequester, stability in solution, buffering action, hot and cold water solubility, emulsifying ability, soil suspension qualities, biodegradability, and the like. Of course, unit cost of the candidate vis-a-vis STPP is important. At present, for instance, the sodium salt of nitrilotriacetic acid is better than three times the cost of STPP. Obviously, if the candidate is three times more effective, i.e., much less thereof is required for comparable cleaning power, the disproportionate unit cost can be obviated. To date, however, the prior art has not come up with a substitute for STPP which is economically attractive.

Polyelectrolytes as detergent builders have previously been investigated with varying degrees of success. U.S. Pat. No. 3,308,067 to F.L. Diehl teaches the use, in conventional detergent compositions, of water-soluble salts of polyelectrolyte builders, such as poly(maleic acid), poly(itaconic acid), poly(fumaric acid), poly(citraconic acid), and other like aliphatic polycarboxylic acids, as well as copolymers thereof with, say, alkylenes and monocarboxylic acids, e.g., acrylic acid, methacrylic acid. While a smaller amount of these

polyelectrolytes is needed to provide cleaning effects comparable to STPP, the unit cost differential still favors the latter.

British Pat. No. 935,733 discloses detergents of the alkylaryl sulfonate variety in which a water-soluble salt of a copolymer of acrylic acid and/or methacrylic acid with vinyl-sulfonate is present in small amounts as an anti-redeposition agent. By comparison, "... sodium salts of polyacrylic acid alone have little effect," according to the patent.

British Pat. No. 451,342 (1936), on the other hand, teaches the addition of sodium polyacrylate and an alkali or ammonium salt of orthophosphoric acid, e.g., trisodium phosphate, to washing agents which are stable to the salts that cause the hardness of water, the additive preventing the precipitation of inorganic metal salts. The patent notes that "This fact is surprising, since polymeric carboxylic acids without addition of phosphates do not prevent the formation of precipitates on textiles when they are being washed."

U.S. Pat. No. 3,332,880 to Kessler, et al. discloses three-component detergent compositions comprising (A) a mixture of double-bond positional isomers of water-soluble salts of alkene — 1 — sulfonic acids containing from about 10 to about 24 carbon atoms, (B) a mixture of water-soluble salts of bifunctionally-substituted sulfur-containing saturated aliphatic compounds containing from about 10 to about 24 carbon atoms, the functional units being hydroxy and sulfonate radicals, and (C) a mixture comprising from 30–95 percent water-soluble salts of alkene disulfonates containing from about 10 to about 24 carbon atoms, and from about 5 to about 70 percent water-soluble salts of hydroxy disulfonates containing from about 10 to about 24 carbon atoms. The detergent compositions usually contain, in admixture, water-soluble inorganic and organic alkaline builder-sequestrants, e.g., sodium tripolyphosphate, sodium polyacrylate, sodium nitrilotriacetate, and the like.

Other well known detergent active compounds may be admixed with components (A), (B), and (C), above, e.g., anionic, nonionic, ampholytic and zwitterionic synthetic detergents. One example in the patent, Example III coupled with Table III, shows a mixture of detergent/builder, viz., sodium-4-hydroxy-n-hexadecyl-1-sulfonate/sodium polyacrylate, wherein the ratio is 1:5, parts by weight. It is not clear what the total composition is, or what its efficacy is, let alone the exact nature of the sodium polyacrylate used.

U.S. Pat. No. 3,085,916 to Zimmie et al. discloses the use of sodium polyacrylate as a flocculating agent for fluidizing silt deposits in cooling systems using river, lake or bay water containing mud and like contaminants. In other words, accumulations of mud, rust and silt in the jackets or pipings of cooling systems can be prevented or removed by flushing the system with a small amount of water-soluble, polyelectrolytic organic polymer, typically sodium polyacrylate.

"Surface Active Agents, Their Chemistry and Technology," by Anthony M. Schwartz and James W. Perry, 1949, Interscience Publishers, Inc., New York, p. 235, in discussing organic builders and mixtures states broadly: "Sodium polyacrylate has been used as a thickening agent and a builder for synthetic detergents." Further authors sayeth not.

It is obvious from the above patents and literature that polyacrylic acid salts have been used in detergent compositions in relatively minor roles. Attempts have been made to recognize their anti-redeposition properties in conjunction with other polymers, their flocculating attributes, their additive effect as builders in combination with proven agents, e.g., sodium tripolyphosphate. Alkali metal, ammonium or substituted-ammonium salts of polyacrylic acid have apparently never gone it alone. The present invention demonstrates quite conclusively that sodium polyacrylate, for instance, is anything but an also-ran.

It can be readily appreciated that polymeric acrylic acids and their salts come in many different molecular weights. The patents and literature discussed hereinabove are, for the most part, quite silent as to the inherent viscosity (I.V.), a measure of polymer molecular weight, and other physical properties of the various polyacrylic acid salts suggested as flocculating and anti-redeposition agents. As will be evident hereinafter, the art could not and did not recognize the advantages provided by the present discovery. Clearly the art relegated the polyacrylates to a lesser role in the race to upgrade detergent compositions. Clearly the art had no concept of the efficacy of these polyacrylates as full-fledged substitutes for the "suspect" phosphate and other builder-sequestrants. In fact, as will also be seen hereinafter, attempts to combine alkali metal polyacrylates having the physical properties contemplated herein with, say, STPP to make up a predetermined builder-sequestrant concentration have resulted in detergency compositions which gave less desirable detergency values (cleaning power) when compared with the same predetermined concentration of, say, sodium polyacrylate only.

Very possibly the art was concerned, as it should have been, that alkali metal polyacrylates at higher molecular weights might tend to flocculate and become a redeposition problem themselves. By virtue of the present discovery, however, this inhibition has been eliminated. Quite surprisingly, it has been found, the relatively high molecular weight alkali metal polyacrylates are very effective builder-sequestrants which exhibit superior cleaning power.

Accordingly, it is an object of the present invention to replace in conventional detergent compositions all of the builder-sequestrant commonly used, be it a phosphate, sodium nitrilotriacetic acid, or the like.

Another object of the instant invention is to substitute said builder-sequestrants with an alkali metal, ammonium or substituted ammonium polyacrylate of predetermined molecular weight.

Still another object of the present invention is to provide detergent builder-sequestrants equal to and better than the previously proposed phosphate-free builders, e.g., the trisodium salt of nitriloacetic acid SNTA, the latter itself being "suspect" and at least three times as expensive as STPP.

### DESCRIPTION OF THE INVENTION

According to the present invention a washing composition is prepared in which are present as essential components an active synthetic organic detergent and an organic alkaline builder-sequestrant salt. More particularly, the novel detergent composition of the

present invention contains as essential ingredients a synthetic organic detergent selected from non-soap anionic and non-ionic surface active compounds and an organic alkaline builder-sequestrant selected from alkali metal, ammonium or substituted ammonium polyacrylates, the latter having an inherent viscosity (I.V.), measured in 2 N NaOH as shown hereinafter, in the range of about 0.05 to about 1.25 preferably in the range of about 0.30 to about 1.0.

Pursuant to a typical embodiment of the present invention, a detergent composition is prepared from active ingredient sodium dodecylbenzene sulfonate and builder ingredient sodium polyacrylate having an inherent viscosity of 0.8 in 2N sodium hydroxide, I.V. being a measure of molecular weight. Obviously the efficacy of the builder-sequestrant will vary depending upon the concentration thereof with respect to the synthetic organic detergent component and the total detergent composition. For example, it has been found that at a concentration of 20 percent sodium dodecylbenzene sulfonate, based upon the total formulation (100 percent), excellent results are achieved when using about 40 percent sodium polyacrylate, the remaining 40 percent of the formulation comprising additives, such as inorganic alkaline salts, e.g., silicates, carbonates and sulfates, anti-redeposition agents, such as sodium carboxymethylcellulose (CMC), perfume, coloring agents, bleaching compounds, and many other ingredients which are widely and generally used to improve the overall performance and aesthetic characteristics of detergent compositions, such as anti-tarnishing agents, bactericidal agents, fluorescers, germicidal agents, and the like.

The concentration of active detergent and builder-sequestrant best suited for the novel detergent compositions of the present invention is generally based upon the end use intended for each composition. Obviously, a light duty detergent composition, such as that used for dishwashing or for washing delicate apparel, would not require as high a concentration of active and/or builder-sequestrant as would a heavy duty composition used for laundering soiled outerwear clothing. In general, the concentration of active detergent ranges from about 10 to about 30 percent, preferably from about 15 to about 25 percent, based upon the total formulation as defined hereinabove.

As to the builder-sequestrant contemplated herein, a concentration in the range of about 8 to about 60 percent, preferably from about 10 to 40 percent, likewise based upon the above-defined total formulation, is best suited for the present invention.

The ratio of active detergent to builder-sequestrant suitable for the instant invention may also vary significantly, depending upon end use intended for the detergent composition. Generally, a ratio of about 1:5 to about 2:1, active/builder-sequestrant, is preferred, but ratios in the range of about 1 to 10, or greater, and 5 to 1 may be used.

The detergent compositions of the present invention are usually used at a pH in aqueous solution of from about 8 to about 12.5, preferably from about 9 to about 11. Furthermore, the novel compositions are effective in a wide range of wash water temperatures. Preferably, however, temperatures in the range of 45° to 200° F are used, best results being achieved in the mid range, say, from about 80° to about 160° F.

While sodium polyacrylate is demonstrated as one of the preferred polyacrylic acid salts, other water-soluble alkali metal salts, e.g., potassium, lithium, are contemplated herein, as well as water-soluble ammonium and substituted ammonium salts, such as methylamine and triethylamine salts. Of course, mixtures of these polyacrylate salts may be used effectively under the conditions and concentrations described herein.

Again, while the alkali metal salts of dodecylbenzene sulfonic acid have been singled out hereinbefore as very desirable active detergents (surfactants) for use with the novel builder-sequestrants of the present invention, other anionic surface active compounds may be used very effectively in the concentrations and ratios given above. Anionic surface active compounds can be broadly described as compounds which contain hydrophilic or lyophilic groups in their molecular structure and which ionize in an aqueous medium to give anions containing the lyophilic group. These compounds include the sulfated or sulfonated alkyl, aryl and alkyl aryl hydrocarbons and alkali metal salts thereof, for example, sodium salts of long chain alkyl sulfates, sodium salts of alkyl naphthalene sulfonic acids, sodium salts of sulfonated abietenes, sodium salts of alkyl benzene sulfonic acids, particularly those in which the alkyl group contains from eight to 24 carbon atoms, sodium salts of sulfonated mineral oils and sodium salts of sulfosuccinic acid esters, such as sodium dioctyl sulfosuccinate.

Advantageous anionic surfactants include the higher alkyl aryl sulfonic acids and their alkali metal and alkaline earth metal salts, such as, for example, sodium tridecyl sulfonate, magnesium dodecyl benzene sulfonate, potassium tetradecyl benzene sulfonate, ammonium dodecyl toluene sulfonate, lithium pentadecyl benzene sulfonate, sodium dioctyl benzene sulfonate, disodium dodecyl benzene disulfonate, disodium diisopropyl naphthalene disulfonate, and the like, as well as the alkali metal salts of fatty alcohol esters of sulfuric and sulfonic acids, the alkali metal salts of alkyl aryl (sulfothioic acid) ethers and the alkyl thiosulfuric acid, etc. Preferred anionic organic surface active agents are, as noted hereinbefore, sodium salts of alkyl benzene sulfonic acids and particularly preferred sodium salts of alkyl benzene sulfonic acids are those in which the alkyl group or radical contains 10 to 18 carbon atoms in a straight i.e., unbranched) chain.

As indicated hereinabove, nonionic surface active compounds may be used as the active detergent. Nonionic surface active compounds can be broadly described as compounds which do not ionize but usually acquire hydrophilic characteristics from an oxygenated side chain, such as polyoxyethylene, while the lyophilic part of the molecule may come from fatty acids, phenols, alcohols, amides or amines. Examples of nonionic surfactants include products formed by condensing one or more alkylene oxides of two to four atoms, such as ethylene oxide or propylene oxide, preferably ethylene oxide alone or with other alkylene oxides, with a relatively hydrophobic compound, such as a fatty alcohol, fatty acid, sterol, a fatty glyceride, a fatty amine, an aryl amine, a fatty mercaptan, tall oil, etc. Nonionic surface active agents also include those products produced by condensing one or more relatively lower alkyl alcohol amines (such as methanolamine, ethanolamine, propanolamine, etc.) with a fatty acid

such as lauric acid, cetyl acid, tall oil fatty acid, abietic acid, etc., to produce the corresponding amide.

Still other nonionic surface active compounds include the amine oxides and phosphine oxides and preferably the unsymmetrical trialkyl-amine oxides and phosphine oxides wherein two of the alkyl groups are lower alkyl groups (1 to 4 carbon atoms) and the third alkyl group is a higher alkyl group (eight to 18 carbon atoms). Examples include dimethyldodecylamine oxide, dimethyldodecylphosphine oxide, dimethyltetradecyl amine oxide, dimethyltetradecyl phosphine oxide, diethylhexadecylamine oxide, diethylhexadecylphosphine oxide, and the like.

Particularly advantageous nonionic surface active agents are condensation products of a hydrophobic compound having at least one active hydrogen atom and a lower alkylene oxide (for example, the condensation product of an aliphatic alcohol containing from about eight to about 18 carbon atoms) and from about three to about 30 mols of ethylene oxide per mol of the alcohol, or the condensation product of an alkyl phenol containing from about eight to about 18 carbon atoms in the alkyl group and from three to about 30 mols of ethylene oxide per mol of alkyl phenol. Other advantageous nonionic detergents include condensation products of ethylene oxide with a hydrophobic compound formed by condensing propylene oxide with propylene glycol.

The detergent compositions of the present invention may be made into liquid solutions, granules, flakes, tablets or bars. Regardless of form, however, only small concentrations of these novel detergent compositions are needed in an aqueous medium to realize excellent cleaning power. Generally less than about 0.2 percent by weight, based upon the combined weight of the detergent composition and water, will provide detergent values which are as good and better than those of the conventional detergents presently enjoying the greatest commercial success.

Evidence of the effectiveness of the novel detergent compositions of the present invention is presented hereinafter with a view to providing illustrative compositions within the purview of the present invention. The person skilled in the art will readily appreciate that the specific embodiments in the following examples and illustrations are just that, illustrative and not unduly restrictive:

#### EXAMPLE I

Sodium polyacrylate builder-sequestrant was prepared by first polymerizing acrylic acid and then reacting the resulting polyacrylic acid with NaOH. Polyacrylic acid of suitable molecular weight, as determined by inherent viscosities within the range specified hereinabove, was prepared by using a 2-liter round bottom flask having two (2) superimposed calibrated dropping funnels from which acrylic acid monomer and catalyst sodium persulfate were fed separately and continuously into the 2-liter flask. To record the temperature of the reaction mixture a thermometer was inserted into the mixture through the mouth of the flask; to control the reaction temperature the 2-liter flask was placed in a hot water bath.

Into the flask was placed 690 cc. of H<sub>2</sub>O, and 10 percent of the total monomer feed of 250 cc., as well as 10

cc. of the total catalyst solution (1.2 grams  $\text{Na}_2\text{S}_2\text{O}_8$  in 60 cc. of water) and the resulting mixture heated to 80° C., the hot water in the bath reading 81° C. The remainder of the total monomer and catalyst solution was added continuously and temperature readings taken at 10-minute intervals and recorded as shown:

TABLE I

Time (in min.)	Temperature °C Reactor Bath	Remaining Monomer (cc.)	Remaining Catalyst (c.c)
10	80.0	225	50
20	93.0	206	46
30	94.5	187	42
40	95.5	168	38
50	96.0	149	34
60	96.0	130	30
70	95.5	111	26
80	96.0	92	22
90	96.0	73	18
100	95.0	54	14
110	96.0	35	10
120	96.0	16	5
130	96.0	0	0

The reaction mixture, subsequent to addition of all monomer and catalyst, was maintained at 95° C for 2 hours and then cooled to room temperature. The resulting 25 percent (wt.) polyacrylic acid solution, subjected to viscosity measurement, indicated an inherent viscosity (I.V.) of 0.80, a measure of its molecular weight.

The procedure for measuring viscosity was as follows:

SCOPE: Provides the inherent viscosity of a 0.5 percent (wt.) solution of polyacrylic acid.

REAGENT: 2N NaOH

APPARATUS: Cannon-Fenske Series 75 viscometer. Constant temperature ( $25 \pm 0.02^\circ \text{C}$ ) water bath. (Both above items sold by Cannon Instrument Co.) Stop watch capable of reading 0.1 second. Rubber bulb (ca. 4 oz.) on vacuum source.

#### PROCEDURE:

1. Prepare in 100 mil. volumetric flask a 0.5 percent (wt.) solution of polymer in 2N NaOH by adding 0.5g. polymer/100 mil. solution at 25° C. Shake to dissolve.

2. Pipet 10 mil. of same solvent used to prepare sample into series 75 Cannon-Fenske viscometer which has been firmly clamped in true vertical position in bath. Allow to equilibrate. Using rubber bulb or vacuum source, draw liquid into upper bulb above fiducial mark. Allow to drain, and accurately time flow between upper and lower marks. This is solvent flow time  $t_0$ .

Repeat operation (2) to check flow time. It should be within  $\pm 0.3$  second.

3. Clean viscometer and repeat (2) with polymer solution. Result obtained is solution flow time  $t_1$ .

CALCULATIONS: The inherent viscosity  $[\eta]$  inh. is given approximately by:

$$1nt_1/t_0/C$$

UNITS:  $[\eta]$  inh. dL/g.; C in g./dL

The 25 percent (wt.) polyacrylic solution having a viscosity (I.V.) of 0.80 was then formulated into a de-

tergent composition as follows (all percentages by weight):

#### DETERGENT FORMULATION

Composition		
20%	Active-sodium dodecylbenzene sulfonate*	
40%	<sup>11</sup> Builder - Sodium polyacrylate	
0.5%	Sodium carboxymethylcellulose (CMC)	
6.0%	Sodium Metasilicate	
33.5%	Sodium Sulfate	
100.0%		
Formulation		
Active	7.5g of 40% Sulframin 40	3.0g Active
Builder	18.3g of 25% Polyacrylic Acid	(4.6g Acid)
	10.66ml of 6N NaOH	(2.56g NaOH)
15	These React to Give	6.0g of Builder
CMC		0.075g
Sodium Metasilicate		0.9g
Sodium Sulfate-Sulframin 40	4.35g	
Addition of 0.675g		5.025
Total Solid		15.0g
20	Made up to 1 liter to give a 1.5% Solution	

\*Sulframin 40 - sold by Witco Chemical Corp., Ultra Division

<sup>11</sup>Builder - Sequestrant

The detergent formulation thus prepared was used in the following detergency testing procedure:

1. 100 ml. of 1.5 percent detergent solution is diluted with 900 ml. of hard water to give a 0.15 percent detergent concentration for testing. pH adjusted to 9.5 (if necessary) with sodium hydroxide solution.

2. Hard water has 180 ppm of 2:1 calcium to magnesium.

3. Each pot of the Terg-o-Tometer\* (\*Trademark for apparatus sold by U.S. Testing Co.) is filled filled with 1 liter of the detergent solution.

4. Bath temperature, 120° F: 90 cycles/minute agitation.

5. Four swatches (4 × 4 inches) of standard soiled cloth are added to each pot and washed for 10 minutes.

6. Pot emptied; hand squeeze; dry in commercial dryer for 20 minutes.

7. Read swatches on Hunter D-25\*\* (\*\*Photo-reflectance meter sold by Hunter Laboratories.) front and back; four layers.

8.  $\Delta L$  value determined.

The detergent formulation described just above having 40 percent by weight builder-sequestrant sodium polyacrylate and having an I.V. of 0.80 gave an average  $\Delta L$  (detergency value) of 39.

#### EXAMPLE II

Example I, above, was repeated in every essential respect with the exception that the builder-sequestrant concentration was reduced from 40 to 20 percent, and the sodium sulfate concentration increased proportionately to maintain the 100 percent total formulation. The average  $\Delta L$  (detergency value) was 36.

#### EXAMPLE III

Example II, above, was repeated in every essential respect with the exception that the builder-sequestrant concentration was reduced from 40 percent to 10 percent, and the sodium sulfate concentration increased proportionately to maintain the 100 percent total formulation. The average  $\Delta L$  (detergency value) was 34.

## EXAMPLE IV

Examples I, II and III, above, were repeated in every essential respect with the exception that the  $\text{Na}_2\text{S}_2\text{O}_8$  catalyst concentration used to polymerize acrylic acid was 0.56 gram in 60 cc. of water and the resulting polymer I.V. was 1.21. Using the corresponding sodium polyacrylate polymer (I.V. 1.21) at the concentrations given in Examples I (40 percent), II (20 percent), and III (10 percent), the resulting  $\Delta\text{L}$  detergency value averages were, respectively, as follows: 37, 33 and 28.

## EXAMPLE V

Examples I, II, and III, above, were repeated in every essential respect with the exception that the  $\text{Na}_2\text{S}_2\text{O}_8$  catalyst concentration used to polymerize acrylic acid was 1.3 grams in 60 cc. of water and the resulting polymer I.V. was 0.66. Using the corresponding sodium polyacrylate polymer (I.V. .66) at the concentrations given in Examples I (40 percent), II (20 percent), and III (10 percent), the resulting  $\Delta\text{L}$  detergency value averages were, respectively, as follows: 36, 35 and 33.

## EXAMPLE VI

By comparison, each of Examples I, II and III, above, was repeated using sodium tripolyphosphate (100 percent active) as the builder-sequestrant in lieu of sodium polyacrylate. At the 40 percent, 20 percent and 10 percent concentrations (all other ingredients being present in the concentrations given in Examples I, II and III, above), STPP gave  $\Delta\text{L}$  detergency value averages of 36, 28 and 24, respectively.

## EXAMPLE VII

Example II, above, is repeated in every essential respect only the 20 percent sodium polyacrylate builder-sequestrant was replaced with a 20 percent concentration of builder-sequestrant made up of 2 parts of STPP (100 percent active) and 1 part of the sodium polyacrylate of Example II. The  $\Delta\text{L}$  detergency value average was 29.9.

Quite obviously, the builder-sequestrants of the present invention manifest superior cleaning power and are very effective, suprisingly enough, in a totally phosphate-free formulation. In fact, as Example VII, above, clearly demonstrates, particularly when its  $\Delta\text{L}$  average is compared with that of Example II, above,

sodium polyacrylate works better as a total substitute, rather than as a partial substitute, for sodium tripolyphosphate.

Furthermore, the  $\Delta\text{L}$  values of STPP in Example VI vis-a-vis sodium polyacrylate  $\Delta\text{L}$  values (Examples I, II, III) clearly favor the latter builder-sequestrant's cleaning power.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of this invention as described hereinabove and as defined in the appended claims.

What is claimed is:

1. An essentially phosphate-free detergent composition in which the principal cleaning components are an anionic or non-anionic detergent and an organic alkaline builder-sequestrant selected from alkali metal, ammonium or substituted ammonium polyacrylates having an inherent viscosity, in 2 normal sodium hydroxide, in the range of about 0.30 to about 1.00, the detergent being present in a concentration of about 10 percent to about 30 percent, and the builder-sequestrant being present in a concentration of about 10 percent to about 40 percent, said percentages being based on the total weight of the composition.

2. The composition of claim 1 wherein the builder sequestrant is an alkali metal polyacrylate.

3. The composition of claim 1 wherein the surfactant is selected from non-soap anionic and non-ionic surfactants.

4. The composition of claim 1 wherein the surfactant is present in the concentration of about 15 to about 25 percent this range being based, by weight, on the total formulation weight.

5. An aqueous solution of the detergent composition of claim 1 wherein the solution has a pH in the range of about 8 to about 12.5.

6. An aqueous solution of the detergent composition of claim 1 wherein the solution has a pH in the range of about 9 to about 11.

7. The composition of claim 2 wherein the builder-sequestrant is sodium polyacrylate.

8. The composition of claim 3 wherein the surfactant is an alkali metal alkylaryl sulfonate.

9. The composition of claim 8 wherein the surfactant is sodium dodecylbenzene sulfonate.

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#### Disclaimer

3,706,672.—*Preston Kuhn Martin*, Fanwood, and *Richard Howard Kelly*, West Orange, N.J. DETERGENT POLYELECTROLYTE BUILDERS. Patent dated Dec. 19, 1972. Disclaimer filed Aug. 12, 1974, by the assignee, *Celanese Corporation*.

Hereby enters this disclaimer to claims 1-9 of said patent.

[*Official Gazette April 1, 1975.*]