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(54) **Detergent compositions having improved bleaching effect.**

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Description

This invention relates to detergent compositions, and, in particular, to detergent compositions adapted for fabric washing.

It is known that laundry compositions function more efficiently in soft water than in water containing significant amounts of dissolved "hardness" cations such as calcium ion, magnesium ion and the like. Zeolites or other cation exchange materials were frequently used to pre-soften water. Such pre-softening procedures require an additional expense to the user occasioned by the need to purchase the softener appliance.

The most usual means whereby fabrics can be optionally laundered under hard water conditions involves the use of water-soluble builder salts and/or chelators to sequester the undesirable hardness cations and to effectively remove them from interaction with the fabrics and detergent materials in the laundering liquor. The most efficacious material of this type has been sodium tripolyphosphate and this builder has been in almost universal use during the last ten years. However, the use of such water-soluble builders, especially phosphates, introduces into the water supply certain materials which, in improperly treated sewage effluents, may be undesirable. Accordingly, a means for providing water-softening builders in detergent compositions without the need for such large quantities of soluble builder additives is desirable.

A variety of methods have been suggested for providing builder and water-softening action concurrently with the washing cycle of a home laundering operation, but without the need for water-soluble detergent additives.

One recently developed method for removing water hardness cations in detergent solutions involves the use of certain water-insoluble synthetic aluminosilicates in detergent compositions. A multitude of patent applications have appeared in recent years relating to these materials. Among these can be mentioned British Patent Specifications No. 1,429,143; No. 1,473,201 and No. 1,473,202; German Offenlegungsschriften No. 2,529,685 and No. 2,532,501; Dutch Patent Application No. 75.11455; U.S. Patent No. 3,985,669 and Belgian Patent No. 835,492.

Despite the advances which have been made in replacing phosphate builders by aluminosilicate materials, it is in practice found that detergent compositions built with aluminosilicates are still deficient in a number of areas of detergency performance compared with the commercial phosphate built detergents of today. One such area of deficiency is in the field of oxidizable stain cleaning. In part this deficiency would appear to reflect the poorer peptizing ability of aluminosilicate materials. Also of importance, however, is the fact that aluminosilicates and perbleach components such as perborates, can interact antagonistically, thereby reducing the bleaching effectiveness of compositions containing these materials.

The essence of the present invention lies in the discovery that compositions based on certain crystalline aluminosilicates and having specifically defined low levels of polyphosphonate sequestering agents and specific in-use pH characteristics, have excellent all round detergency performance and especially good cleaning performance on oxidizable-type stains. Moreover, these benefits are delivered in the absence of per-bleach components so that the invention makes it possible to reduce or to eliminate such materials entirely.

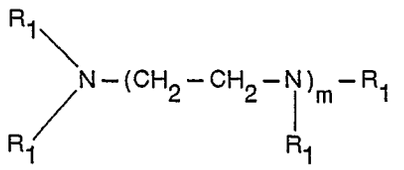
Furthermore, unlike traditional compositions based on per-bleach materials which have optimum effectiveness at a pH well above the optimum pH (8 to 9) of conventional enzyme components, the instant compositions have optimum bleach effectiveness at about the same pH as these enzyme materials making it possible to secure excellent bleaching and enzyme performance from a single composition.

Polyphosphonates have already been suggested for use in detergent compositions containing aluminosilicate. For example, German Offenlegungsschrift 2,544,035, 2,539,071, 2,527,388, 2,559,631 and Austrian Patent No. 338,947 all disclose the use of various polyphosphonates notably as dispersing agents in aluminosilicate built products. However, it appears that the usefulness of polyphosphonates in improving bleachable-stain performance in low pH aluminosilicate built products has not hitherto been recognized.

Accordingly, the present invention provides a detergent composition comprising from 2—75% of an anionic, nonionic, zwitterionic or amphoteric surfactant, from 5—60% of a water insoluble crystalline aluminosilicate builder of formula

$$M_2(AlO_2)_z(SiO_2)_yxH_2O$$

where M is a calcium-exchange cation, z and y are integers of at least 6; the molar ratio of z:y is in the range from 1:1 to 0.5:1 and x is an integer from 15 to 264, said aluminosilicate material having a particle size diameter from 0.1 micron to 10 microns and an ion exchange capacity of at least 200 mg eg of $CaCO_3$ per gram, together with a polyphosphonate component, wherein the polyphosphonate compound has the formula



wherein each R_1 is $CH_2PO_3H_2$ or a water soluble salt thereof, and m has the value 0, 1 or 2, the polyphosphonate being present in an amount of from 0.01—4% by weight of the composition, and in that the composition contains from 5—25% by weight of a pH regulating agent selected from sodium or potassium bicarbonate, such that a 1% aqueous solution of the detergent composition has a pH in the range from 7.0 to 9.5.

Laundry detergent compositions of the same type wherein citric acid and its water soluble salts are used as a pH regulating agent are described in EP—A—1310 (Prior date 26.09.77, Appl. date 13.09.78, Publ. dat 04.04.79).

The various essential and optional components of the composition of the invention will now be discussed.

Organic Detergent

The detergent active component of the present compositions can be anionic, nonionic ampholytic or zwitterionic in nature or can be mixtures thereof.

The detergent compositions of the invention contain the active system in an amount of from 2% to 75% by weight. For solid granular compositions, the active systems is generally in the range from 4% to 30%, more preferably from 6% to 15% of the compositions. In liquid compositions, higher active contents, for example 20% to 70% are normally employed. A typical-listing of anionic, nonionic, zwitterionic and amphoteric surfactants useful herein appears in USP 3,925,678. The following list of detergent compounds which can be used in the instant compositions is representative of such materials.

Water-soluble salts of the higher fatty acids, i.e. "soaps", are useful as the anionic detergent component of the compositions herein. This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids containing from 8 to 24 carbon atoms and preferably from 10 to 20 carbon atoms. Soaps can be made by direct saponification of fats and soils or by the neutralisation 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.

A highly preferred class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 8 to 22, especially from 10 to 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 detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8—C_{18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil; and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from 9 to 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in USP 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

A preferred alkyl ether sulfate surfactant component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of 12 to 16 carbon atoms, preferably from 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from 1 to 4 mols of ethylene oxide.

Other anionic detergent 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 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts of esters of α-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms; water-soluble salts of paraffin sulfonates containing from 8 to 24, especially 14 to 18 carbon atoms, and β-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactant mixtures can also be employed, for example 5:1 to 1:5 mixtures of an alkyl benzene sulfonate having from 9 to 15 carbon atoms in the alkyl radical and mixtures thereof, the cation being an

alkali metal preferably sodium; and from 2% to 15% by weight of an alkyl radical and from 1 to 30 ethoxy groups and mixtures thereof, having an alkali metal cation, preferably sodium.

Water-soluble nonionic synthetic detergents 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 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 water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic detergents include:

1. The polyethylene oxide condensates of alkyl phenol, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; nonylphenol condensed with 20 moles of ethylene oxide per mole of nonylphenol and di-isooctylphenol condensed with 15 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 1 to 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils, and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulphonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or prepared by the Ziegler process from ethylene, e.g., myristyl, cetyl, stearyl, alcohols), or partly branched such as the Dobanols and Neodols (being Trade Names of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a trade name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45—4, Dobanol 45—7, Dobanol 45—11, Dobanol 91—3, Dobanol 91—6, Dobanol 91—8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from 9 to 16 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of 1500 to 1800. Such synthetic nonionic detergents are available on the market under the trade name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Semi-polar nonionic detergents include water-soluble amine oxides containing one alkyl moiety of from 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxide detergents containing one alkyl moiety of 10 to 23 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxide detergents containing one alkyl moiety of from 10 to 28 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Ampholytic detergents 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.

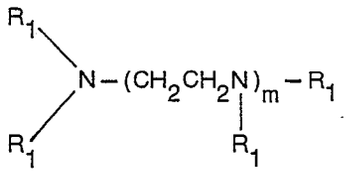
Zwitterionic detergents include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group. Further use of zwitterionic detergents are discussed in US Patents Nos. 3,925,262 and 3,929,678.

It is to be recognised that any of the foregoing detergents can be used separately herein or as mixtures.

A highly preferred mixture of surfactants is an anionic/nonionic mixture, especially a mixture of a C_8—C_{22} alkyl benzene sulfonate and a C_{10}—C_{20} alkanol ethoxylated with from 3 to 30 moles of ethylene oxide per mole of alkanol. Highly preferred mixtures include C_{12} alkyl benzene sulfonate and C_{14}—C_{15} alcohol-(7)-ethoxylate, in ratios of from 5:1 to 1:3, preferably 3:1 to 1:1. In still more preferred compositions, a fatty acid soap is added to the above-described mixture, preferably a C_{10}—C_{20} soap at a level of from 1% to 5%.

The Polyphosphonate

Polyphosphonates useful in the present invention have the formula



wherein each R_1 is $CH_3PO_3H_2$ or a water soluble salt thereof and m has the value 0, 1 or 2.

The polyphosphonate is present in an amount of from 0.01% to 4% by weight of the composition preferably in an amount of from 0.1% to 2% by weight. Examples of compounds within this class are aminotri(methylenephosphonic acid), ethylene diamine tetra (methylenephosphonic acid) and diethylene triamine penta (methylene phosphonic acid).

Preferred polyphosphonates can also be defined in terms of their calcium and iron sequestering ability as reflected in their calcium and iron logarithmic stability constants, pK_{Ca++} and $pK_{Fe}3+$. These are defined by reference to the equilibrium.

$$M + A \rightleftharpoons MA$$

where M is the metal cation and A is the polyphosphonate anion predominating in aqueous solution at the in-use pH of the detergent composition.

The equilibrium constant is therefore

$$K_m = \frac{[MA]}{[M]\ [A]}$$

$$\text{and } pK_m = \log_{10} K_m$$

Preferably, the polyphosphonate has a $pKpK_{Ca++}$ of less than 6, more preferably less than 5 and especially less than 4. The value of $pK_{Fe}3+$, on the other hand is preferably greater than 6, more preferably greater than 9, and especially greater than 12. Literature values of stability constants are taken where possible, (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, the Chemical Society, London). Otherwise, the stability constant is defined at 25°C and 0.1 molar KCl, using a glass electrode method of measurement as described in Complexation in Analytical Chemistry by Anders Ringbom (1963).

pH Regulating Agent

The pH regulating agent is selected from sodium or potassium bicarbonates.

The pH regulating agent is present in an amount sufficient to provide a pH in 1% aqueous solution of the detergent composition, in the range from 7 to 9.5, preferably from 7 to 9, especially from 7.5 to 8.5. Generally, from 5 to 25% especially from 10 to 20% of the regulating agent is sufficient for this purpose.

The Aluminosilicate Builder

The aluminosilicate ion exchange materials used herein are prepared by a process which results in the formation of materials which are particularly suitable for use as detergency builders and water softeners. Specifically, the aluminosilicates herein have both a higher calcium ion exchange capacity and a higher exchange rate than similar materials previously suggested as detergency builders. Such high calcium ion exchange rate and capacity appear to be a function of seveal interrelated factors which result from the method of preparing said aluminosilicate ion exchange materials.

It is highly preferred that these ion exchange builder materials are in the "sodium form".

A second essential feature of the ion exchange builder materials herein is that they be in a hydrated form ie. contain 10% to 28%, preferably 10% to 22% of water. Highly preferred aluminosilicates herein frequently contain from 18% to 22% water in their crystal matrix. It has been found, for example, that less highly hydrated aluminosilicates eg. those containing about 6% water, do not function effectively as ion exchange builders when employed in the context of a laundry detergent composition.

A third essential feature of the ion exchange builder materials herein is their particle size range. Proper selection of small particle sizes results in fast, highly efficient builder materials.

The method set forth below for preparing the aluminosilicates herein takes into consideration all of the foregoing essential elements. First, the method avoids contamination of the aluminosilicate product by cations other than sodium. For example, product washing steps involving acids or bases other than sodium hydroxide are avoided. Second, the process is designed to form the aluminosilicate in its most highly hydrated form. Hence, high temperature heating and drying are avoided. Third, the process is designed to form the aluminosilicate materials in a finely-divided state having a narrow range of small particle sizes. Of

course, additional grinding operations can be employed to still further reduce the particle size. However, the need for such mechanical reduction steps is substantially lessened by the process herein.

The aluminosilicates herein are prepared according to the following procedure:

(a) dissolve sodium aluminate ($NaAlO_2$) in water to form a homogeneous solution

(b) add sodium hydroxide to the sodium aluminate solution of step (a) at a weight ratio of NaOH: $NaAlO_2$ of 1:1.8 (preferred) and maintain the temperature of the solution at about 50°C until all the NaOH dissolves and a homogeneous solution forms;

(c) add sodium silicate (Na_2SiO_3) having a SiO_2:Na_2O weight ratio of 3.2 to 1) to the solution of step (b) to provide a solution having a weight ratio of Na_2SiO_3:NaOH of 1.14:1 and a weight ratio of Na_2SiO_3:$NaAlO_2$ of 0.63:1;

(d) heat the mixture prepared in step (c) to 90°C—100°C and maintain at this temperature range for about one hour.

In a preferred embodiment, the mixture of step (c) is cooled to a temperature below 25°C, preferably in the range from 17°C to 23°C, and maintained at that temperature for a period from 25 hours to 500 hours, preferably from 75 hours to 200 hours.

The mixture resulting from step (d) is cooled to a temperature of 50°C and thereafter filtered to collect the desired aluminosilicate solids. If the low temperature (<25°C) crystallization technique is used, then the precipitate is filtered without additional preparatory steps. The filter cake can optionally be washed free of excess base (deionized water wash preferred to avoid cation contamination). The filter cake is dried to a moisture content of 18% to 22% by weight using a temperature below 150°C to avoid excessive dehydration. Preferably, the drying is performed at 100°C—105°C.

Following is a typical pilot-point scale preparation of the aluminosilicates herein.

PREPARATION OF ALUMINOSILICATE BUILDER

Component	kg (as is)	kg (Anhydrous)	Water	Wt.% of Total
$NaAlO_2$	57.72	49.454	8.27	16.40 (Anh.)
Sodium silicate (3.2:1 SiO_2:Na_2O)	82.52	30.945	51.57	10.26 (Anh.)
NaOH	54.96	27.304	27.66	9.05 (Anh.)
N_2O (deionized)	106.40		106.40	64.29

The sodium aluminate was dissolved in the water with stirring and the sodium hydroxide added thereto. The temperature of the mixture was maintained at 50°C and the sodium silicate was added thereto with stirring. The temperature of the mixture was raised to 90°C—100°C. and maintained within this range for 1 hour with stirring to allow formation of a synthetic aluminosilicate ion exchange material having the formula $Na_{12}(AlO_2:SiO_2)_{12}.27\ H_2O$. The mixture was cooled to 50°C, filtered, and the filter cake washed twice with 100 kg. of deionized water. The case was dried at a temperature of 100°C—105°C to a moisture content of 18%—22% by weight to provide the aluminosilicate builder material. This synthetic aluminosilicate ion exchange material is known under the commercial denomination ZEOLITE A; in the dehydrated form it can be used as a molecular sieve and catalyst carrier. The synthetic aluminosilicate known commercially as ZEOLITE X is also suitable for use in the present invention, as are the amorphous synthetic aluminosilicates.

The aluminosilicates prepared in the foregoing manner are characterized by a cubic crystal structure and may additionally be distinguished from other aluminosilicates on the basis of the X-ray powder diffraction equipment. This included a nickel filtered copper target tube at about 1100 watts of input power. Scintillation detection with a strip chart recorder was used to measure the diffraction from the spectrometer. Calculation of the observed d-values was obtained directly from the spectrometer chart. The relative intensities were calculated with Io as the intensity of the strongest line or peak. The synthetic aluminosilicate ion exchange material having the formula

$$Na_{12}\ [(AlO_2)_{12}.(SiO_2)_{12}].27\ H_2O$$

prepared as described hereinbefore had the following X-ray diffraction pattern:

d	I/Io	d	I/Io
12.3	100	2.15	10
8.67	70	2.11	4
7.14	35	2.09	4
6.35	1	2.06	10
5.50	25	1.92	8
5.04	2	1.90	4
4.36	6	1.86	2
4.11	35	1.84	4
3.90	2	1.76	2
3.71	50	1.74	14
3.42	16	1.69	6
3.29	45	1.67	2
3.08	2	1.66	2
2.99	55	1.63	4
2.90	10		
2.76	12		
2.69	4		
2.62	20		
2.52	6		
2.47	4		
2.41	1		
2.37	4		
2.29	1		
2.25	4		
2.18	8		

The above diffraction pattern substantially corresponds to the pattern of ASTM powder diffraction card file #11—590.

Water-insoluble aluminosilicates having a molar ratio of $(AlO_2):(SiO_2)$ smaller than 1, ie. in between 1.0 and about 0.5, preferably in between 1.0 and about 0.8, can be prepared in a similar manner. These aluminosilicate ion exchange materials ($AlO_2:SiO_2 < 1$) are also capable of effectively reducing the free polyvalent hardness metal ion content of aqueous washing liquor in a manner substantially similar to the aluminosilicate ion exchange material having a molar ratio of $AlO_2:SiO_2 = 1$ as described hereinbefore. Examples of aliminosilicates having a molar ratio: $AlO_2:SiO_2 < 1$, suitable for use in the instant compositions include:

$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] . 264\ H_2O$; and $Na_6[(AlO_2)_6(SiO_2)_{10} . . 15\ H_2O$

Although completely hydrated aluminosilicate ion exchange materials are preferred herein, it is recognised that the partially dehydrated aluminosilicates having the general formula given hereinbefore are also excellently suitable for rapidly and effectively reducing the water hardness during the laundering operation. Of course, in the process of preparing the instant aluminosilicate ion exchange material, reaction-crystallization parameter fluctuations can result in such partially hydrated materials. As pointed out previously, aluminosilicates having 6% or less water do not function effectively for the intended purpose in a laundering context.

The water-insoluble, inorganic aluminosilicate ion exchange materials prepared in the foregoing manner are characterized by a particle size diameter from 0.1 micron to 10 microns. Preferred ion exchange materials have a particle size diameter from 0.2 micron to 10 microns. The term "particle size diameter" herein represents the number-average particle size diameter of a given ion exchange material as determined by conventional analytical technique such as, for example, microscopic determination, scanning electron microscope (SEM).

Preferred detergent compositions of the present invention contain from 10% to 50% of the aluminosilicate, more preferably from 15% to 25%.

Optional Components

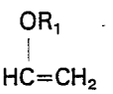
It is to be understood that granular compositions of the invention can be supplemented by all manner of detergent components, either by including such components in the aqueous slurry for spray drying or by admixing such components with the compositions of the invention after the drying step. Soil suspending agents at about 0.1% to 10% by weight such as water-soluble salts of carboxymethylcellulose, carboxyhydroxymethylcellulose, and polyethylene glycols having a molecular weight of about 400 to 10,000 are common components of the present invention. Dyes, pigment optical brighteners, and perfumes can be added in varying amounts as desired.

Other materials such as fluorescers, antiseptics, germicides, enzymes in minor amounts, anti-caking agents such as sodium sulfosuccinate, and sodium benzoate may also be added. Enzymes suitable for use herein include those discussed in U.S. Patents 3,519,570 and 3,553,139 to McCarty and McCarty et al issued 7 July, 1970 and 5 January, 1971 respectively. Particularly preferred are proteolytic enzymes having maximum intrinsic enzyme activity in the range from about pH 8 to about pH 9, especially preparations derived from B. subtilis such as ALCALASE (Registered Trade Mark) manufactured by Novo Industri A.S. Copenhagen, Denmark, and MAXATASE (Registered Trade Mark) manufactured by GIST-BROCADES N.V. Delft. These can be used in levels from about 0.1 to about 2% by weight of the composition.

Bleaches such as perborates and percarbonates and activators therefor can also be added to the instant composition, although it is a feature of the invention that such materials can be reduced in level or eliminated entirely. Suitably, therefore, per-bleaches can be present in amounts up to about 15%, especially up to about 10% by weight of the compositions.

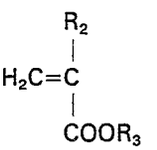
An optional but highly desirable ingredient of the present compositions is from 0.1% to 3% of a polymeric material having a molecular weight of from 2000 to 2,000,000 and which is a copolymer of maleic acid or anhydride and a polymerisable monomer selected from compounds of formula:

(i)

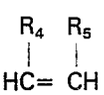


wherein R_1 is CH_3 or a C_2 to C_{12} alkyl group;

(ii)

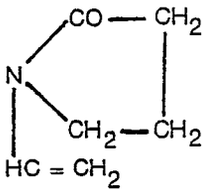


wherein R_2 is H or CH_3 and R_3 is H, or a C_1 to C_{10} alkyl group;



wherein each of R_4 and R_5 is H or an alkyl group such that R_4 and R_5 together have 0 to 10 carbon atoms;

(iv)



(v)

and (vi) mixtures of any two or more thereof, said copolymers being optionally wholly or partly neutralised at the carboxyl groups by sodium or potassium.

Preferred examples of polycarboxylates in the above classes are polymaleic acid/acrylic acid copolymer, 70:30 acrylic acid/hydroxy ethyl maleate copolymer, 1:1 styrene/maleic acid copolymer, propylene/maleic acid copolymer, isobutylene/maleic acid copolymer, diisobutylene/maleic acid copolymer, methylvinylether/maleic acid copolymer, ethylvinylether/maleic acid copolymer, ethylene/maleic acid copolymer and vinyl pyrrolidone/maleic acid copolymer. The preferred material is a methylvinylether/maleic acid copolymer having an average molecular weight from 12000 to 1,500,000.

Inorganic alkaline detergency builder salts can also be added, although high levels of highly alkaline builder salts and of phosphorus containing builder salts should be avoided. In particular, the phosphorus content of the compositions of the invention is preferably less than 6% by weight, and highly preferred compositions comprise no more than 1% by weight of phosphorus.

Inorganic builder salts include, for instance, alkali metal carbonates, tetraborates, pentaborates, aluminates, sesquicarbonates, polyphosphates such as sodium tripolyphosphate and pentapolyphosphate, and metaphosphates such as tetrametaphosphate, pentametaphosphate and hexametaphosphate, as well as orthophosphates and pyrophosphates.

A further optional component of the present compositions is a suds depressant. Soap is an effective suds depressant, especially C_{16-22} soaps, for instance those derived by neutralisation of Hyfac (trade name) fatty acids. These are hardened marine fatty acids of chain length predominantly C_{18} to C_{20}. However, non-soap suds depressants are preferred. A preferred suds depressant comprises silicones. In particular, there may be employed a particulate suds depressant comprising silicone and silica releasably enclosed in a water soluble or water dispersable substantially non-surface active detergent-impermeable carrier. Suds depressing agents of this type are disclosed in British Patent Specification 1,407,997.

A very suitable granular (prilled) suds depressant product comprises 7% silica/silicone (85% by weight silanated silica, 15% silicone obtained from Messrs. Dow Corning), 65% sodium tripolyphosphate, 25% tallow alcohol (EO) 25 (ie. condensed with 25 molar proportions of ethylene oxide), and 3% moisture. Also suitable and preferred is a combination of 0.02% to 5% by weight, especially about 0.3% of the composition, of a substantially water insoluble wax or mixture of waxes, melting at from 35°C to 125°C, and having saponification value less than 100, and a suds depressing amount, usually about 2% of the composition, of particulate suds depressant mentioned above. Suds depressant mixtures of this type are described in British Patent Specification No. 1492939.

Another desirable component of the compositions of the invention is a water-soluble cationic surfactant such as those described in European Published Application No. 225. The cationic surfactant, when used in combination with anionic and nonionic surfactants in defined ratios and amounts, improves the oil stain detergency performance of the formulation. Preferred cationic surfactants have the general formula

$$R^1{}_m R^2{}_{4-m}\ \overset{+}{N}\ \overset{-}{A}$$

wherein R^1 is selected from C_{8-20} alkyl, alkenyl and alkaryl groups; R^1 is selected from C_{1-4} alkyl and benzyl; A is an anion; and m is 1, 2, or 3; provided that when m is 2, R^1 has less than 15 carbon atoms, and when m is 3, R^1 has less than 9 carbon atoms.

C_{12} and C_{14} alkyl trimethyl ammonium salts are highly preferred.

In preparing granular detergent compositions of the invention the components may be mixed together in any order and in powdery or in fluid form, eg. in an aqueous dispersion. The composition may be sprayed dried, drum dried, freeze dried or dried by other means, to provide a granular composition. Usually

a moisture content of 3% to 10% is suitable to provide non-sticky free-flowing granules.

Liquid detergent compositions of the invention can contain, as optional ingredients, organic carriers or solvents such as lower aliphatic alcohols having from 2 to 6 carbon atoms and 1 to 3 hydroxyl groups; ethers of diethylene glycol and lower aliphatic mono-alcohols having 1 to 4 carbon atoms; and mixtures thereof. Liquid compositions can also contain hydrotropes such as the water-soluble alkylaryl sulfonates having up to 3 carbon atoms in an alkyl group such as sodium, potassium, ammonium and ethanolamine salts of xylene-, toluene-, ethylbenzene- and isopropylbenzene sulfonic acids.

Examples 1—5

Built low-sudsing detergent compositions were prepared having the formulae given below. To make the products a slurry was prepared containing all the components except the bleach and enzyme and the slurry was then spray dried to form a granular intermediate. Bleach and enzyme were dry mixed with the intermediate granules to form the stated composition. All figures are given as % by weight.

		1	2	3	4	5
Linear C_{12} alkyl benzene sulphonate		7.0	—	9.5	5.0	3.0
Myristyl trimethyl ammonium chloride		—	6.0	—	5.0	3.0
Tallow alcohol sulphate		3.0	—	—	—	—
Dobanol 45—E—7	(8)	—	8.0	—	1.5	3.0
Tallow alcohol $(EO)_{11}$		3.0	—	3.0	—	—
Dobanol 45—E—4	(9)	—	4.0	—	—	—
C_{12} soap		—	2.0	—	—	2.0
C_{18} soap		2.0	—	0.75	4.0	—
Sodium tripoly-phosphate		1.0	2.5	4.0	—	8.0
Sodium pentapoly-phosphate		—	—	—	1.5	—
Zeolite A		25.0	—	20.0	—	15.0
Zeolite X		—	30.0	—	12.0	—
Gantrez AN 119	(7)	0.8		1.5	—	—
Dequest 2040	(5)	1.0	—	1.0	—	0.1
Dequest 2060	(3)	—	2.0	—	0.2	—
Dequest 2006	(4)	—	—	—	—	—
Sodium Citrate		15.0	—	4.0	—	—
Protease enzyme	(6)	0.5	0.5	1.2	0.5	—
Sodium perborate		—	—	—	5.0	—
Sodium bicarbonate		5.0	15.0	12.0	14.0	10.0
Polyethylene glycol (Mol Wt. 6000)		—	1.0	1.5	—	—

		1	2	3	4	5
Silicone Prills	(1)	2.0	8	—	2.0	—
Microcrystalline wax	(2)	0.3	—	—	0.3	—
Sodium sulphate, moisture Miscellaneous		to 100				
In-Use pH		<9				

Notes:

(1) Comprising 0.14 parts by weight of an 85:15 by weight mixtures of silanated silica and silicone, granulated with 1.3 parts of sodium tripolyphosphate, and 0.56 parts of tallow alcohol condensed with 25 molar proportions of ethylene oxide.

(2) Witcodur 272 M.pt. 83°C. (Trade name)

(3) Trade name for diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto.

(4) Trade name for nitrilo tri(methylenephosphonic acid) marketed by Monsanto.

(5) Trade name for ethylenediamine tetra (methylene phosphonic acid), marketed by Monsanto

(6) Alcalase: Marketed by Novo Industri A.S., Copenhagen.

(7) Trade name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 240,000 marketed by GAF. This was prehydrolysed with NaOH before addition.

(8) Trade name: primary C_{14-15} alcohols condensed with 7 molar proportions of ethylene oxide, marketed by Shell.

(9) Trade name: primary C_{14-15} alcohols condensed with 4 molar proportions of ethylene oxide, marketed by Shell.

The compositions of the above Examples all provide good detergency performance, particularly on bleachable type soils and stains and at wash low temperatures compared with compositions containing no polyphosphonate material, and compared with compositions containing polyphosphonates but having pH in use outside the claimed range.

Similar results are achieved when the tripolyphosphate is replaced by a P_{12} glassy phosphate. The anionic/nonionic active systems of Examples 3—6 can be replaced by all nonionic systems, for example, with Dobanol 45—E—7 and Dobanol 45—E—4. The Zeolite A in Examples 1, 3, 5 and 6 can be replaced in whole or in part by an amorphous sodium aluminosilicate. Enhanced performance is also obtained when myristyl trimethyl ammonium chloride is replaced by lauryl trimethyl ammonium bromide, decyl trimethyl ammonium chloride, dioctyl dimethyl ammonium bromide, lauryl dichlorobenzyl dimethyl ammonium chloride, and cetyl trimethyl ammonium ethosulphate.

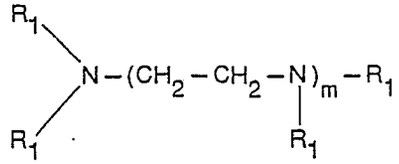
Products with enhanced performance are obtained when the sodium alkyl benzene sulphonate is replaced by C_{10-22} olefine sulphonates, C_{10-20} paraffin sulphonates, and by zwitterionic detergents such as C_{10-18} alkyl dimethyl ammonium propane sulphonate or hydroxypropane sulphonate.

Claims

1. A laundry detergent composition comprising from 2—75% of an anionic, nonionic, zwitterionic or amphoteric surfactant, from 5—60% of a water insoluble crystalline aluminosilicate builder of formula

$$M_z(AlO_2)_z(SiO_2)_yxH_2O$$

where M is a calcium-exchange cation, z and y are integers of at least 6; the molar ratio of z:y is in the range from 1:1 to 0.5:1 and x is an integer from 15 to 264, said aluminosilicate material having a particle size diameter from 0.1 micron to 10 microns and an ion exchange capacity of at least 200 mg eq of $CaCO_3$ per gram, together with a polyphosphonate component, characterised in that the polyphosphonate compound has the formula



wherein each R_1 is $CH_2PO_3H_3$ or a water soluble salt thereof, and m has the value 0, 1 or 2, the polyphosphonate being present in an amount of from 0.01—4% by weight of the composition, and in that the composition contains from 5—25% by weight of a pH regulating agent selected from sodium or potassium bicarbonate, such that a 1% aqueous solution of the detergent composition has a pH in the range from 7.0 to 9.5.

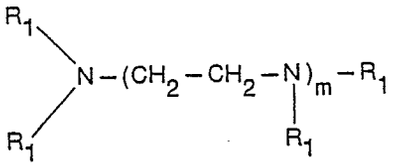
2. A composition according to Claim 1 comprising, in addition, from 0.1—2% of a proteolytic enzyme derived from B. subtilis and form 0—15% of a peroxy bleach.

Patentansprüche

1. Ein Waschmittel, umfassend 2 bis 75% eines anionischen, nichtionischen, zwitterionischen oder amphoteren oberflächenaktiven Mittels, 5 bis 60% eines wasserunlöslichen kristallinen Aluminosilikatgerüststoffes der Formel

$$M_z(AlO_2)_z(SiO_2)_yxH_2O$$

worin M ein Calciumaustauschkation darstellt, z und y ganze Zahlen von mindestens 6 bedeuten; das Molverhältnis von z zu y im Bereich von 1:1 bis 0,5:1 liegt und x eine ganze Zahl von 15 bis 264 ist, wobei das Aluminosilikatmaterial einen Teilchengrößendurchmesser von 0,1 µm bis 10 µm und eine Ionenaustauschkapazität von mindestens 200 mg Äquivalenten $CaCO_3$ pro g aufweist, zusammen mit einem Polyphosphonatbestandteil, dadurch gekennzeichnet, daß die Polyphosphonatverbindung die Formel



aufweist, worin jedes R_1 $CH_2PO_3H_2$ oder ein wasserlösliches Salz davon bedeutet und m den Wert 0, 1 oder 2 hat, wobei das Polyphosphonat in einer Menge von 0,01 bis 4 Gew.-%, bezogen auf das Waschmittel, vorhanden ist, und daß das Waschmittel 5 bis 25 Gew.-% eines pH-regulierenden Mittels ausgewählt aus Natrium- oder Kaliumbicarbonat enthält, so daß eine 1%ige wäßrige Lösung des Waschmittels einen pH im Bereich von 7,0 bis 9,5 aufweist.

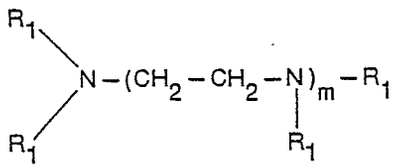
2. Waschmittel nach Anspruch 1, umfassend zusätzlich 0,1 bis 2% eines proteolytischen Enzyms abgeleitet von B. subtilis und 0 bis 15% eines Peroxy-bleichmittels.

Revendications

1. Composition détergente pour blanchissage comprenant 2 à 75% d'un surfactif anionique, non ionique, zwitterionique ou amphotère, 5 à 60% d'un adjuvant de détergence à base d'alumino-silicate cristallin insoluble dans l'eau de formule:

$$M_z(AlO_2)_z(SiO_2)_yxH_2O$$

dans laquelle M est un cation échangeur de calcium, z et y sont des nombres entiers d'au moins 6; le rapport molaire de z:y se situe entre 1:1 et 0,5:1 et x est un nombre entier de 15 à 264, ladite matière à base d'alumino-silicate ayant un diamètre de particule de 0,1 micron à 10 microns et une capacité d'échange d'ions d'au moins 200 mg éq. de $CaCO_3$ par gramme, ensemble avec un composant à base de polyphosphonate, caractérisée en ce que le composé de polyphosphonate répond à la formule:



dans laquelle chaque R_1 est $CH_2PO_3H_2$ ou un de ses sels hydrosolubles et m possède la valeur 0,1 ou 2, le polyphosphonate étant présent à raison de 0,01 à 4% en poids de la composition et en ce que la composition renferme 5 à 25% en poids d'un agent régulateur de pH choisi parmi le bicarbonate de sodium ou de potassium de façon qu'une solution aqueuse à 1% de la composition détergente possède un pH compris entre 7 et 9,5.

2. Composition selon la revendication 1, caractérisée en ce qu'elle comporte, en outre 0,1 à 2% d'une enzyme protéolytique dérivée du B. subtilis et 0 à 15% d'un agent de blanchiment peroxydique.