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64 Detergents containing polyacrylate polymer.

⑤ Detergents containing organic surfactant, non-phosphorus detergent builder and polyacrylate polymer having a weight average molecular weight of from about 2,000 to about 10,000 are disclosed.

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#### DETERGENTS CONTAINING POLYACRYLATE POLYMER

# Antoinette L. Larrabee Gianfranco Luigi Spadini

#### Technical Field

The present invention relates to detergent compositions containing organic surfactant, non-phosphate detergent builder, preferably an alkali metal silicate, and polyacrylate polymer having a weight average molecular weight of from about 2,000 to about 10,000.

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## Background Art

U.S. Patent 4,072,621, Rose, issued Feb. 7, 1978, discloses the addition of a water-soluble copolymer of a vinyl compound and maleic anhydride to granular detergents containing aluminosilicate builders.

British Patent 2,048,841, Burzlo, published Dec. 17, 1980, discloses the use of polymeric acrylamides to stabilize aqueous suspensions of zeolites. The suspensions are said to be suitable for spray-drying to obtain detergent compositions.

- U.S. Patent 3,933,673, Davies, issued Jan. 20, 1976, describes the use of partial alkali metal salts of homo- or copolymers of unsaturated aliphatic mono- or polycarboxylic acids as builders which provide improved storage properties.
- U.S. Patent 3,794,605, Diehl, issued Feb. 26, 1974, relates to the use of from 0.1% to 20% of a mixture of salts of cellulose sulfate esters and copolymers of a vinyl compound with maleic anhydride to provide whiteness maintenance benefits to detergent compositions.
- U.S. Patent 3,922,230, Lamberti et al, issued November 25, 1975, discloses detergent compositions containing oligomeric polyacrylates.
- 30 U.S. Patent 4,031,022, Vogt et al, issued June 21, 1977, discloses detergent compositions containing copolymers of alphahydroxyacrylic acid and acrylic acid.
  - U.S. Patent 4,378,080, Murphy, issued April 5, 1983, discloses low levels of film forming polymers for improving detergent granules' structure.

British Patent Application 2,097,419A, published November 3,

1982, discloses "base bead" compositions containing low levels of low molecular weight especially 1,000-2,000, polyacrylate for structure reasons.

British Patent 1,333,915, published Oct. 17, 1973, discloses that polyacrylic acids of molecular weight greater than 1000 and having from 5-55% of its carboxyl groups neutralized as the sodium salt are free-flowing powders useful as detergent builders.

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British Patent 1,380,402, Pritchard et al, published Jan. 15, 1975, relates to the addition of low levels of reactive and non-reactive polymers to provide free-flowing granular detergents containing nonionic surfactants.

## Summary of the Invention

The present invention encompasses a detergent composition comprising:

- (a) from about 5% to about 50% by weight of organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof;
- (b) from about 5% to about 80% by weight of non-phosphor-20 ous detergent builder;
  - (c) from about 0.3% to about 5% by weight of a polyacrylate polymer soluble in an aqueous slurry comprising the above components and having a weight average molecular weight of from about 2,000 to about 10,000.

#### Detailed Description of the Invention

The detergent compositions of the present invention contain organic surfactant, water-soluble non-phosphorus detergent builder, and a polyacrylate polymer of selected molecular weight at a low level. The polyacrylate polymers herein provide a surprising boost to the removal of clay soils even at these low levels which do not provide substantial builder capacity.

The compositions of the present invention can be prepared by drying an aqueous slurry comprising the components, by agglomeration or by mixing the various ingredients, either dry or in liquid form, either aqueous or anhydrous. The effect is obtained regardless of the method of preparation. It is believed that the effect is obtained by some kind of surface modification.

## Organic Surfactant

The detergent compositions herein contain from about 5% to about 50% by weight of an organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof. The surfactant preferably represents from about 10% to about 30% by weight of the detergent composition. Surfactants useful herein are listed in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin, et al, issued December 30, 1975, both incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both incorporated herein by reference.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and substituted ammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and substituted ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ( $C_8$ - $C_{18}$  carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon

atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as  $C_{11-13} LAS$ .

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Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and from about 10 to about 20 carbon atoms in the alkyl group.

Other useful anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 8 to 20 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Water-soluble nonionic surfactants are also useful in the compositions of the invention. Such nonionic materials include 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 polyoxyalkylene group which is condensed with any particular

hydrophobic group can be readily adjusted to yield a watersoluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 8 moles of ethylene oxide per mole of alcohol.

Semi-polar nonionic surfactants useful herein include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

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Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Particularly preferred surfactants herein do not comprise substantial amounts of nonionic detergent surfactants and, preferably, are anionic surfactants, especially those selected from the group consisting of the alkali metal salts of  $C_{11-13}$  alkylbenzene sulfonates,  $C_{14-18}$  alkyl sulfates,  $C_{14-18}$  alkyl linear polyethoxy sulfates containing from about 1 to about 4 moles of ethylene oxide, and mixtures thereof.

## The Non-Phosphorous Detergent Builder

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The compositions of the present invention also contain from about 5% to about 80%, preferably from about 10% to about 70%, and most preferably from about 15% to about 60%, by weight of a non-phosphorous detergent builder. The non-phosphorous detergent builder can be either organic or inorganic in nature. They function as detergency builder materials in the laundering solution.

Non-phosphorous detergent builder are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium carbonates, silicates, carboxylates, and polycarboxylates other than the polyacrylates as defined hereinafter, especially non-polymeric polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. However, the present compositions preferably contain less than about 6%, more preferably less than about 4%, by weight of silicate materials for optimum granule solubility.

Specific examples of non-phosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of SiO<sub>2</sub> to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4.

An especially preferred detergency builder is crystalline aluminosilicate ion exchange material of the formula

$$Na_z[(AIO_2)(SiO_2)_v] \times H_2O$$

wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.5 and x is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula

 $M_z(zAlO_2.ySiO_2)$ 

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wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO<sub>3</sub> hardness per gram of anhydrous aluminosilicate.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg. equivalent of CaCO, water hardness/g. of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from mq. eq./g. to about 352 mg. aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca<sup>++</sup>/gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from

about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

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The amorphous aluminosilicate ion exchange materials usually have a Mg<sup>++</sup> exchange capacity of at least about 50 mg. eq. CaCO<sub>3</sub>/g. (12 mg. Mg<sup>++</sup>/g.) and a Mg<sup>++</sup> exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Patent 3,985,669, Krummel et al, issued October 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material in Zeolite A and has the formula

 $Na_{12}[A1O_2)_{12}.(SiO_2)_{12}].xH_2O$ wherein x is from about 20 to about 30, especially about 27.

Water-soluble, non-phosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium, carboxylates, polycarboxylates and polyhydroxysulfonates. Examples of non-polymeric polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. The compositions of this invention only contain the limited amount of polyacrylate defined hereinafter.

Other useful builders herein are sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclo-

hexanehexacarboxylate, cis-cyclopentanetetracarboxylate, and phloroglucinol trisulfonate.

Other suitable polycarboxylates are the polyacetal carboxy-lates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield, et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield, et al., both incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Other detergency builder materials useful herein are the "seeded builder" compositions disclosed in Belgian Patent No. 798,856, issued October 29, 1973, incorporated herein by reference. Specific examples of such seeded builder mixtures are: 3:1 wt. mixtures of sodium carbonate and calcium carbonate having 5 micron particle diameter; 2.7:1 wt. mixtures of sodium sesquicarbonate and calcium carbonate having a particle diameter of 0.5 microns; 20:1 wt. mixtures of sodium sesquicarbonate and calcium hydroxide having a particle diameter of 0.01 micron; and a 3:3:1 wt. mixture of sodium carbonate, sodium aluminate and calcium oxide having a particle diameter of 5 microns.

Preferably the builder is selected from the group consisting of zeolites, especially Zeolite A; carbonates, especially sodium carbonate; and citrates, especially sodium citrate.

Soaps, as described hereinbefore, can also act as builders depending upon the pH of the wash solution, the insolubility of the calcium and/or magnesium soaps, and the presence of other builders and soap dispersants.

The compositions herein preferably contain from about 0% to about 6%, preferably from about 0.5% to about 5%, and most preferably from about 1% to about 4%, by weight of an alkali metal silicate having a molar ratio of SiO<sub>2</sub> to alkali metal oxide of from about 1.0 to about 3.2, preferably from about 1.6 to about 2.4. Sodium silicate, particularly one having a molar ratio of from about 1.8 to about 2.2, is preferred.

The alkali metal silicates can be purchased in either liquid or granular form. Silicate slurries can conveniently be used to avoid having to dissolve the dried form in the aqueous slurry (e.g., crutcher mix) of the components herein.

#### Polyacrylate Polymer

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The compositions of the present invention contain from about 0.3% to about 5%, preferably from about 1.0% to about 3%, and more preferably from about 1.5% to about 2%, by weight of a polyacrylate polymer having a molecular weight of from about 2,000 to about 10,000, preferably from about 3,000 to about 8,000, and more preferably from about 3,000 to about 6,000. Optimum solubility of the polymer is obtained when it is in the form of an at least partially neutralized alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanol ammonium) salt. The alkali metal, especially sodium, salts are most preferred.

Lower levels of polyacrylate are preferred for cost reasons and there is less chance of an adverse effect on other detergent properties, e.g., cleaning of other soils, performance by minor ingredients such as enzymes or brighteners, etc.

Suitable polymers herein are the at least partially neutralized salts of polymers of acrylic acid. One can also use copolymers formed with small amounts of other copolymerisable monomers. The percentage by weight of the polymer units which is derived from acrylic acid is preferably greater than about 80%. Suitable copolymerisable monomers include, for example, methacrylic acid, hydroxyacrylic acid, vinyl chloride, vinyl alcohol, furan, acrylonitrile, methacrylonitile, vinyl acetate, methyl acrylate,

methyl methacrylate, styrene, alpha-methylstyrene, vinyl methyl ether, vinyl ether, vinyl propyl ether, acrylamide, ethylene, propylene and 3-butenoic acid.

Preferred copolymers of the above group contain at least about 90% by weight of units derived from the acrylic acid. Preferably essentially all of the polymer is derived from acrylic acid. Particularly preferred is sodium polyacrylate, especially when it has an average molecular weight of from about 3,000 to about 6,000.

#### Optional Components

The compositions of the invention preferably contain from about 0.3% to about 6.0%, preferably from about 0.5% to about 4.0%, and more preferably from about 0.7% to about 3.0% by weight of a water-soluble polymeric material, or mixtures thereof, containing at least about 50% ethylene oxide by weight, said polymer or mixtures thereof having a melting point not less than about 35°C. Preferably the polymeric material will have a melting point not less than about 45°C, more preferably not less than about 50°C and most preferably not less than about 55°C. Because the polymeric materials useful in the practice of the invention are generally mixtures representing a range of molecular weights, the materials tend to soften and begin to become liquid over a range of temperatures of from about 3°C to about 7°C above their melting point. Mixtures of two or more polymeric materials can have an even wider range.

Preferred polymers contain at least about 70% ethylene oxide by weight and more preferred polymers contain at least about 80% ethylene oxide by weight. Polyethylene glycol which can be said to contain essentially 100% ethylene oxide by weight is particularly preferred.

Preferred polyethylene glycols have an average molecular weight at least about 1000, and more preferably from about 2500 to about 20,000 and most preferably from about 3000 to about 10,000.

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Other suitable polymeric materials are the condensation products of  $C_{10-20}$  alcohols or  $C_{8-18}$  alkyl phenols with sufficient ethylene oxide, not less than about 50% by weight of the polymer, so that the resultant product has a melting point above about 35°C.

Block and heteric polymers based on ethylene oxide and propylene oxide addition to a low molecular weight organic compound containing one or more active hydrogen atoms are suitable in the practice of the invention. Polymers based on the addition of ethylene oxide and propylene oxide to propylene glycol, ethylenediamine, and trimethylolpropane are commercially available under the names Pluronics®, Pluronic® R, Tetronics® and Pluradots® from the BASF Wyandotte Corporation of Wyandotte, Michigan. Corresponding nonproprietary names of the first three trade names are poloxamer, meroxapol and poloxamine, respectively.

Preferably these ethylene oxide polymers are incorporated into the detergent crutcher and dried with a major portion of the detergent composition when forming granular compositions.

Other ingredients commonly used in detergent compositions can be included in the compositions of the present invention. These include solvents, diluents, sources of ionic strength, color speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, soil release agents, dyes, fillers, optical brighteners, germicides, non-builder alkalinity sources, enzymes, enzyme-stabilizing agents, and perfumes.

The following non-limiting examples illustrate the detergent compositions of the present invention.

All percentages, parts, and ratios used herein are by weight unless otherwise specified.

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## EXAMPLE I

	Component		Wt %
		A	<u>B</u>
	Na C <sub>13</sub> alkylbenzene sulfonate (C <sub>13</sub> LAS)	7.3	9.25
5	Na C <sub>14-15</sub> alkyl sulfate (C <sub>14-15</sub> AS)	7.3	9.25
	C <sub>12-13</sub> alkylpolyethoxylate (6.5) stripped		
	to remove unexthoxylated alcohol and		
	monoethoxylated alcohol ( $C_{12-13}$ $E_{6.5}$ )	2.0	<b>-</b> .
	C <sub>12</sub> alkyltrimethylammonium chloride	1.0	-
10	Na Zeolite A, hydrated (2-3μ)	23.8	23.8
	Na <sub>2</sub> CO <sub>3</sub>	13.1	13.1
	Na silicate (1.6r)	1.0	1.0
	Na <sub>2</sub> SO <sub>4</sub> , water, minors, Na polyacrylate		
	as indicated, etc.	Bal	ance

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The above compositions with the indicated amounts of the tested sodium polyacrylates were in miniwashers with assorted soils and stains present including the particulate soil (clay) that defines the "Cleaning Index". "Cleaning Index" is obtained by finding the panel score grades for each product using a scale in which 0 means "There is no difference."; 1 means "I think I see a difference."; 2 means "I see a difference."; and 3 means "I see a big difference.". The control product contains no polyacrylate and the best performing product is set at 100 with all other grades being ranked as a percent of the difference.

Test 1

Conditions: 95°F; indicated water hardness; Product A with different molecular weight sodium polyacrylates at the 1.5% level.

	Polyacrylate molecular weight	Cleaning	
30	as indicated	Index	LSD
	Pollycotton Fabric, 12 grains per gallon		
	none	0	30
	650	71	. 30
	2000	57	30
35	4500	100	30

	Cotton Fabric, 12 grains per gallon		
	none	0	30
	650	45	30
	4500	100	30
5	Polyester and Cotton Fabric (Polycotton),	5 grains per	gallon
	none	0	30
	650	0	30
	4500	100	30

# Test 2

10 Conditions: 95°F, indicated hardness, Product B with 1.5% of sodium polyacrylate with the indicated molecular weight.

		Cleaning		
		Index	LSD	
	Cotton Fabric (12 gpg)			
15	none	0	50	
	4500	100	50	
	8840	55	50	
	15,000	· 0	50	
	60,000	-167	50	
20	Polycotton Fabric (5 gpg)			
	none	0	40	
	4500	100	40	
	8840	100	40	
	15,000	46	40	
25	60,000	-31	40	
	Cotton Fabric (5 gpg)			
	none	0	30	
	4500	100	30	
	8840	70	30	
30	15,000	-20	30	
	60,000	-200	30	

As can be seen from the above, there is essentially no benefit from using a polyacrylate with a molecular weight above about 10,000 and for a consistent meaningful benefit, the molecular weight should be less than about 8,000. For optimum

LSD

performance, the molecular weight should not exceed about 6,000. Polymers containing less than 100%, e.g., 80%, acrylate monomers can be used with substantially equivalent results.

#### Test 3

Cleaning Index

Conditions: 95°F; underbuilt, and Product A containing the indicated amounts of Na Zeolite A and Na Polyacrylate (M.W. 4500).

		<b>5</b>				
		Polycotton				
10	% Polyacrylate	% Zeolite	Cotton Fabric	Fabric		
	none	23	0	0	25	
	1.5	23	100	95	25	
	9.6	18	85	100	25	
	11.8	none	72	59	<b>- 25</b>	

As can be seen from the above, the clay improvement is essentially independent of the amount of other detergent builder present and there is essentially no advantage in using more than about 5% of the polyacrylate.

#### **EXAMPLE II**

20	Component	<u>8</u>
	C <sub>13</sub> LAS	10
	C <sub>14-15</sub> AS	10
	Na Zeolite A, hydrated (2-3μ)	24.4
	Na <sub>2</sub> CO <sub>3</sub>	5
25	Na silicate (1.6r)	2
	Na sulfosuccinate	2
	Polyethylene glycol (M.W8000)	1.5
	Minors including protease and amylase,	
	Na <sub>2</sub> SO <sub>4</sub> and water	Balance

30 The above composition was prepared as a spray-dried granule and tested with (control) and without 1.5% added sodium polyacrylate (M.W. 4500). The temperature was 95°F., the water had 10 grains/gal. hardness and the results in panel score grade units difference were as follows for clay removal.

Clay on cotton fabric: 0.9 LSD = 0.51

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Clay on polycotton fabric: 1.0 LSD = 0.41

Based on these results, it is clear that a small amount of a low molecular weight polyacrylate provides a substantial cleaning boost for clay removal.

Preferred compositions are (1) spray-dried detergent granules wherein at least the surfactant and, preferably, the detergent builder are both in the detergent crutcher mix prior to spray drying and (2) liquid compositions.

#### CLAIMS

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- 1. A detergent composition comprising:
- (a) from about 5% to about 50% by weight of an organic detergent surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof;
- (b) from about 5% to about 80% by weight of a non-phosphorus detergent builder;
- (c) from about 0.3% to about 5% by weight of a polyacrylate polymer soluble in an aqueous slurry comprising the above components and having a weight average molecular weight of from about 2,000 to about 10,000.
- 2. The composition of Claim 1 wherein the organic surfactant comprises an anionic surfactant selected from the group consisting of alkali metal salts of  $C_{11-13}$  alkylbenzene sulfonates,  $C_{14-18}$  alkyl sulfates,  $C_{14-18}$  alkyl polyethoxy sulfates containing from about 1 to about 4 moles of ethyl-ne oxide, and mixtures thereof.
- 3. The composition of Claim 1 wherein the non-phosphate detergent builder comprises a zeolite, a carbonate or mixtures thereof.
- 4. The composition of Claim 1 comprising from about 1% to about 4% by weight of an alkali metal silicate having a molar ratio of from about 1.6 to about 2.4.
- 5. The composition of Claim 1 wherein the polyacrylate is a salt of a homopolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid, or a copolymer thereof containing at least about 80% by weight of units derived from said acids.
- 6. The composition of Claim 5 wherein the polymer has a weight average molecular weight of from about 3,000 to about 6,000.
- 7. The composition of Claim 6 wherein the polymer is sodium polyacrylate.

8. The composition of Claim 2 comprising from about 10% to about 30% by weight of the organic surfactant; from about 15% to about 60% by weight of non-phosphate detergent builder salt comprising hydrated sodium Zeolite A, carbonate, nitrilotriacetate, or mixtures thereof.

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- 9. The composition of Claim 8 comprising from about 1% to about 3% by weight of sodium polyacrylate having a weight average molecular weight of from about 3,000 to about 8,000.
- 10. The composition of Claim 9 prepared by spray-drying an aqueous slurry of the components.
- 11. The composition of Claim 10 comprising from about 10% to about 30% by weight of aluminosilicate ion exchange material of the formula  $Na_{12}[(AlO_2)_{12}.(SiO_2)_{12}].x$   $H_2O$ , wherein x is from about 20 to about 30.
- 12. The composition of Claim 1 which is substantially free of nonionic detergent surfactant.
- 13. The composition of Claim 12 wherein the non-phosphate detergent builder comprises a zeolite, a carbonate or mixtures thereof.
- 14. The composition of Claim 12 comprising from about 1% to about 4% by weight of an alkali metal silicate having a molar ratio of from about 1.6 to about 2.4.
- 15. The composition of Claim 12 wherein the polyacrylate is a salt of a homopolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid, or a copolymer thereof containing at least about 80% by weight of units derived from said acids.

- 16. The composition of Claim 12 wherein the polymer has a weight average molecular weight of from about 3,000 to about 6,000.
- 17. The composition of Claim 12 wherein the polymer is sodium polyacrylate.
- 18. The composition of Claim 1 prepared by spray-drying in which the organic detergent surfactant is in the spray-dried portion.
- 19. The composition of Claim 1 in the form of a liquid.
- 20. The composition of Claim 19 which is an aqueous liquid.





# **EUROPEAN SEARCH REPORT**

EP 84 20 0874

Category		h indication, where appropriate,	Releva		CLASSIFICATION	
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х	EP-A-O 080 222 GAMBLE CO.) * Pages 14,15, 1-3,5 *	(PROCTER & example 1, claims	1-3	,5,	C 11 D	3/3
}	1-3,5 "					
A			13,	15		
D,A	US-A-3 922 230 al.) * Claims 1,4 *	(V. LAMBERTI et				
D,A	US-A-4 031 022	(W. VOGT et al.)				
	* Claim 1 *					
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X: pa Y: pa do	CATEGORY OF CITED DOCU rticularly relevant if taken alone rticularly relevant if combined w cument of the same category chnological background on-written disclosure	JMENTS T: theory or E: earlier par after the first another D: documen L: documen	principle tent docui iling date t cited in t	underly ment, b the app other r	ying the invention out published on, dication reasons	or