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(54) Title: LOW pH GRANULAR LAUNDRY DETERGENT COMPOSITIONS CONTAINING ALUMINOSILICATE, CITRIC ACID AND CARBONATE BUILDERS**(57) Abstract**

Low pH, dense granular laundry detergent compositions contain a specific aluminosilicate, citric acid and carbonate builder system, and little or no phosphate. The composition provide good cleaning and have good physical properties.

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LOW PH GRANULAR LAUNDRY DETERGENT COMPOSITIONS
CONTAINING ALUMINOSILICATE; CITRIC ACID
AND CARBONATE BUILDERS

5

Technical Field

The present invention relates to low pH, granular laundry detergent compositions. Certain preferred compositions herein contain a low level of a chlorine scavenger, preferably an ammonium salt. The compositions minimize fading of fabric colors sensitive to higher wash water pHs and to the low levels of chlorine present in the wash and rinse water. Other preferred compositions herein are dense, low or no phosphate detergents containing a specific aluminosilicate, citric acid and carbonate builder system. These compositions provide good cleaning performance while maintaining good physical properties.

Background Art

Granular laundry detergents typically are formulated to provide a wash water pH of about 9.8 to 10.5. This pH range can cause fading of some fabric dyes after multiple laundry cycles. When the wash solution is diluted in the rinse, the pH is lowered to a range of about 7 to 9 where some fabric dyes are generally less sensitive to pH.

Chlorine is used in many parts of the world to purify water. To make sure that the water is safe, a small residual amount, typically about 1 part per million (ppm), of chlorine is left in the water. It has been found that even this small amount of chlorine can cause fading of chlorine-sensitive fabric dyes. In a typical wash, there is usually enough soil on the fabrics to scavenge residual chlorine and minimize damage to chlorine-sensitive dyes. However, in the rinse the soil levels are greatly reduced, as is the pH, and chlorine-sensitive dyes can fade after multiple laundering cycles. Chlorine is also more aggressive to dyes at the lower pHs. Thus, fading of fabric colors over time is a result of both the high pH of typical granular laundry

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detergents and the presence of residual chlorine in the wash and rinse water.

Delivering good cleaning performance from a low or no phosphate condensed detergent is difficult due to limitations in conventional spray dry processing. Additionally, trying to compensate with higher levels of actives (surfactant and builder) is limited without significantly diminishing product physical properties (solubility, lumping/caking, scoopability).

Summary of the Invention

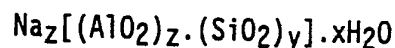
The present invention encompasses granular laundry detergent compositions comprising, by weight:

(a) from about 15% to about 25% of a mixture of a C₁₁-C₁₃ alkylbenzene sulfonate surfactant and a C₁₂-C₁₆ alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from about 4:1 to about 1:1;

(b) from about 1% to about 3% of an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from about 1.0 to about 2.4;

(c) from about 20% to about 30% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

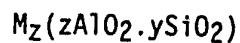
(i) crystalline aluminosilicate material of the formula:



wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from about 0.1 micron to about 10 microns, a calcium ion exchange capacity of at least about 200 mg CaCO₃ eq./g and a calcium ion exchange rate of at least about 2 grains Ca⁺⁺/gallon/minute/gram/gallon;

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(ii) amorphous hydrated aluminosilicate material of the empirical formula:



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 ion exchange capacity of at least about 50 milligram equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon; and

(iii) mixtures thereof;

(d) from about 4% to about 10% of citric acid;

(e) from about 5% to about 20% of an alkali metal carbonate; said composition having a pH of from about 7 to about 9.3 at a concentration of 1% by weight in water at 20°C, and said composition having a density of from about 500 to about 600 grams per liter.

Preferably, the present compositions also contain a chlorine scavenger employed in an effective amount to control residual chlorine in the wash and rinse water. The amount of chlorine scavenging material needed will vary, but only a small amount is used to avoid destroying hypochlorite bleach that may be added deliberately to treat bleach-sensitive stains.

Detailed Description of the Invention

The granular laundry detergent compositions of the present invention are formulated to provide a pH of from about 7 to about 9.3, preferably from about 8 to about 9.1, more preferably from about 8.5 to about 9.0, at a concentration of 1% by weight in water at 20°C. The individual components of the compositions herein are described in detail below.

Chlorine Scavenger

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When present in the compositions of the invention chlorine scavengers should not be used in a large excess since they will interfere with normal hypochlorite bleaches added to the wash water for stain removal and whitening. The level should be from about 0.01% to about 10%, preferably from about 0.05% to about 5%, most preferably from about 0.08 to about 2%, based on the molar amount equivalent to react with about 0.5 to about 2.5, typically about 1, ppm of available chlorine, per average rinse. If both the cation and the anion of the scavenger react with chlorine, which is desirable, the level is adjusted to react with an equivalent amount of available chlorine.

Suitable chlorine scavengers include the following polymers which can be divided into four groups according to their structural construction: polyethyleneimines, polyamines, polyamineamides and polyacrylamides, of which the polyethyleneimines, the polyamines and polyamineamides are especially preferred.

Suitable polyethyleneimines are obtained by acid-catalyzed polymerization of ethyleneimine and can be modified by urea and epichlorhydrin or dichlorethane. Polyethyleneimines can contain primary, secondary or tertiary amino groups as well as quaternary ammonium groups. Aqueous solutions of polyethyleneimines show basic reaction. The molecular weight can amount up to about 1,000,000.

Polyamines are addition or condensation products from multivalent aliphatic amines and compounds with several groups capable of reacting, for example, epichlorhydrin or alkylene dihalides. Therefore, they always contain several secondary, tertiary or even quaternary nitrogen atoms, as well as eventually also hydroxyl groups in the molecule. They are accordingly hydrophilic, polar compounds, which behave as polyelectrolytes and are water soluble, inasmuch as they do not contain large hydrophobic groups in the molecule. The polyamines exhibit basic

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reaction in aqueous solution. Suitable compounds, for example, are described in U.S. Patent 2,969,302.

5 Polyamineamides contain amino- and amido groups in the molecule at the same time. They are made, for example, by condensation of multibasic acids, for example, dibasic, saturated, aliphatic C₃ to C₈ acids and polyamines, as well as with compounds, which contain several groups capable of reacting, such as, for example, epichlorhydrin. These compounds also demonstrate
10 basic reaction in aqueous solution. Suitable polyamineamides are described, for example, in U.S. Patent 2,926,154.

Polyacrylamides having amino groups and molecular weights up to several million are suitable for use herein. By building in carboxyl groups, which are formed, for example, by partial
15 hydrolysis, anionic polyacrylamides are obtained in addition to amido groups, while polyacrylamides containing amino groups exhibit basic reaction in aqueous solution. Amino groups can be introduced, for example, by reaction with alkali and hypobromite or hypochlorite.

20 It is common to all polymers that they are water soluble. Such polymers are commercial products. Compounds especially well suited as inserts to the detergents conforming to the discovery are the polyethyleneimines and polyamines, which exhibit strong basic reaction in water. Examples of commercially available
25 polyethyleneimines, which are particularly appropriate, are "Epomin SP-003" from Nippon Shokubai, "Lugalvan G20 and G35" from BASF, and "Ethyleneamine E-100" from Dow Chemical. These polymers can be added either alone or together with water soluble polymers from melamine or urea and formaldehyde. Other polymers suitable
30 for the detergents conforming to the discovery are, for example, the water soluble polymers based on alkyleneimines, acrylamides as well as melamine or urea and formaldehyde, which are described in the "Encyclopedia of Polymer Science and Technology", John Wiley & Sons, Inc., New York, 1968, Vol. 9, p. 762. An addition of these
35 polymers to the detergents conforming to the discovery in

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combination with the amino- and/or amido group-containing polymers causes an intensification of the dye-protective effect.

5 Preferred polymers for use in the preferred anionic surfactant containing compositions herein are polyethyleneimines. Polyethyleneimines are believed to be particularly efficient chlorine scavengers because they adsorb to cotton fibers. In an anionic surfactant matrix, ion pairing of the amines with surfactant or polymeric carboxylates tends to dramatically lower
10 the solubility of the polymeric amine. The solubility of the polymeric amine complexes can be maintained by utilizing materials of relatively low molecular weight. The molecular weight of the chosen amine polymer should be controlled to achieve a fabric substantivity of preferably at least 50%. A low substantivity
15 will not allow efficient carryover into the rinse. Preferred polyethyleneimines have a molecular weight of less than about 800, more preferably from about 200 to about 400.

The cationic charge and the solubility of the polymeric amine allow the deposition of the polymer onto cotton fabric. The
20 affinity the polymer has for fabric increases with lower pH, or higher molecular weight. Thus, a balance of these properties (solubility, solution pH, and polymer molecular weight) controls the efficiency of the chlorine scavenger on fabric and in solution. The optimal composition will allow a balance of polymer
25 on fabric (for carryover from wash to rinse) and in solution (for an efficiency rate of reaction with chlorine).

Other chlorine scavengers herein are anions selected from the group consisting of reducing materials like sulfite, bisulfite, thiosulfite, thiosulfate, iodide, nitrite, etc. and antioxidants
30 like carbamate, ascorbate, etc. and mixtures thereof. Conventional non-chlorine scavenging anions like sulfate, bisulfate, carbonate, bicarbonate, nitrate, chloride, borate, phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, salicylate, etc. and mixtures thereof can be
35 used with ammonium cations.

Other chlorine scavengers useful herein include ammonium

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sulfate (preferred), and primary and secondary amines of low volatility such as ethanolamines, amino acids and their salts, polyamino acids and their salts, fatty amines, glucoseamine and other aminated sugars. Specific examples include tris(hydroxymethyl) aminomethane, monoethanol amine, diethanol amine, sarcosine, glycine, iminodiacetic acid, lysine, ethylenediamine diacetic acid, 2,2,6,6-tetramethyl piperinol, and 2,2,6,6-tetramethyl piperinone.

Other chlorine scavengers include phenol, phenol sulfonate, 2,2-biphenol, tiron, and t-butyl hydroquinone. Preferred are meta-polyphenols such as resorcinol, resorcinol monoacetate, 2,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, and 2,4-dihydroxyacetophenone.

Peroxide bleach sources, e.g. perborate, percarbonate and other persalts, can also be used in minor amounts (less than 3% by weight, preferably less than about 2%) as a chlorine scavenger herein. However, peroxides are not efficient chlorine scavengers because they cannot be used at high enough levels to carry over to the rinse water without risk of bleach damage to colors.

Detergent compositions comprising the chlorine scavenger and the detergent component can be provided having various ratios and proportions of these two materials. Of course, the amount of the chlorine scavenger can be varied, depending upon the level of residual chlorine expected by the formulator. Moreover, the amount of detergent component can be varied to provide either heavy-duty or light-duty products, as desired. This invention relates primarily to detergent compositions that contain essentially no additional ingredients which are chlorine scavengers. For example, the other materials present should not provide any substantial additional amounts of ammonium cations in the wash solution.

Detergent Additives

The amount of the detergent surfactant component can, as noted hereinabove, vary over a wide range which depends on the desires of the user. In general, the compositions contain from about 5% to about 50%, preferably from about 10% to about 30% by

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weight, of detergent surfactant, which preferably is an anionic surfactant.

5 The detergent compositions of the instant invention can contain all manner of organic, water-soluble detergent surfactant compounds. A typical listing of the classes and species of detergent compounds useful herein appear in U.S. Patent 3,664,961, incorporated herein by reference. The following list of detergent
10 compounds and mixtures which can be used in the instant compositions is representative of such materials, but is not intended to be limiting.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful as the detergent component of the composition herein. This class of detergents includes ordinary alkali metal soaps such
15 as the sodium, potassium, salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 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
20 salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Another class of detergents includes water-soluble salts, particularly the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl group
25 containing from about 8 to about 22 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 detergents which form a part of the detergent compositions of the present invention are the sodium and potassium
30 alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; and 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
35 configuration, e.g. those of the type described in United States

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Patents 2,220,099 and 2,477,383, incorporated herein by reference. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average of the alkyl groups is about 12 carbon atoms, abbreviated as C₁₂ LAS.

Other anionic detergent surfactant compounds herein include 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; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 13 carbon atoms.

Water-soluble nonionic synthetic detergent surfactants are also useful as the detergent component of the instant composition. Such nonionic detergent materials can be broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

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 a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Other suitable nonionic synthetic detergents 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 about 13 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 4 to about 15 moles of ethylene oxide per mole of alkyl phenol.

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The water-soluble condensation products of aliphatic alcohols having from about 8 to about 22 carbon atoms, in either straight chain or branched configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from about 3 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms, are also useful nonionic detergents herein.

Semi-polar nonionic detergent surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 20 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxide detergents containing one alkyl moiety of from about 10 to 20 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; and water-soluble sulfoxide detergents containing one alkyl or hydroxyalkyl moiety of from about 10 to about 20 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to about 3 carbon atoms.

Ampholytic detergent 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 about 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic detergent surfactants include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group. The quaternary compounds, themselves, e.g. cetyltrimethyl ammonium bromide, can also be used herein.

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Other useful detergent surfactant compounds herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to about 20 carbon atoms in the fatty acid group and from 1 to about 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to about 9 carbon atoms in the acyl group and from about 9 to about 20 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to about 20 carbon atoms in the alkyl group and from about 1 to about 12 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred water-soluble organic detergent compounds herein include linear alkylbenzene sulfonates containing from about 11 to about 13 carbon atoms in the alkyl group; C₁₀₋₁₈ alkyl sulfates; the C₁₀₋₁₆ alkyl glyceryl sulfonates; C₁₀₋₁₈ alkyl ether sulfates, especially wherein the alkyl moiety contains from about 14 to 18 carbon atoms and wherein the average degree of ethoxylation between 1 and 6; C₁₀₋₁₈ alkyl dimethyl amine oxides, especially wherein the alkyl group contains from about 11 to 16 carbon atoms; alkyl dimethyl ammonio propane sulfonates and alkyl dimethyl ammonio hydroxy propane sulfonates wherein the alkyl group in both types contains from 14 to 18 carbon atoms; soaps, as hereinabove defined; and the condensation product of C₁₀₋₁₈ fatty alcohols with from about 3 to about 15 moles of ethylene oxides.

Specific preferred detergents for use herein include: sodium linear C₁₀₋₁₃ alkylbenzene sulfonates; sodium C₁₂₋₁₈ alkyl sulfates; sodium salts of sulfated condensation product of C₁₂₋₁₈ alcohols with from about 1 to about 3 moles of ethylene oxide; the condensation product of a C₁₀₋₁₈ fatty alcohols with from about 4 to about 10 moles of ethylene oxide; and the water-soluble sodium

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and potassium salts of higher fatty acids containing from about 10 to about 18 carbon atoms.

5 It is to be recognized that any of the foregoing detergents can be used separately herein, or as mixtures. Examples of preferred detergent mixtures herein are as follows.

10 An especially preferred alkyl ether sulfate detergent component of the instant compositions is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of from about 12 to 16 carbon atoms, preferably from about 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 to 4 moles of ethylene oxide, preferably from about 1 to 3 moles of ethylene oxide.

15 The detergent compositions of the present invention can contain, in addition to the detergent surfactant, water-soluble or water-insoluble builders such as those commonly taught for use in detergent compositions. Such auxiliary builders can be employed to sequester hardness ions and to help adjust the pH of the
20 laundering liquor. Such builders can be employed in concentrations of from about 5% to about 95% by weight, preferably from about 10% to about 50% by weight, of the detergent compositions herein to provide their builder and pH-controlling functions. The builders herein include any of the conventional
25 inorganic and organic water-soluble builder salts.

Such builders can be, for example, water-soluble salts of phosphates including tripolyphosphates, pyrophosphates, ortho-phosphates, higher polyphosphates, carbonates, silicates, and
30 organic polycarboxylates. Specific preferred examples of inorganic phosphate builders include sodium and potassium tripolyphosphates and pyrophosphates.

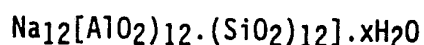
Nonphosphorus-containing materials can also be selected for use herein as builders.

35 Specific examples of nonphosphorus, inorganic detergent builder ingredients include water-soluble inorganic carbonate,

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bicarbonate, and silicate salts. The alkali metal, e.g., sodium and potassium, carbonates, bicarbonates, and silicates are particularly useful herein.

5 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
10 aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al, issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline
15 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



wherein x is from about 20 to about 30, especially about 27.

20 Water-soluble, organic builders are also useful herein. For example, the alkali metal, polycarboxylates are useful in the present compositions. Specific examples of the polycarboxylate builder salts include sodium and potassium, salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acid, polyacrylic
25 acid, polymaleic acid, and citric acid.

Other desirable polycarboxylate builders are the builders set forth in U.S. Patent 3,308,067, Diehl, incorporated herein by reference. Examples of such materials include the water-soluble
30 salts of homo- and co-polymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid, and methylenemalononic acid.

Other suitable polymeric polycarboxylates are the polyacetal carboxylates described in U.S. Pat. No. 4,144,226, issued Mar. 13, 1979 to Crutchfield et al, and U.S. Pat. No. 4,246,495, issued
35 Mar. 27, 1979 to Crutchfield et al, both incorporated herein by

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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.

Preferred builders herein are polycarboxylic acids, especially citric acid, which preferably are used at a level of from about 5% to about 10% by weight, and sodium acid pyrophosphate, which preferably is used at a level of from about 5% to about 15% by weight. Such materials function as both builder and acid source to adjust pH to the desired range.

Detergent Adjuvants

The detergent compositions herein can contain all manner of additional materials, detergent adjuvants, commonly found in laundering and cleaning compositions. For example, the compositions can contain thickeners and soil-suspending agents such as carboxymethylcellulose and the like. Various enzymes, enzyme stabilizers, suds suppressors, perfumes, optical bleaches, fillers, anticaking agents, fabric softeners and the like can be present in the compositions to provide the usual benefits occasioned by the use of such materials in detergent compositions.

The compositions herein are essentially free of oxygen bleaching agents, since if they are present, there is no need for the chlorine scavenger. Similarly, there should be no chlorine bleaching agent present since the chlorine scavenger would not be effective against a large amount of available chlorine.

A finished detergent composition of this invention can contain minor amounts of materials which make the product more attractive. The following are mentioned by way of example: a tarnish inhibitor such as benzotriazole or ethylene thiourea can be added in amounts up to 2% by weight; fluorescers, perfumes and dyes, while not essential, can be added in small amounts. An

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alkaline material such as sodium or potassium carbonate or hydroxide can be added in minor amounts as supplementary pH adjusters. There may also be mentioned, as suitable additives:
5 bacteriostats, bactericides, corrosion inhibitors such as soluble alkali silicates (preferably sodium silicates having an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of from 1:1 to 2.8:1), and textile softening agents.

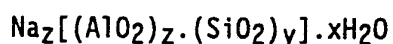
Particularly preferred compositions herein are granular laundry detergents comprising by weight:

10 (a) from about 15% to about 25% of a mixture of a C_{11} - C_{13} (preferably C_{12} - C_{13}) alkylbenzene sulfonate surfactant and a C_{12} - C_{16} (preferably C_{14} - C_{15}) alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from about 4:1 to about 1:1;

15 (b) from about 1% to about 3% of an alkali metal (preferably sodium) silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 1.0 to about 2.4;

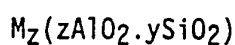
(c) from about 20% to about 30% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

20 (i) crystalline aluminosilicate material of the formula:



25 wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from about 0.1 micron to about 10 microns, a calcium ion exchange capacity of at least about 200 mg CaCO_3 eq./g and a calcium ion exchange rate of at least about 2 grains Ca^{++} /gallon/minute/gram/gallon;

30 (ii) amorphous hydrated aluminosilicate material of the empirical formula:



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5 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 ion exchange capacity of at least about 50 milligram equivalents of CaCO_3 hardness per gram of anhydrous aluminosilicate and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon; and

10 (iii) mixtures thereof;
 (d) from about 4% to about 10% of citric acid;
 (e) from about 5% to about 20% of an alkali metal (preferably sodium) carbonate;
 15 said composition having a pH of from about 7 to about 9.3 at a concentration of 1% by weight in water at 20°C , and said composition having a density of from about 500 to about 600 grams per liter.

20 Preferred aluminosilicate ion exchange material is of the formula $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]\cdot x\text{H}_2\text{O}$, wherein x is from about 20 to about 30.

The above granular detergent compositions provide good cleaning performance due to the relatively high levels of anionic surfactants and aluminosilicate, citric acid, and carbonate
 25 builders. Despite having a density of from about 500 to about 600 grams per liter, the compositions have good physical properties, i.e., they are free-flowing and are readily soluble in the laundering solution. The citric acid and carbonate levels are selected to obtain the required pH range and provide additional
 30 builder function to the aluminosilicate material.

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

The following examples illustrate the compositions herein.

EXAMPLES

35 Granular detergent compositions of the present invention comprise the following ingredients:

<u>Ingredient</u>	<u>Percent (Wt)</u>		
	<u>I</u>	<u>II</u>	<u>III</u>
Sodium 12.3 linear alkyl			

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	benzene sulfonate	13.6	12.7	15.8
	Sodium C ₁₄ -C ₁₅ alkyl sulfate	5.8	5.4	6.8
	C ₁₂ -C ₁₃ alcohol ethoxylate			
5	(EO 6)	0.0	0.0	0.5
	Citric acid	5.5	4.9	0.0
	Sodium tripolyphosphate	0.0	0.0	6.8
	Sodium pyrophosphate	0.0	0.0	13.1
	Sodium acid pyrophosphate	0.0	0.0	12.4
10	Zeolite A, hydrate			
	(1-10 micron size)	26.9	27.3	0.0
	Sodium carbonate	10.0	8.9	0.0
	Sodium silicate (1.6			
	ratio NaO/SiO ₂)	2.2	2.1	7.6
15	Polyethylene glycol 8000	1.4	1.3	0.6
	Sodium polyacrylate (MW 4500)	3.2	3.0	3.4
	Protease enzyme*	1.8	1.7	0.7
	Sodium perborate tetrahydrate	0.0	0.0	1.9
	Ammonium sulfate	2.0	2.0	0.0
20	Sodium sulfate	18.3	17.1	14.4
	Balance (including water, brightener,			
	perfume, suds suppressor)	-----	to 100.0	-----
	pH 1% aqueous solution at 20°C	8.7	8.9	9.2

*Activity of 1.8 Anson units per gram.

25 Aqueous crutcher mixes of the detergent compositions are prepared and spray-dried, except for the citric acid, sodium acid pyrophosphate, enzyme, perfume, and ammonium sulfate or perborate, which are admixed, so that they contain the above ingredients at the levels shown.

30 Fabrics laundered using the above compositions retain their color over time better than similar compositions not containing the chlorine scavenger or formulated to provide a higher wash pH.

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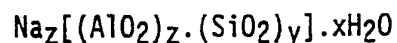
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Claims

1. A low or no phosphate granular laundry detergent composition characterized in that it comprises, by weight:

- (a) from 15% to 25% of a mixture of a C₁₁-C₁₃ alkylbenzene sulfonate surfactant and a C₁₂-C₁₆ alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:1;
- (b) from 1% to 3% of an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.0 to 2.4;
- (c) from 20% to 30% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

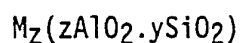
- (i) crystalline aluminosilicate material of the formula:



wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle

size diameter of from 0.1 micron to 10 microns, a calcium ion exchange capacity of at least 200 mg CaCO₃ eq./g and a calcium ion exchange rate of at least 2 grains Ca⁺⁺/gallon/minute/gram/gallon;

- (ii) amorphous hydrated aluminosilicate material of the empirical formula:



wherein M is sodium, potassium, ammonium, or substituted ammonium, z is from 0.5 to 2 and y is 1, said material having a magnesium ion exchange ion exchange capacity of at least 50 milligram equivalents of CaCO₃ hardness per

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gram of anhydrous aluminosilicate and a Mg^{++} exchange rate of at least 1 grain/gallon/minute/gram/gallon; and

(iii) mixtures thereof;

(d) from 4% to 10% of citric acid;

(e) from 5% to 20% of an alkali metal carbonate;

said composition having a pH of from 7 to 9.3 at a concentration of 1% by weight in water at 20°C, and said composition having a density of from 500 to 600 grams per liter.

2. The composition of Claim 1 wherein the sulfonate surfactant is sodium C₁₂-C₁₃ linear alkylbenzene sulfonate and the sulfate surfactant is sodium C₁₄-C₁₅ linear alkyl sulfate.

3. The composition of any one of the preceding claims comprising from 18% to 23% of the sulfonate and sulfate surfactants, in a weight ratio of sulfonate surfactant to sulfate surfactant of 2:1.

4. The composition of any one of the preceding claims wherein the alkali metal silicate is sodium silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.4 to 2.0.

5. A composition according to any one of the preceding claims wherein the aluminosilicate ion exchange material is of the formula

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$,
wherein x is from 20 to 30.

6. A composition according to any one of the preceding claims comprising from 22% to 28% of the aluminosilicate ion exchange material.

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7. A composition according to any one of the preceding claims comprising from 5% to 8% of citric acid.

8. A composition according to any one of the preceding claims comprising from 8% to 12% of sodium carbonate.

9. The composition of any one of the preceding claims wherein said composition has a pH of from 8 to 9.1, preferably from 8.5 to 9.0, at a concentration of 1% by weight in water at 20°C.

10. The composition of any one of the preceding claims which is substantially free of phosphate builder materials.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/03109

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5) CL: C11D 1/28, 1/02, 3/08, 7/20, 7/14

US CL: 252/174.19, 174.13, 174.25, 174.20, 140 95, 134, 135, 108

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
US CL	252/174.19, 174.13, 174.25, 174.20, 140, 95, 134, 135, 108

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4,715,979 (MOORE et al) 29 December 1987 See example II Col.7, line 60 to Col.8, line 30 col.4, lines 38-46, col.4, lines 11-21 col.2, lines 14-18	1-10
Y	US, A, 4,560,492 (CURRY ET AL) 24 December 1985 See col.7 lines 39-41 col.9 lines 60-64	1-10
Y	US, A, 4,810,413 (PANCHERI et al) 7 April 1989 See col 11 lines 14-21 col 10 lines 58-63 col 10 line 63 to col 11 line 13	1-10

- * Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed


"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report	
25 June 1991		26 JUL 1991	
International Searching Authority		Signature of Authorized Officer	
ISA/US		 KEVIN MC CARTHY	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A US, A, 4,983,315 (GLOGOWSKI et al) 8 January 1991
See entire document

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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

3. ☐ Claim numbers, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.