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(54) Low-phosphate detergent composition for fabric washing.

(57) A detergent composition containing surfactant and an insoluble aluminosilicate builder salt includes defined, low levels of a phosphate builder salt and of certain polymeric materials based on maleic acid. The presence of these low levels of phosphate and polymaleate enhances the builder effectiveness of the eluminosilicate and the compositions have surprisingly good cleaning performance and show enhanced removal of bleachable stains.

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DETERGENT COMPOSITIONS

This invention relates to detergent compositions, and, in particular, to detergent compositions having only a specific low level of phosphorous-containing builder salt.

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 this material. 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.

Although these, and other, patent applications suggest the possibility that useful detergent compositions can be prepared that are entirely free of water-soluble builders, especially phosphate salts, it has been found in practice that the aluminosilicate material, even in large amounts, tends to be undesirably slow in its exchange of cations preferably at low wash temperatures and the most useful compositions have been those which contain mixtures of aluminosilicate materials and water-soluble builder salts, especially sodium tripolyphosphate.

The essence of the present invention lies in the discovery that compositions based on aluminosilicate and having specifically defined low levels of phosphate builder can have excellent all-round detergency performance provided that they also include a small amount of certain specific polymeric materials, namely polymers including maleic acid or similar dibasic acid groups.

Copolymers containing maleic acid moieties have already been suggested for use in detergent compositions containing aluminosilicate. For example, in Dutch Patent Application No. 75.11455, a copolymer of maleic acid and methylvinylether is used at a high level essentially acting as a co-builder with the aluminosilicate. Also, in Belgian Patent No. 835, 492, there is a suggestion that such copolymers can be used in mixed aluminosilicate/tripolyphosphate systems to improve the processing characteristic of spray-dried detergent compositions. The Dutch Patent Specification No. 74.03382 also discloses compositions containing various polymers but these compositions normally contain substantial amounts of phosphate or, if free of phosphate, contain builder levels of the polymers. Furthermore, these polymers are normally polyacrylates and the polymers selected for use in the present invention have been shown to provide benefits in bleachable stain removal not shared by polyacrylate materials.

It is an object of this invention to provide detergent compositions containing water-insoluble aluminosilicate ion exchange materials which are free of large amounts of phosphate and yet are capable of providing superior detergency performance.

According to the invention there is provided a detergent composition comprising :

(a) from 2% to 60% of a surfactant selected from anionic, nonionic, zwitterionic and amphoteric surfactants and mixtures thereof; (b) from 5% to 60% of a water-insoluble aluminosilicate ion exchange material of the formula

$$M_z\left[(AlO_2)_z\cdot(SiO_2)_y\right]x\ H_2O$$

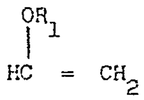
wherein M is a calcium-exchange cation; z and y are integers of at least 6; the molar ratio of z to y is in the range from 1.0 to about 0.5; and x is an integer from about 15 to about 264; said aluminosilicate ion exchange material having a particle size diameter from about 0.1 micron to about 100 microns; a calcium ion exchange capacity of at least about 200 mg. eq. [illegible]

[illegible] least abo [illegible]

(c) from 0.5% to 6% of a phosphate builder salt;

and (d) 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 :

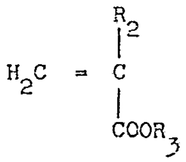
(i)



$$\overset{\mathrm{OR_1}}{\overset{|}{\mathrm{HC}}} = \mathrm{CH_2}$$

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

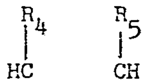
(ii)



$$\mathrm{H_2C} = \underset{\underset{\mathrm{COOR_3}}{|}}{\overset{\mathrm{R_2}}{\overset{|}{\mathrm{C}}}}$$

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

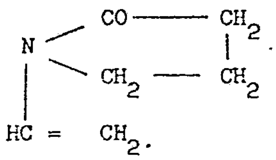
(iii)



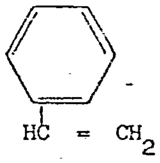
$$\overset{\mathrm{R_4}}{\overset{|}{\mathrm{HC}}} \qquad \overset{\mathrm{R_5}}{\overset{|}{\mathrm{CH}}}$$

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 compositions of the invention contain from 1% to 4 % of phosphate salts, especially a tripolyphosphate. Other water-soluble builder salts, while not excluded from the present invention are also preferably absent except in small amounts. Highly preferred compositions are in granular form and contain from 5% to 20% surfactant and from 15% to 50% of the aluminosilicate.

In the following detailed description of the invention, the "percent" indications mean percent by weight, unless otherwise stated.

The detergent compositions of the instant invention contain a surfactant selected from anionic, nonionic, zwitterionic and ampholytic surfactants. The surfactant is used in an amount from about 2% to about 60%, preferably from about 5% to about 50% of the detergent compositions. A typical listing of the classes and species of surfactants useful herein appears in U.S. Patent 3,929,678, incorporated herein by reference. The following list of detergent 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 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 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 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, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group 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. [illegible] detergents which form [illegible] 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 about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in United States Patents 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 13 carbon atoms, abbreviated as C_{13} LAS.

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

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.

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 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 water-soluble condensation products of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms, are also useful nonionic detergents herein.

Semi-polar nonionic detergents include water-soluble amine oxides containing one alkyl moiety of from about 10 to 28 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 about 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxide detergents containing one alkyl moiety of from about 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 [illegible] 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 aliph[illegible]

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 about 8 to 18 carbon atoms and one contains an anionic water solubilizing group.

Other useful detergent compounds herein include the water-soluble salts of esters of α-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 β-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.

It is to be recognized 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 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 several 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, i.e. contain 10%-28%, preferably 10%-22%, of water. Highly preferred aluminosilicates herein frequently contain from about 18% to about 22% water in their crystal matrix. It has been found, for example, that less highly hydrated aluminosilicates, e.g. 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.

A suitable method for preparing such materials is described in British Patent No. 1 501 498, the disclosure of which is incorporated herein by reference. This patent also characterises the aluminosilicate materials in terms of their physical properties.

A highly preferred synthetic aluminosilicate ion exchange material for use in the present invention 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 ZEOLIT X is also suitable for use in the present invention, as are the amorphous synthetic aluminosilicates. A preferred synthetic aluminosilicate ion exchange material has the formula

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

Examples of aluminosilicates having a molar ratio: $AlO_2:SiO_2$ 1, suitable for use in the instant compositions include:

$Na_{86}(AlO_2)_{86}(SiO_2)_{106} \cdot 264\ H_2O$; and

$Na_6(AlO_2)_6(SiO_2)_{10} \cdot 15\ H_2O$.

Although completely hydrated aluminosilicate ion exchange materials are preferred herein, it is recognized 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 about 6% or less water do not function effectively for the intended purpose in laundering context. The suitability of particular partially dehydrated water-insoluble aluminosilicates for use in the compositions of this invention can easily be asserted and does only involve routine testing as, for example, described herein (Ca-ion exchange capacity; rate of exchange).

The ion exchange properties of the aluminosilicates herein can conveniently be determined by means of a calcium ion electrode. In this technique, the rate and capacity of Ca^{++} uptake from an aqueous solution containing a known quantity of Ca^{++} ion is determined as a function of the amount of aluminosilicate ion exchange material added to the solution.

The water-insoluble, inorganic aluminosilicate ion exchange materials prepared in the foregoing manner are characterized by a particle size diameter from about 0.1 micron to about 100 microns. Preferred ion exchange materials have a particle size diameter from about 0.2 micron to about 10 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, scanning electron microscope (SEM).

The aluminosilicate ion exchangers herein are further characterized by their calcium ion exchange capacity, which is at least about 200 mg. equivalent of $CaCO_3$ hardness/gram of aluminosilicate, calculated on an anhydrous basis, and which generally lies within the range of from about 300 mg. eq./g. to about 352 mg. eq./g.

The ion exchange materials herein are still further characterized by their calcium ion exchange rate, which is at least about 2 grains (Ca^{++})/gallon/minute/gram of aluminosilicate (anhydrous basis), and lies within the range of about 2 grains/gallon/minute/gram to about 6 grains/gallon/minute/gram, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a Ca^{++} exchange rate of at least about 4 grains/gallon/minute/gram.

Preferred detergent compositions of the present invention contain from 15% to 50% of the aluminosilicate, more preferably from 20% to 45%.

Another essential component herein is a minor amount, 0.5% to to 6%, of a water-soluble phosphate salt. Particularly preferred compositions contain from 1% to 3% of a polyphosphate salt, especially sodium or potassium tripolyphosphate or higher polyphosphates, such as the tetra-,penta-, and hexaphosphates up to the so called glassy metaphosphates with some 12-14 or more phosphorous atoms in the molecule. The use of such phosphates does of course reduce the economy of phosphate usage achieved by the compositions, but it also improves some aspects of their cleaning power, especially whiteness maintenance and removal of particulate soils, such as clay-like materials. Preferred compositions contain from 1% to 3% of tripolyphosphate, or from 0.5% to 2% pentaphosphate. Such phosphates are obtainable commercially under trade names, such as those of Messrs. Albright and Wilson, viz. Phosphate Glass 627 (believed to be sodium pentaphosphate) Calgon N12 (believed to be the P_{12} glassy phosphate and alternatively known as glassy sodium phosphate, sodium metaphosphate, sodium hexametaphosphate or Graham's Salts).

It is a most surprising effect in the present invention that the presence of such small quantities of phosphate salts can contribute so effectively to the overall performance of the detergent composition. While not intending to be limited by theory, it appears that certain defined,minor quantities of phosphate have a substantial influence on the kinetics of the calcium exchange reaction with the aluminosilicate, so that the effectiveness of the zeolite material, especially in short wash cycles is markedly improved.

The fourth essential component herein is a water-soluble copolymer or derivative thereof as defined above. The copolymeric ingredient is used in an amount from about 0.1% to about 3%, preferably from 0.25% to 1.5%.

Copolymers useful in the present invention are all copolymers of maleic acid with certain olefinic monomers, optionally wholly or partly neutralised by sodium or potassium. All may be made by heating together maleic anhydride and the other monomer in an appropriate solvent, such as benzene, cyclohexene, or in some cases in excess of one of the monomers, in the presence of a catalyst such as an organic peroxide or azo-bisbutyronitrile. As will be appreciated by those skilled in the art, different solvent, catalysts, and reaction conditions are most suitable according to the type of copolymer and molecular weight thereof being prepared. In particular in order to make the high molecular weight polymers for the present invention, it is often desirable to use up the initiator (catalyst) to make a macro-radical and then to add further monomers employing the macro-radical as sole initiator. Methods of preparing these compounds are described in U.S. Patent 2,430,313 (Vana to E.I. Dupont de Nemours Co.). The polymers so prepared are, of course, copolymers of maleic anhydride and the selected monomer. Either before or during the manufacture of the compositions of the invention, these are usually hydrolysed to the acid form and optionally neutralised as indicated above. In the present specification, unless stated otherwise, the molecular weight of the compolymer is expressed as that of the unneutralised acid form thereof. It so happens that when copolymers formed from olefins of the classes (i), (iii),and (v) above are prepared, the copolymer consists substantially entirely of alternating units of each monomer even though the original monomers reacted were present in other than a 1:1 molar ratio. In the case of the acrylic-maleic copolymers of class [illegible] it is necessary to ensure an excess of maleic anhydride in the reaction mixture to obtain substantially 1:1 molar ratio of the [illegible] in acrylic units can be obtained by p[illegible] of acrylic monomer in the reactor

The alkyl vinyl ethers constituting coponent (i) of the composition of the invention are preferably methyl vinyl ethers. Preferred molecular weights for these copolymers are in the range from 12,000 to 1,500,000, more preferably 50,000 to 300,000. Copolymers in anhydride form believed to be of this class are commercially available from GAF Corporation under the trade names Gantrez AN119 (MWt.200,000 in anhydride form) Gantrez AN139 (MWt.500,000 in anhydride form), AN149 (MWt.750,000 in anhydride form) and AN169 (MWT.1,125,000 in anhydride form). Ethyl and methyl vinyl ether/maleic anhydride copolymers are also available from BASF under the trade name Sokalan and having molecular weight about 30,000. Higher than methyl alkyl vinyl ethers, especially C_2 to C_4 alkyl, have been found to be most effective in copolymers of much lower molecular weight, preferably in the range from 2,000 to 20,000, especially about 4,000 to 12,000.

The molecular weight of these copolymers is the viscosity average molecular weight and is determined as follows :

A number of polymer solutions of known concentration ($<1\%$ w/v) are made up in a suitable solvent and their viscosities determined as described in F. Daniels et al Experimental Physical Chemistry pp.71-74, 242-246, McGraw-Hill (1949), at 25°C, using an Ostwald viscometer. A plot of (specific viscosity/concentration) against concentration is then constructed and the best line extrapolated to zero concentration. The value of (specific viscosity/concentration) at zero concentration is termed the intrinsic viscosity, $[\eta]$. This parameter is used to determine a viscosity-average molecular weight, $\bar{M}_v$.

For the above copolymers as anhydrides the equation applicable employing acetone as solvent, and giving the molecular weight of the anhydride form is :

$$\log[\eta] = 0.94 \log \bar{M}_v - 3.27 \qquad \text{I}$$

In 1M NaOH, giving the molecular weight of the sodium salt of the copolymer, the equation is :

$$\log[\eta] = 0.86 \log \bar{M}_v - 2.88 \qquad \text{II}$$

The acrylic-maleic copolymers derived from olefin (ii) above are preferably based upon methyl acrylate or methyl methacrylate, although higher alkyl esters may be employed. The manufacture of these polymers, and the control of the molar ratio of the monomers one to other is described by Seymour, Harris and Branum in Industrial and Engineering Chemistry, Volume 41, pages 1509 to 1513, 1949. Preferably copolymers wherein the molar ratio of acrylate ester to maleic acid is from about 2:1 to 1:1 are employed herein, especially close to 1:1; their molecular weight is preferably in the range from 3,000 to 1,500,000, especially from about 5,000 to 30,000.

The molecular weight of these copolymers is determined by the method described above.

When the olefin (iii) is used, the copolymers are preferably of high molecular weight and are preferably based on ethylene. The preferred molecular weight range is from 275,000 to 1,500,000.

Another preferred group of materials within this class are copolymers of maleic anhydride or acid with propylene, isobutylene, alkyl substituted isobutylene and, especially, di-isobutylene, having molecular weight in the range from about 500 to 50,000 and molar ratio of olefine to maleic acid in the range from 1:1 to 1:2. Suitable materials of this type are available under the trade names "Empicryl" of Albright and Wilson Ltd. and "Orotan" of Rohm and Haas.

The molecular weight of these polymers is determined by the method described above but employing ethanol as solvent and using the equation :

$$\log[\eta] = 1.18 \log \bar{M}_v - 3.85 \qquad \text{III}$$

The vinyl pyrrolidone maleic copolymers (using olefin (iv) above) preferably have molecular weight in the range from about 3,000 to

50,000, especially about 20,000 to 30,000. The molecular weight is determined by the method described above but employing 1M NaOH as solvent and using the equation II above.

The styrene-maleic acid copolymers (olefin (v) above) preferably have molecular weight about 300,000. The molecular weight is determined by the same method but employing acetone as solvent and using the equation I above.

The most preferred copolymers are those of methyl and ethyl vinyl ether-maleic described above.

Although polymers of the above type have been suggested for use in compositions containing aluminosilicate, these prior art disclosures have either been in compositions containing substantial amounts of phosphate co-builder (e.g. Belgian Patent No. 835 492) or have utilised relatively large levels of polymer, at least 5% (e.g. German Offenlegungsschrift No. 25 39 071), at which levels the polymer acts mainly as a co-builder.. It was entirely unexpected that, in an aluminosilicate built composition substantially free of phosphate, the presence of very small amounts of these polymeric materials could give a substantial improvement in detergency performance, especially on bleachable stain removal.

There may also be included in the composition other inorganic salts which have some detergency building effect and effect upon the alkalinity of the compositions, or act as fillers, such as sodium or potassium carbonates, borates, sulphates and silicates.

In solid granular or particulate compositions it is preferred that an alkali metal, especially sodium, silicate be present.

The alkali metal silicate preferably is used in an amount from 0.5% to 10%, preferably from 3% to 8%. Suitable silicate solids have a molar ratio of SiO_2/alkali $metal_2O$ in the range from about 0.5 to about 4.0, but much more preferably from 1.0 to 1.8, especially about 1.6. The alkali metal silicates suitable herein can be commercial preparations of the combination of silicone dioxide and alkali metal oxide, fused together in varying proportions.

Crystalline silicate solids normally possess a high alkalinity content; in addition hydration water is frequently present as, for example, in metasilicates which can exist having 5, 6 or 9 molecules of water. The alkalinity is provided through the monovalent alkali metal ions such as, for example, sodium, potassium, lithium and mixtures thereof. The sodium and potassium silicate solids are generally used. Highly preferred for the compositions herein are the commercially widespread available sodium silicate solids.

The alkali metal silicate solids are preferably incorporated into the instant detergent compositions during the crutching operation together with the other major constituents, particularly the surface-active agent and the water-insoluble aluminosilicate ion exchange material. The required amount of silicate solids can also be incorporated into the detergent composition in the form of colloidal silicates called water glass which are frequently sold as a 20-50% aqueous solution.

Silicate solids, particularly sodium silicate solids, are frequently added to heavy-duty granular detergent compositions as corrosion inhibitors to provide protection to the metal parts of the washing machines in which the alkali washing liquor is utilized. In addition, sodium silicates provide a certain degree of crispness and pourability to detergent granules which is very desirable to avoid lumping and caking, particularly during prolonged storage. It is known, however, that silicate solids cannot easily be incorporated into detergent compositions comprising major amounts of water-insoluble aluminosilicate ion exchange materials as they are capable of enhancing and facilitating the deposition of these water-insoluble particles on the textiles being laundered as well as on the machine. In addition, the concurrent use of alkali metal silicate solids and water-insoluble aluminosilicates apparently adversely affects the capacity and rate of hardness depletion of the ion exchange material in laundry liquor. It is believed that this can be due to a physical blocking of the ion exchange sites on the synthetic zeolites herein. Unexpectedly, a minor effective amount of alkali metal silicate solids has been found to be compatible with a major amount of synthetic aluminosilicate materials in the presence of organic syntnetic detergents, thereby providing effective corrosion inhibition and crispness benefits without concurrently enhancing the deposition of the synthetic aluminosilicate particles on the textiles and on the walls of the washing machine.

As noted hereinabove, the detergent compositions of the present invention can contain, in addition to the aluminosilicate ion exchange builders, small amounts of other non-phosphate builders.

These include the water-soluble salts of phosphonates, bicarbonates, carbonates, citrates, polyhydroxysulfonates, polyacetates, carboxylates, polycarboxylates and succinates. The polyphosphonates specifically include, for example, the sodium and postassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Examples of these and other phosphorous builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Specific examples of the polyacetate and polycarboxylate builder salts include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Highly preferred non-phosphorous auxiliary builder materials herein include sodium carbonate, sodium bicarbonate, sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetate, and sodium ethylenediaminetetraacetate, and mixtures thereof.

The compositions of this invention can require the presence of a suds regulating or suppressing agent.

Suds regulating components are normally used in an amount from about 0.001% to about 5%, preferably from about 0.05% to about 3% and especially from about 0.10% to about 1%. The suds suppressing (regulating) agents which are known to be suitable as suds suppressing agents in detergent context can be used in the compositions herein. These include the silicone suds suppressing agents, especially the mixtures of silicones and silica described in U.S. Patent No.3,933,672, the disclosure of which is incorporated herein by reference. A particularly preferred suds suppressor is the material known as "HYFAC", the sodium salt of a long-chain (C_{20}-C_{24}) fatty acid.

Microcrystalline waxes having a melting point in the range from 35°C-115°C and saponification value of less than 100 represent an additional example of a preferred suds regulating component for use in the subject compositions. The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes have a melting point from about 65°C to 100°C, a molecular weight in the range from 400-1 000; and a penetration value of at least 6, measured at 77°C by ASTM-D1321. Suitable examples of the above waxes include : microcrystalline and oxidized microcrystalline petrolatum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax; candelilla; and carnauba wax.

The detergent compositions herein can contain all manner of other materials commonly found in laundering and cleaning compositions. For example, such compositions can contain thickeners and soil suspending agents such as carboxymethylcellulose and the like. Enzymes, especially the proteolytic and lipolytic enzymes commonly used in laundry detergent compositions, can also be present herein. Various perfumes, optical bleaches, fillers, anti-caking agents, fabric softeners and the like can

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be present in the compositions to provide the usual benefits occasioned by the use of such materials in detergent compositions. It is to be recognized that all such adjuvant materials are useful herein inasmuch as they are compatible and stable in the presence of the aluminosilicate ion exchange builders.

The granular detergent compositions herein can also advantageously contain a peroxy bleaching component in an amount from about 3% to about 40% by weight, preferably from about 8% to about 33% by weight. Examples of suitable peroxy bleach components for use herein include perborates, persulfates, persilicates, perphosphates, percarbonates, and more in general all inorganic and organic peroxy bleaching agents which are known to be adapted for use in the subject compositions. The composition can also advantageously include a bleach activator which is normally an organic compound containing an N-acyl, or an O-acyl (preferably acetyl) group. Preferred materials are N,N,N',N'-tetraacetyl ethylene diamine and N,N,N',N'-tetraacetylglycouril.

The detergent compositions of this invention can be prepared by any of the several well known procedures for preparing commercial detergent compositions. For example, the compositions can be prepared by simply admixing the aluminosilicate ion exchange material with the water-soluble organic detergent compound. The adjuvant builder material and optional ingredients can be simply admixed therewith, as desired. Alternatively, an aqueous slurry of the aluminosilicate ion exchange builder containing the dissolved water-soluble organic detergent compound and the optional and auxiliary materials can be spray-dried in a tower to provide a granular composition. The granules of such spray-dried detergent compositions contain the aluminosilicate ion exchange builder, the organic detergent compound and the optional and auxiliary materials.

In a preferred process, the surfactant ingredients, the aluminosilicate and the polymeric material are slurried in an aqueous medium, together with sodium silicate and sodium sulfate, if present. This mixture is then spray-dried and the necessary quantities of the phosphate salt, e.g. sodium tripolyphosphate, is added separately to the spray-dried mixture. Other ingredients which are normally added after the spray-drying step are enzyme and bleach.

It is highly preferred that the sodium tripolyphosphate be dry-mixed in this fashion because this avoids the possibility of reversion of the tripolyphosphate to ortho and/or pyrophosphate, it being known that such reverted phosphate materials tend to deposit noticebly on both the laundered fabrics and on washing machine surfaces. The compositions of the present invention show very little or no tendency to deposit insoluble phosphate salts on to fabric or machine surfaces and are very advantageous in this regard.

In an especially preferred process of the present invention, a specific type of sodium silicate and specific drying conditions are used to avoid agglomeration of the aluminosilicate material.

Agglomeration of the aluminosilicate tends to cause a high level of insolubles, an unsightly solution appearance, deposits on fabrics, and blocking of cation exchange sites with resulting reduced calcium depletion capacity.

The two parameters controlling the tendency for the aluminosilicate to agglomerate are ratio and level of silicate and the level of base powder moisture.

The chemistry of silicate solutions involves what has become known as the crystalloid-colloïdal (amorphous) balance with the break-point at the ratio 2.0 molar or 1.96 weight (based on SiO_2/Na_2O). Below 2.0 ratio the silicate anion consists of either one or two nonionic crystalline species. Above 2.0 the molecular weight of silicates increases as polymerization occurs, with a step change in intrinsic viscosity.

It has been found that the degree of aluminosilicate agglomeration is dramatically reduced by the use of low, e.g. 1.6 ratio si silicate. In addition, it has been found that decreasing base powder moisture tends to increase agglomeration of aluminosilicate, especially if the base granules are overdried below the level corresponding to the aluminosilicate bound moisture.

It is therefore highly preferred that the process uses 1.6 ratio silicate at a level from 3% to 8% and the base powder is dried to a free moisture level of from 2% to 6%, especially about 4%.

The detergent compositions herein are employed in aqueous liquros to cleanse surfaces, especially fabric surfaces, using any of the standard laundering and cleansing techniques. For example, the compositions herein are particularly suited for use in standard automatic washing machines at concentrations of from about 0.1% to about 1.5% by weight. Optimal results are obtained when the compositions herein are employed in an aqueous laundry bath at a level of at least about 0.5% by weight. As is the case of most commercial laundry detergent compositions, the dry compositions herein are usually added to a conventional aqueous laundry solution at a rate of about 1.0 cup/17 gallons of wash water.

The detergent compositions containing such materials have a pH in the range of from about 8.0 to about 11, preferably about 9.5 to about 10.2. As in the case of other standard detergent compositions, the compositions herein function optimally within the basic pH range to remove soils e.g. triglyceride soils and stains. While the aluminosilicates herein inherently provide a basic solution, the detergent compositions comprising the aluminosilicate and the organic detergent compound can additionally contain from about 5% to about 25% by weight of a pH adjusting agent. Such compositions can, of course, contain the auxiliary builder materials and optional ingredients as hereinbefore described.

The optional pH adjusting agents useful herein include any of the water-soluble, basic materials commonly employed in detergent compositions. Typical examples of such water-soluble materials include the sodium phosphates; sodium hydroxide; potassium hydroxide; triethanolamine; diethanolamine; ammonium hydroxide and the like. Preferred pH adjusting agents herein include sodium hydroxide and triethanolamine.

In the Examples which follow, the abbreviations used have the following designations:

LAS : Linear C_{12} alkyl benzene sulfonate
TAS : Tallow alkyl sulfate
TAE_{11}: Tallow alcohol ethoxylated with 11 moles of ethylene oxide per mole alcohol
Dobanol 45-E-7 : A C_{14}-C_{15} oxo-alcohol with 7 moles of ethylene oxide
Dobanol 45-E-3 : A C_{14}-C_{15} oxo-alcohol with 3 moles of ethylene oxide
P_5 : Sodium pentapolyphosphate
Silicate : Sodium silicate having an SiO_2:Na_2O ratio of 1.6
DIMA : Copolymer of di-isobutylene and maleic anhydride of molecular weight 30,000 (Empicryl)
SMA : Styrene/maleic acid copolymer of molecular weight 300,000.

The level of Zeolite A is given on an anhydrous basis; the material contains 21% water of crystallisation.

The present invention is illustrated by the following Examples.

EXAMPLES I-III

The following compositions were prepared by spray-drying an aqueous slurry of the ingredients except for sodium perborate which was dry-mixed to the spray-dried granular composition.

	EXAMPLES		
	1 %	2 %	3 %
LAS	8	8	13
Dobanol 45-E-7	3	-	-
TAE_{11}	-	3	3.5
C_{22} soap	3	4	2
Sodium tripolyphosphate	2	3	4
Zeolite A (particle size 5 μ)	28	26	45
Gantrez AN 119	1	1	1.5
Silicate	4	5	-
Protease enzyme	0.5	0.5	0.8
Sodium perborate	30	32	-
Sodium sulfate	7	4	20
Moisture and miscellaneous		to 100	

The compositions of the above examples provided excellent detergency on a wide range of fabrics and soils, and were equivalent in performance to conventional fully phosphate-built detergents.

EXAMPLES IV-IX

	Examples				
	4	5	6	7	8
LAS	5	-	8	5	5	[illegible]
TAS	3	-	-	-	2	-
Dobanol 45-E-7	-	8	2.4	1.5	-	-
TAE_{11}	3	-	-	-	-	1
Dobanol 45-E-3	-	4	-	-	-	-
C_{12} soap	-	2	-	-	4	-
C_{22} soap	2	-	3	4	-	2
Sodium tripolyphosphate	1.0	2.5	4.5	-	3.0	1.5
P_5	-	-	-	1.5	-	-
Zeolite A	25	30	45	-	-	18
Zeolite X	-	-	-	28	[illegible]	-
Gantrez AN 119	0.8	2.5	-	2.0	-	-
Gantrez AN 136	-	-	1.5	-	-	-
DIMA	-	-	-	-	2.5	-
SMA	-	-	-	-	-	1.5
Silicate	3	4	3	-	4	-
Sodium citrate	15	-	-	-	-	10
Protease enzyme	0.5	0.5	-	0.5	-	[illegible]
Sodium perborate	32	18	19	25	-	[illegible]
TAED *	1	5	-	-	-	-
Sodium sulphate	-	10	-	20	[illegible]	[illegible]
Moisture and miscellaneous				100		

* Tetra-acetyl ethylene diamine

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The compositions of the above Examples all provide good detergency performance, comparable to conventional high-phosphate compositions and superior to compositions built with Zeolite A but without the minor content of phosphate and polymeric material.

Similar results are achieved when the tripolyphosphate in Examples 4-6 is replaced by a P_{12} glassy phosphate. The anionic.nonionic active systems of Examples 6-9 can be replaced by all nonionic systems, for example, with Dobanol 45-E-7 alone or with 8:1 mixtures of, for example, Dobanol 45-E-7 and Dobanol 45-E-3. The Zeolite A in Examples 4-6 and 9 can be replaced in whole or in part by an amorphous sodium aluminosilicate.

What we claim is:

1. A detergent composition comprising

(a) from 2% to 60% of a surfactant selected from anionic, nonionic, zwitterionic and amphoteric surfactants and mixtures thereof; and

(b) from 5% to 60% of a water-insoluble aluminosilicate ion exchange material of the formula

$$M_z\left[(AlO_2)_z.(SiO_2)_y\right]x\ H_2O$$

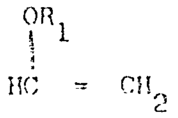
wherein M is a calcium-exchange cation; z and y are integers of at least 6; the molar ratio of z to y is in the range from 1.0 to about 0.5; and X is an integer from about 15 to about 264; said aluminosilicate ion exchange material having a particle size diameter from about 0.1 micron to about 100 microns; a calcium ion exchange capacity of at least about 200 mq. eq. $CaCO_3$/g.; and a calcium ion exchange rate of at least about 2 grains(Ca^{++})/gallon/minute/gram,

characterized in that the composition additionally comprises:

(c) from 0.5% to 6% of a phosphate builder salt; and

(d) 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)



$$\overset{\displaystyle OR_1}{\overset{|}{HC}} = CH_2$$

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

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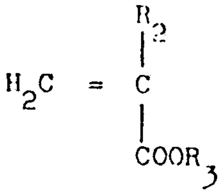
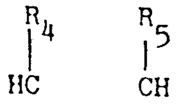
(ii)



$H_2C=\underset{COOR_3}{\overset{R_2}{C}}$

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

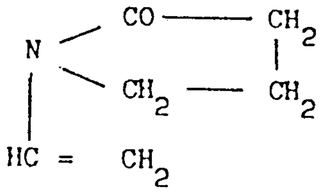
(iii)



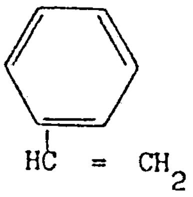
$\overset{R_4}{HC} \quad \overset{R_5}{CH}$

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.

2. A composition according to Claim 1, characterised in that the phosphate salt is present in an amount of from 1% to 4%.

3. A composition according to Claim 1 or Claim 2, characterised in that the phosphate salt is an alkali metal tripolyphosphate.

4. A composition according to any one of Claims 1-3, characterised in that the aluminosilicate is Zeolite A having a particle size from 0.2 microns to 10 microns.

5. A composition according to any one of Claims 1-4, characterised in that the surfactant comprises a 5:1 to 1:3 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.

6. A composition according to Claim 5, characterised in that the surfactant additionally comprises from 1% to 5% of a C_{10}-C_{20} soap.

7. A composition according to any one of Claims 1-8, characterised in that the polymeric material is a copolymer of maleic acid or anhydride and methyl vinyl ether, or a water-soluble salt thereof.

8. A composition according to any one of Claims 1-7, characterised in that the phosphate salt is dry-mixed in the composition.

European Patent Office

EUROPEAN SEARCH REPORT

0000215

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	FR - A - 2 291 268 (PROCTER & GAMBLE) & BE 835 492 (quoted in the present application) * Claims, in particular claim 11 *	1-8
	--	
	DE - A - 2 547 389 (HENKEL) * Claims *	1

TECHNICAL FIELDS SEARCHED

C 11 D 3/12
C 11 D 3/37

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	[illegible]	[illegible]

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