

# PATENT SPECIFICATION

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## (54) COMPOSITIONS FOR WASHING OR BLEACHING TEXTILES

(71) We, HENKEL & CIE. GMBH., a German Company, of 67 Henkelstrasse, Duesseldorf-Holthausen 4000, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The main patent (Patent Application 15797/74 (Serial No. 1,473,201)) relates to a process for washing and/or bleaching textiles by treatment with an aqueous liquor which contains in suspension a water soluble synthetically produced, finely-divided crystalline aluminium or boron silicate cation exchanger containing bound water, having a calcium binding capacity (as hereinafter defined) of at least 50 mg of CaO/g of anhydrous active substance (=AS), of the general formula:



in which Cat represents a cation of valency n and exchangeable with calcium, x is a number from 0.7 to 1.5 Me represents boron or aluminium and y is a number from 0.8 to 6, preferably 1.3 to 4.

The expression "calcium binding capacity" is to be understood as being the value obtained by the following test:—

1 litre of an aqueous solution containing 0.594 g of CaCl<sub>2</sub> (= 300 mg CaO/litre) and adjusted to a pH value of 10 with dilute NaOH is mixed with 1 g of aluminium silicate (referred to AS). The suspension is vigorously stirred at a temperature of 22° C (± 2° C) for 15 minutes after which time the aluminium silicate is immediately filtered off and the residual hardness x in mg CaO/litre of the filtrate is determined. The calcium binding capacity is then determined from the formula

$$\text{calcium binding capacity} = 300 - x$$

The calcium binding capacity may reach

values of 200 mg CaO/g AS and lies preferably in the range from 100 to 200 mg CaO/g AS.

If the above test for calcium binding capacity is carried out at higher temperatures than 22° C e.g. at 60° C the values formed are consistently higher than those formed for the standard test at 22° C. This fact distinguishes the aluminium silicates from most of the soluble complex-forming substances previously proposed for use in washing agents.

Sodium is the preferred cation, but it may also be replaced by lithium, potassium, ammonium or magnesium, as well as by the cations of water-soluble organic bases, for example those of primary, secondary or tertiary amines or alkylolamines having not more than 2 carbon atoms per alkyl residue and not more than 3 carbon atoms per alkylol residue.

The above-defined cation-exchanging compounds to be used according to the invention instead of phosphates, especially tripolyphosphates, are for the sake of simplicity denoted below as "aluminium silicates". Sodium aluminium silicates are preferably used. All details given for their preparation and use obviously apply to the other compounds claimed.

Compounds of the composition



are of special practical interest. The calcium binding capacity of these substances lies in the region of 100 to 200 mg CaO/g AS.

The present invention provides a further development of the process of the main patent, in which the aqueous treatment liquor for the textiles contains a surface-active component consisting of 1 part by weight of non-ionic and 0 to 3 parts by weight of anionic surfactants, and wherein the non-ionic surfactant comprises a mixture of different ethoxylated condensates having an aliphatic hydrocarbon residue with 10 to 18 carbon atoms, in which

0.2 to 2 parts by weight of condensate hav-

ing 2 to 6 ethyleneglycolether residue in the molecule are present per part by weight of condensate with 8 to 20 ethyleneglycolether residues in the molecule.

5 The said surface-active component, of which the concentration used preferably amounts to 0.1 to 3 g/l, in combination with the above-described, cation-exchanging aluminium silicates causes an improved removal of dirt,  
10 especially in the case of fatty and oily contaminations.

The above-defined aluminium silicates can be prepared synthetically in a simple way, for example by reaction of a water-soluble silicate with a water-soluble aluminate in the presence of water in appropriate concentrations. For this purpose, aqueous solutions of the water-soluble silicate and water-soluble aluminate may be mixed with one another or  
20 the water-soluble silicate or the water-soluble aluminate present in the solid state may be reacted with the water-soluble aluminate or the water-soluble silicate present as an aqueous solution respectively. Also on mixing the water-soluble silicate and the water-soluble aluminate present as solids, the desired aluminium silicate is obtained when water is present. Aluminium silicates can also be prepared from  $\text{Al}(\text{OH})_3$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{SiO}_2$  by reaction with alkali metal silicate or aluminate solutions.  
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The aluminium silicates prepared by precipitation or converted by other processes into the finely divided state in an aqueous suspension are converted from the amorphous into the crystalline state by heating at temperatures from 50° to 200° C.  
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The crystalline aluminium silicate present in aqueous suspension can be separated by filtration from the remaining aqueous solution and dried at temperatures of, for example, 50° to 800° C. The product contains more or less bound water, depending on the drying conditions. Anhydrous products are obtained  
40 at 800° C. If the water is to be completely driven off, this is possible by heating at 800° C for one hour; in this way the AS contents of the aluminium silicates are also determined.

Such high drying temperatures are not recommended in the case of the aluminium silicates to be used according to the invention; suitably one does not go beyond 400° C. It is a particular advantage that products dried even at substantially lower temperatures of, for example, 80° to 200° C until the adhering liquid water is removed are utilisable for the purpose of the invention. The aluminium silicates containing varying amount of bound water thus prepared after the splitting up of  
50 the dried filter cake are obtained as a fine powder, of which the initial particle size is not more than 0.1 mm, but is usually substantially less and goes to a dust-fine product, for example up to 0.1  $\mu$ . It is to be borne in  
60 mind that the initial particles may be agglomer-

ated to larger structures. The size of the initial particles lies preferably in the region of 50 to 1  $\mu$ .

The aluminium silicates of other cations, for example of potassium, magnesium or water-soluble organic bases, can be prepared in a simple way from the sodium aluminium silicates by base exchange. The use of these compounds instead of the sodium aluminium silicates may be suitable when a special effect is to be obtained by transfer on the said cations, for example if it is desired to influence the state of solution of simultaneously present surface-active substances.

The amount of aluminium silicate required to obtain a good washing and cleaning effect depends on its calcium binding capacity, on the amounts and degree of contamination of the materials to be treated and on the hardness and the quantity of water used. When hard water is used, it is expedient to proportion the amount of aluminium silicate so that the residual hardness of the water is not more than 5° German hardness (corresponding to 50 mg  $\text{CaO/l}$ ), preferably 0.5 to 2° German hardness (5 to 20 mg  $\text{CaO/l}$ ). To obtain an optimal washing and cleaning effect it is advisable to use a certain excess of aluminium silicates, especially in the case of heavily soiled substrates, so as to bind wholly or partly the substance producing the hardness contained in the detached impurities. Consequently the concentration of aluminium silicates used is preferably from 0.2 to 10 g AS/litre, especially from 1 to 6 g AS/litre.  
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As already found in the main patent, the removal of the impurities is substantially accelerated and/or improved when a conventional builder is added to the treatment liquor which exerts a complex-forming and/or precipitating action on the calcium present in the water as the hardness-producing substance. Although the complex-forming builders for calcium for use in the invention are substances which have so small a complex-forming ability that they have not previously been regarded as typical complex-forming substances for calcium, they often have the ability to delay the precipitation of calcium carbonate from aqueous solution.  
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Preferably small added amounts of, for example, 0.05 to 2 g/litre of complex-forming or calcium-precipitating builders are used in order to accelerate or improve the removal of the impurities markedly. In particular, additions of 0.1 to 1 g/litre are used. Substantially larger amounts may also be used, but when phosphorus-containing builders are used, amounts should be chosen such that the phosphorus carried by the waste water is distinctly less than that obtained by use of the washing agents based on the triphosphate usually present.  
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The complex-forming and calcium-precipitating builders can be inorganic compounds,  
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such as pyrophosphate, triphosphate, higher polyphosphates and metaphosphates.

Organic compounds which serve as complex-forming and calcium-precipitating builders are found among the polycarboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids, carboxyalkylethers, polyanionic polymeric carboxylic acids and the phosphonic acids, these compounds being used mostly in the form of their water-soluble salts.

Examples of polycarboxylic acids are dicarboxylic acids of the general formula



in which  $n = 0$  to 8, also maleic acid, methylenemalononic acid, citraconic acid, mesaconic acid, itaconic acid, non-cyclic polycarboxylic acids with at least 3 carboxyl groups in the molecule such as tricarballic acid, aconitic acid, ethylenetetracarboxylic acid, 1,1,3,3-propane-tetracarboxylic acid, 1,1,3,3,5,5-pentane-hexacarboxylic acid, hexanehexacarboxylic acid, cyclic di- or poly-carboxylic acids such as cyclopentane-tetracarboxylic acid, cyclohexane-hexacarboxylic acid, tetrahydrofuran-tetracarboxylic acid, phthalic acid, terephthalic acid, benzenetri-, benzenetetra- or benzenepentacarboxylic acids and mellitic acid.

Examples of hydroxymono- or -poly-carboxylic acids are glycollic acid, lactic acid, malic acid, tartronic acid, methyltartronic acid, gluconic acid, glyceric acid, citric acid, tartaric acid, and salicylic acid.

Examples of aminocarboxylic acids are glycine, glycyglycine, alanine, asparagine, glutamic acid, aminobenzoic acid, iminodi- or tri-acetic acid, hydroxyethyl-iminodiacetic acid, ethylenediamino-tetraacetic acid, hydroxyethyl-ethylenediamino-triacetic acid, diethylenetriamino-pentaacetic acid as well as higher homologues, which may be prepared by polymerisation of an N-aziridylcarboxylic acid derivative, for example of acetic acid, succinic acid, tricarballic acid, and subsequent saponification, or by condensation of polyamines with a molecular weight of 500 to 10,000 with chloroacetic acid or bromoacetic acid salts.

Examples of carboxyalkylethers are 2,2-oxydisuccinic acid and other etherpolycarboxylic acids, especially polycarboxylic acids containing carboxymethylether groups, to which belong the corresponding derivatives or the following polyhydric alcohols or hydroxycarboxylic acids, which may be completely or partly etherified with the glycollic acid: glycol, di- or tri-glycols, glycerine, di- or tri-glycerine, glycerinemonomethylether, 2,2-dihydroxymethylpropanol, 1,1,1-trihydroxymethylethane, 1,1,1-trihydroxymethylpropane, erythritol, pentaerythritol, glycollic acid, lactic acid, tartronic acid, methyltartronic acid, glyceric acid, erythronic acid, malic acid, citric acid,

tartaric acid, trihydroxyglutaric acid, saccharic acid, and mucic acid.

As transition types to the polyanionic polymers, the carboxymethylethers of sugar, starch and cellulose may be mentioned.

Among the polyanionic polymers, the polymeric carboxylic acids play a special part such as the polymers of acrylic acid, hydroxyacrylic acid, maleic acid, itaconic acid, mesaconic acid, aconitic acid, methylenemalononic acid and citraconic acid the copolymers of the above-mentioned carboxylic acids with one another or with ethylenically unsaturated compounds such as ethylene, propylene, isobutylene, vinyl alcohol, vinylmethylether, furan, acrolein, vinyl acetate, acrylamide, acrylonitrile, methacrylic acid, crotonic acid etc. such as the 1,1-copolymer from maleic anhydride and ethylene or propylene or furan.

Further polyanionic polymers of the type of the polyhydroxypolycarboxylic acids or polyaldehyde-polycarboxylic acids are substantially substances built up from acrylic acid and acrolein units or acrylic acid and vinyl alcohol units, which are obtainable by copolymerisation of acrylic acid and acrolein or by polymerisation of acrolein followed by the Cannizzaro reaction, possibly in the presence of formaldehyde.

Examples of phosphorus-containing organic complex-forming builders are alkanepolyphosphonic acids, amino- and hydroxy-alkanepolyphosphonic acids and phosphonocarboxylic acids such as the compounds methanediphosphonic acid, propane-1,2,3-triphosphonic acid, butane-1,2,3,4-tetraphosphonic acid, polyvinylphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, 1-amino-1-phenyl-1,1-diphosphonic acid, aminotrimethylenetriphosphonic acid, methylamino- or ethylamino-dimethylenediphosphonic acid, ethylenediaminotetramethylenetetraphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, phosphonoacetic acid, phosphonopropionic acid, 1-phosphonoethane-1,2-dicarboxylic acid, 2-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 2-phosphonobutane-2,3,4-tricarboxylic acid as well as copolymers from vinylphosphonic acid and acrylic acid.

By using the above-described aluminium silicates according to the invention it is readily possible to keep the phosphorus content of the treatment liquors at not more than 0.6 g/litre, preferably at not more than 0.3 g/litre of organically and/or inorganically bound phosphorus, even if phosphorus-containing inorganic or organic complex-forming or calcium-precipitating builders are used. Good results are still obtained when the treatment liquors are completely free from phosphorus.

The process according to the invention for washing all types of textiles can be carried out in industry, in commercial laundries and in the household.

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The textiles to be washed by the compositions of the invention may consist of a large variety of fibres of natural or synthetic origin. These include cotton, regenerated cellulose or linen as well as textiles which contain highly finished cotton or synthetic chemical fibres such as polyamide, polyester, polyacrylonitrile, polyurethane, polyvinyl chloride or polyvinylidene chloride fibres. The washing compositions according to the invention can also be used for washing textiles consisting of synthetic fibres-cotton mixed fabrics denoted as "easy-care", or "non-iron" fabrics.

In the washing and cleaning of such substrates using aqueous cleaning baths containing aluminium silicates suspended therein according to the invention, the washing or cleaning effect can be improved by the addition of other surfactants, builders and conventional additives. These include surface-active substances, surface-active or non-surface-active foam stabilisers or inhibitors, textile softeners, neutral or alkaline reacting builder substances other than the aforesaid complex-forming or calcium-precipitating builders, chemically acting bleaching agents, e.g. percompounds, as well as stabilisers and/or activators for these, dirt carriers, corrosion inhibitors, antimicrobial substances, enzymes, brighteners, dyes and perfumes and so on.

On use of one or more of the above-mentioned substances usually present in washing and cleaning liquors, the following concentrations are suitably maintained:

0-6 g/litre builder substances, including the above-defined complex-forming or precipitating builders for calcium,

0-0.4 g/litre active oxygen or equivalent amounts of active chlorine

The pH value of the treatment baths may lie in the region of 6 to 13, preferably 8.5 to 12, depending on the substrate to be washed or cleaned.

The invention further relates to a composition for carrying out of the process of the invention which contains as calcium binding substances the above-defined aluminium silicates. These compositions are a further development of the compositions of the main patent characterised by containing the above-defined surface-active components.

The compositions preferably contain 3 to 40, especially 3 to 30% of a surface-active component of this kind.

The content of aluminium silicate of the composition may lie in the region of 5 to 95, preferably 15 to 60%.

The compositions according to the invention may further contain conventional complex-forming or calcium-precipitating builders, the action of which, depending on the chemical nature of the agent, is to be recognised preferably with contents of 2 to 15%.

The quantity of the inorganic phosphates and/or organic phosphorus compounds present

in the agents according to the invention should not be greater than that which corresponds to a total phosphorus content of 6% of the agent, preferably of 3%.

Apart from this, other constituents of washing compositions may be present.

All these percentage data are percentages by weight: in the case of the aluminium silicates they relate to the anhydrous active substance (= AS).

The other components of washing compositions include surface-active or non-surface-active foam stabilisers or inhibitors, textile softeners, neutral or alkaline reacting builder substances other than the complex-forming or calcium-precipitating builders referred to above, chemically acting bleaching agents such as percompounds, as well as stabilisers and/or activators therefor. Constituents usually present in smaller quantity include corrosion inhibitors, antimicrobial substances, dirt carriers, enzymes, brighteners, dyes and perfumes and so on.

The composition of typical textile washing compositions to be used at temperatures in the region of 50 to 100° C lies within the following formulation:

- (A) 3-30% by weight of a surface-active component according to the above definition
- (B) 5-70% by weight of a silicate cation exchanger as defined above (corresponding to AS)
- (C) 2-45% by weight of a complex-forming or calcium-precipitating builder
- (D) 0-50% by weight of an inorganic and/or an organic builder not being a complex-forming or calcium-precipitating builder
- (E) 0-50% by weight of a bleaching agent as well as other detergent additives.

Now follows an enumeration of the washing composition constituents suitable for incorporation in the compositions of the invention.

The non-ionic surface-active compounds (= nonionics) to be used according to the invention are products of addition of 2 to 6 or 8 to 18 mol of ethylene oxide to 1 mol of fatty alcohol, alkylphenol, fatty acid, fatty amine, fatty acid amide or alkanesulphonamide. The purely aliphatic nonionics derived for example from coconut or tallow fatty alcohols, oleyl alcohol or secondary alcohols having 8 to 18, preferably 12 to 18 carbon atoms, are specially important.

The products of addition of ethylene oxide to terminal or non-terminal vicinal alkanediols can also be used as nonionics, those with 2 to 4 or 8 to 14 ethyleneglycolether residues in the molecule are preferred.

The anionic surface-active compounds contain in the molecule at least one hydrophobic organic residue and a water-solubilising anionic group. The hydrophobic residue is usually an

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aliphatic hydrocarbon residue having 8 to 26, preferably 10 to 22 and especially 12 to 18 carbon atoms or an alkyl-aromatic residue having 6 to 18, preferably 8 to 16 aliphatic carbon atoms.

Utilisable anionic surface-active compounds include soaps from natural or synthetic, preferably saturated fatty acids, possibly also from resin or naphthene acids. Suitable synthetic anionic surface-active compounds are those of the sulphonate, sulphate and synthetic carboxylate types.

Suitable surface-active compounds of the sulphonate type are alkylbenzenesulphonates ( $C_8$ — $_{15}$ -alkyl), mixtures of alkene and hydroxyalkane-sulphonates as well as disulphonates, such as are obtained from monoolefines with terminal or non-terminal double bonds by sulphonation with gaseous sulphur trioxide and subsequent alkaline or acid hydrolysis of the sulphonation products. Further suitable surface-active compounds are alkane-sulphonates, which are obtainable from alkanes by sulphochlorination or sulfoxidation and subsequent hydrolysis or neutralisation, or by bisulphite addition to olefines. Further useful surface-active compounds of the sulphonate type are the esters of  $\alpha$ -sulpho-fatty acids, for example the  $\alpha$ -sulphonic acids from hydrogenated methyl or ethyl esters of coconut, palm kernel or tallow fatty acids.

Suitable surface-active compounds of the sulphate type are the sulphuric acid monoesters of primary alcohols (for example from coconut fatty alcohols, tallow fatty alcohols or oleyl alcohol) and secondary alcohols. In addition, sulphated fatty acid alkanolamides, fatty acid monoglycerides or reaction products from 1 to 4 mol of ethylene oxide with primary or secondary fatty alcohols or alkylphenols are suitable.

Further suitable anionic surface-active compounds are the fatty acid esters or amides of hydroxy- or amino-carboxylic acids or sulphonic acids, such as the fatty acid sarcosides, glycollates, lactates, taurides or isethionates.

The foaming power of the surface-active component can be increased or reduced by the combination of suitable surface-active types; a reduction can likewise be obtained by additions of non-surface-active organic substances.

A reduced foaming power, which is desired for working in machines, is frequently attained by combination of different types of surface-active compound, for example, of sulphates and/or sulphonates with nonionics and/or with soaps. In the case of soaps the foam inhibition increases with the degree of saturation and the carbon number of the fatty acid residue; soaps of the saturated  $C_{20-24}$ -fatty acids are therefore specially suitable as foam inhibitors.

Some chlorine-containing N-alkylated aminotriazines, which are obtained by reacting 1 mol of cyanuric chloride with 2 to 3 mol of a mono- and/or di-alkylamine having 6 to 20,

preferably 8 to 18 carbon atoms in the alkyl residue, belong to the non-surface-active foam inhibitors. Propoxylated and/or butoxylated aminotriazines have a similar action, for example products which are obtained by addition of 5 to 10 mol of propylene oxide to 1 mol of melamine and further addition of 10 to 50 mol of butylene oxide to this propylene oxide derivative.

Water-insoluble organic compounds such as paraffins or halogenated paraffins with melting points below  $100^\circ\text{C}$ , aliphatic  $C_8$ — $C_{40}$  ketones, and aliphatic carboxylic acid esters which contain at least 18 carbon atoms in the acid or alcohol residue, possibly also in each of these two residues (for example triglycerides or fatty acid-fatty alcohol esters), are also suitable as non-surface-active foam inhibitors. They can be used particularly in combinations of surface-active compounds of the sulphate and/or sulphonate type with soaps for reduction of the foam. Alkali-stable silicones have also proved useful for suppressing foam.

Weakly acid, neutral and alkaline reacting inorganic or organic salts are suitable as builders.

Weakly acid, neutral or alkaline reacting salts useful according to the invention are, for example, the bicarbonates, carbonates, borates or silicates of the alkali metals, alkali metal sulphates and the alkali metal salts of organic non-surface-active sulphonic acids, carboxylic acids and sulphocarboxylic acids containing 1 to 8 carbon atoms. Examples of these are water-soluble salts of benzene, toluene- or xylene-sulphonic acids, water-soluble salts of sulphoacetic acid, sulphobenzoic acid or sulphodicarboxylic acids.

The compounds mentioned above as complex-forming or calcium-precipitating builders are useful throughout as builders; they can therefore also be present in the compositions according to the invention in larger amounts than are needed to fulfil their function as complex-forming or calcium-precipitating builders.

The components of the textile washing compositions, especially the builders are usually chosen so that the preparations have a neutral to strongly alkaline reaction, so that the pH value of a 1% solution of the preparation lies mostly in the region from 7 to 12. In this case fine washing compositions have usually a neutral to weakly alkaline reaction (pH value = 7—9.5), while steeping, pre-washing and boiling washing compositions are adjusted to have a more strongly alkaline reaction (pH value = 9.5—12, preferably 10—11.5). If for special cleaning purposes higher pH values are desired, these can be easily adjusted by use of alkali metal silicates with suitable  $\text{Na}_2\text{O}:\text{SiO}_2$  ratios or of caustic alkalis.

Of the compounds providing  $\text{H}_2\text{O}_2$  in water

and serving as bleaching agents, sodium perborate tetrahydrate ( $\text{NaBO}_3 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ ) and the monohydrate ( $\text{NaBO}_3 \cdot \text{H}_2\text{O}_2$ ) have special importance. However, other borates providing  $\text{H}_2\text{O}_2$  are also useful, for example perborax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}_2$ . These compounds may be partly or wholly replaced by other active oxygen carriers, especially by peroxyhydrates, such as peroxyarbonates ( $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ ), peroxyphosphates, citrate perhydrates, urea- $\text{H}_2\text{O}_2$ - or melamine- $\text{H}_2\text{O}_2$ -compounds as well as peracid salts providing  $\text{H}_2\text{O}_2$ , such as salts of Caro's acid ( $\text{KHSO}_5$ ), perbenzoates or peroxyphthalates.

It is advisable to incorporate the usual water-soluble and/or water-insoluble stabilisers for the peroxy-compounds together with the latter in amounts from 0.25 to 10% by weight. Suitable water-insoluble stabilisers, which constitute, for example, 1 to 8, preferably 2 to 7% of the weight of the total preparation, are mostly magnesium silicates  $\text{MgO}:\text{SiO}_2 = 4:1$  to  $1:4$ , preferably  $2:1$  to  $1:2$  and especially  $1:1$ , obtained by precipitation from aqueous solutions. Alkaline earth metal, cadmium or tin silicates of corresponding composition are utilisable in their place. Water-containing oxides of tin are also suitable as stabilisers. Water-soluble stabilisers, which may be present together with the water-insoluble stabilisers, are the organic complex-forming substances, the amount of which may constitute 0.25 to 5, preferably 0.5 to 2.5% of the weight of the total preparation.

In order to obtain during the washing a satisfactory bleaching action even at temperatures below  $80^\circ\text{C}$ , especially in the range from  $60^\circ$  to  $40^\circ\text{C}$ , activator-containing bleaching components are preferably incorporated in the preparations.

Certain N-acyl and O-acyl compounds forming organic peracids with the  $\text{H}_2\text{O}_2$  serve as activators for percompounds yielding  $\text{H}_2\text{O}_2$  in water, especially acetyl-, propionyl- or benzoyl compounds, as well as carbonic acid or pyrocarbonic acid esters. Among other useful compounds may be mentioned: N-diacylated and N,N'-tetraacylated amines as for example, N,N,N',N' - tetraacetyl - methylenediamine or ethylenediamine, N,N - diacetylaniline and N,N - diacetyl - p - toluidine or 1,3-diacylated hydantoin, alkyl - N - sulphonyl-carbonamides, for example N - methyl - N - mesyl - acetamide, N - methyl - N - mesyl-benzamide, N - methyl - N - mesyl - p-nitrobenzamide, and N - methyl - N - mesyl-p - methoxybenzamide, N - acylated cyclic hydrazides, acylated triazoles or urazoles as for example, the monoacetylmaleic acid hydrazide, O,N,N - trisubstituted hydroxylamines as for example, O - benzoyl - N,N - succinylhydroxylamine, O - acetyl - N,N - succinylhydroxylamine, O - p - methoxybenzoyl - N,N - succinylhydroxylamine, O - p - nitrobenzoyl - N,N - succinylhydroxylamine and

O,N,N - triacetyl - hydroxylamine, N,N'-diacyl - sulphonylamides, as for example, N,N' - dimethyl - N,N' - diacetyl - sulphonyl-amide, and N,N' - diethyl - N,N' - dipropionyl - sulphonyl-amide, triacylcyanurates, for example triacetyl- or tribenzoyl-cyanurate, carboxylic acid anhydrides, for example benzoic anhydride, m-chlorobenzoic anhydride, phthalic anhydride, 4-chloro-phthalic anhydride, sugar esters, as for example, glucose pentaacetate, 1,3 - diacetyl - 4,5 - diacyloxy, imidazolidines, for example the compounds 1,3 - diformyl - 4,5 - diacetoxy - imidazolidine, 1,3 - diacetyl - 4,5 - diacetoxy - imidazolidine, 1,3 - diacetyl - 4,5 - dipropionyloxy-imidazolidine, acylated glycolurils, as for example tetrapropionylglycoluril or diacetyl-dibenzoyl - glycoluril, diacylated 2,5 - diketopiperazines, as for example 1,4-diacetyl - 2,5 - diketopiperazine, 1,4 - dipropionyl - 2,5 - diketopiperazine, 1,4 - dipropionyl - 3,6 - dimethyl - 2,5 - diketopiperazine, acetylation or benzoylation products of propylenediurea or 2,2 - dimethyl - propylenediurea 2,4,6,8 - tetraaza - bicyclo - (3,3,1) - nonane - 3,7 - dione or its 9,9 - dimethyl derivative), sodium salts of p - (ethoxycarbonyloxy) - benzoic acid and p - (propoxycarbonyloxy) - benzenesulphonic acid.

The active chlorine compounds serving as bleaching agents may be inorganic or organic.

Suitable inorganic active chlorine compounds include alkali metal hypochlorites, especially when in the form of their mixed salts or addition compounds to orthophosphates or to condensed phosphates as for example to pyro- and polyphosphates, or to alkali metal-silicates. If the washing compositions contain monopersulphates and chlorides, active chlorine is formed in aqueous solution.

Suitable as organic active chlorine compounds are especially the N-chloro-compounds in which one or two chlorine atoms are linked to a nitrogen atom, the third valency of the nitrogen atoms preferably leading to a negative group, especially a CO— or SO<sub>2</sub>— group. These compounds include dichloro- and trichloro-cyanuric acids or their salts, chlorinated alkylguanides or alkylbiguanides, chlorinated hydantoin and chlorinated melamines.

Furthermore, in the preparations according to the invention dirt carriers may be contained which hold the dirt detached from the fibres suspended in the bath and thus prevent greying. Water-soluble colloids of mostly organic nature are suitable for this purpose, as for example the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ethercarboxylic acids or ether-sulphonic acids of starch or cellulose or salts of acid sulphuric acid esters of cellulose or starch. Water-soluble polyarnides containing acid groups are also suitable for this purpose. In addition, soluble starch preparations and starch products other than those mentioned above can be used, as for example,

imine,  $N'$ -  
for example,  
1 - sulphuryl-  
 $N'$  - dipro-  
anurates, for  
70  
oyl-cyanurate,  
for example  
dic anhydride,  
thalic anhy-  
dride, glucose  
75  
- diacyloxy,  
: compounds  
- imidazolid-  
toxy - imida-  
propionyl-  
80  
- rils, as for  
or diacetyl-  
d 2,5 - di-  
ampl 1,4-  
1,4 - dipro-  
85  
1,4 - dipro-  
topiperazine,  
products of  
hyl - propyl-  
clo - (3,3,1)-  
90  
9 - dimethyl  
- (ethoxycar-  
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acid esters  
120  
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than those  
or example,  
130

degraded starch, aldehyde starches and so forth. Polyvinylpyrrolidone is also utilisable.

The enzyme preparations to be used are usually a mixture of enzymes with different action, for example of proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases. The enzymes obtained from strains of bacteria or fungi such as *Bacillus subtilis* or *Streptomyces griseus* are of special interest, especially proteases or amylases, which are relatively stable towards alkalis, percompounds and anionic surface-active compounds and are still active at temperatures up to 70° C.

Enzyme preparations are usually marketed by the manufacturers as aqueous solutions of the active substances or as powders, granulates or as cold-sprayed products. They frequently contain as diluent or blending agent sodium sulphate, sodium chloride, alkali metal ortho-, pyro- or poly-phosphates, especially tripolyphosphates. Dust-free preparations are regarded as particularly valuable; they are obtained in known way by incorporation of oily or pasty nonionics or by granulating by means of melts of salts in their own water of crystallisation.

Enzymes may be incorporated which are specific for a particular type of dirt, for example proteases or amylases or lipases; it is preferred to use combinations of enzymes of different action, especially combinations of proteases and amylases.

The washing compositions may contain as optical brighteners for cotton, especially derivatives of diaminostilbenedisulphonic acid or its alkali metal salts. For example, salts of 4,4' - bis(2 - anilino - 4 - morpholino - 1,3,5-triazine - 6 - yl - amino) - stilbene - 2,2'-disulphonic acid or similarly constructed compounds, which carry instead of the morpholino group a diethanolamino group, a methylamino group or a 2-methoxyethylamino group, are suitable. Suitable brighteners for polyamide fibres are those of the type of 1,3-diaryl - 2 - pyrazolines, for example the compound 1 - (p - sulphamoylphenyl) - 3 - (p - chlorophenyl) - 2 - pyrazoline as well as similarly constructed compounds which carry instead of the sulphamoyl group, for example, the methoxycarbonyl-, 2-methoxyethoxycarbonyl-, acetylamino- or vinylsulphonyl group. The substituted aminocoumarins for example 4 - methyl - 7 - dimethylamino- or 4 - methyl - 7 - diethylaminocoumarin, are also useful polyamide brighteners. Furthermore, the compounds 1 - (2 - benzimidazolyl) - 2 - (1 - hydroxyethyl - 2 - benzimidazolyl) - ethylene and 1 - ethyl - 3 - phenyl - 7 - diethylamino-carbostyryl are useful as polyamide brighteners. The compounds 2,5-di-(2 - benzoxazolyl) - thiophene, 2 - (2 - benzoxazolyl) - naphtho [2,3 - b] - thiophene and 1,2 - di - (5 - methyl - 2 - benzoxazolyl) -

ethylene are suitable as brighteners for polyester and polyamide fibres. In addition, brighteners of the type of the substituted 4,4'-distyryldiphenyl may be present; for example the compound 4,4' - bis(4-chloro - 3 - sulphostyryl) - diphenyl. Mixtures of the above-mentioned brighteners may also be used.

Compositions according to the invention of powdery to granular state, which may be prepared by all processes known in the art, are of special practical interest.

Thus, for example, the powdery aluminium silicates can be mixed in a simple way with the other components of the washing compositions, while oily or pasty products, as for example nonionics, are sprayed on the powder. Another possible method of preparation consists in the incorporation of the powdery aluminium silicates in the other constituents of the composition present as an aqueous slurry, which is then converted into a powder by processes of crystallisation or by drying the water by heat. After the hot drying, for example on rollers or in spraying towers, then heat- and moisture-sensitive constituents can be incorporated, as for example bleaching components and activators for these, enzymes, antimicrobial substances and so on.

#### Examples.

The preparation of the aluminium silicates used and the determination of the calcium binding capacity are described in the main patent. The water contents were determined by heating the products at 800° C for one hour.

All percentage data are weight percentages; in the case of the aluminium silicates they relate to anhydrous active substance (= AS).

An enumeration of aluminium silicates utilisable according to the invention follows:

- I: 0.9 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2.04 SiO<sub>2</sub>, 4.3 H<sub>2</sub>O  
(= 21.6% of H<sub>2</sub>O)  
completely crystalline  
Calcium binding capacity: 150 mg  
CaO/g AS 110
- Ia: 0.9 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2.04 SiO<sub>2</sub>, 2.0 H<sub>2</sub>O (= 11.4% H<sub>2</sub>O)
- II: 0.8 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2.655 SiO<sub>2</sub>, 5.2 H<sub>2</sub>O  
completely crystalline  
Calcium binding capacity: 120 mg  
CaO/g AS 115
- IIa: 0.8 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2.65 SiO<sub>2</sub>, 0.2 H<sub>2</sub>O 120
- XII: 0.9 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2 SiO<sub>2</sub>, 3 H<sub>2</sub>O  
(= 11% H<sub>2</sub>O)  
Completely crystalline  
Calcium binding capacity: 160 mg  
CaO/g AS 125
- XIII: 0.28 Na<sub>2</sub>O, 0.62 K<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2.04 SiO<sub>2</sub>, 4.3 H<sub>2</sub>O  
Completely crystalline

- Calcium binding capacity: 170 mg  
CaO/g AS
- 5 XV: 1.5 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 2 SiO<sub>2</sub>, x H<sub>2</sub>O  
Completely crystalline  
Calcium binding capacity: 170 mg  
CaO/g AS
- XVI: 1.5 Na<sub>2</sub>O, 1 B<sub>2</sub>O<sub>3</sub>, 2 SiO<sub>2</sub>, 1.5 H<sub>2</sub>O  
Predominantly crystalline  
10 Calcium binding capacity: 120 mg  
CaO/g AS
- XVII: 0.92 Na<sub>2</sub>O, 1 Al<sub>2</sub>O<sub>3</sub>, 1.8 SiO<sub>2</sub>, 3.71 H<sub>2</sub>O  
Completely crystalline  
15 Calcium binding capacity: 180 mg  
CaO/g AS

The constituents in the form of salts contained in the washing compositions of the Examples—namely surface-active compounds, other organic salts as well as inorganic salts—were present as the sodium salts, provided any other is not expressly stated. The terms and abbreviations used have the following meanings:

20 "ABS" is the salt of an alkylbenzenesulphonic acid having 10 to 15, preferably 11 to 13 carbon atoms in the alkyl chain and obtained by condensation of straight-chain olefines with benzene and sulphonation of the alkylbenzene thus obtained,

25 "OS" is a sulphonate obtained from  $\alpha$ -olefine mixtures having 15 to 18 carbon atoms by sulphonation with SO<sub>3</sub> and hydrolysis of

the sulphonation product with alkali, which consists substantially of alkenesulphonate and hydroxyalkanesulphonate, but in addition also still contains small amounts of disulphonates,

The "soap" contains as fatty acid component a hardened mixture of equal parts by weight of tallow and rape oil fatty acid (C<sub>16</sub>—C<sub>22</sub>),

"TA + x EO" and "SA + x EO", are the products of addition of ethylene oxide (EO) to a tallow fatty alcohol (I.V. = 0.5), and to a secondary aliphatic C<sub>11</sub>—C<sub>15</sub> alcohol (SA) and while the numbers represented by x characterise the molar amount of ethylene oxide added on to 1 mol of alcohol,

"CTMS" is the salt of O-carboxymethyl-tartronic acid,

"EDTA" is the salt of ethylenediamine-tetraacetic acid,

"CMC" is the salt of carboxymethylcellulose.

The following Table contains formulations for some washing compositions according to the invention, in which the formulation 1 represents a complete washing composition, which is used in the household, in industrial operations and in industry for washing coloured or white textiles at temperatures from 40° to 100° C, preferably from 50° to 100° C. The two products according to the formulations 2 and 3 are intended for trade and industrial laundries, the first being used in the prewashing process, and the latter in the main washing process.

| Constituent                                                            | % constituent in the washing composition according to Example |      |      |
|------------------------------------------------------------------------|---------------------------------------------------------------|------|------|
|                                                                        | 1                                                             | 2    | 3    |
| TA + 14 EO                                                             | 3.8                                                           | -    | 9.6  |
| TA + 5 EO                                                              | 2.2                                                           | -    | 4.4  |
| SA + 9 EO                                                              | -                                                             | 4.5  | -    |
| SA + 3 EO                                                              | -                                                             | 1.8  | -    |
| ABS                                                                    | 7.0                                                           | -    | -    |
| OS                                                                     | -                                                             | 3.5  | -    |
| Soap                                                                   | 3.4                                                           | 2.0  | -    |
| Foam inhibitor                                                         | -                                                             | 0.6  | -    |
| Aluminium silicate I                                                   | 20.0                                                          | -    | -    |
| Aluminium silicate XII                                                 | -                                                             | 28.0 | -    |
| Aluminium silicate XVII                                                | -                                                             | -    | 40.0 |
| Na <sub>3</sub> P <sub>3</sub> O <sub>10</sub>                         | 10.0                                                          | -    | -    |
| CMTS                                                                   | -                                                             | 7.5  | 10.0 |
| EDTA                                                                   | 0.3                                                           | -    | -    |
| Na <sub>2</sub> O, 3.3 SiO <sub>2</sub>                                | 5.0                                                           | 4.5  | 5.0  |
| Na <sub>2</sub> CO <sub>3</sub>                                        | -                                                             | 7.0  | 8.5  |
| NaBO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , 3 H <sub>2</sub> O | 28.5                                                          | -    | -    |
| Na <sub>2</sub> SO <sub>4</sub>                                        | 0.5                                                           | 29.5 | 9.3  |
| MgSiO <sub>3</sub>                                                     | 2.0                                                           | -    | -    |
| CMC                                                                    | 1.5                                                           | 1.8  | 1.5  |
| H <sub>2</sub> O                                                       | 15.8                                                          | 9.3  | 11.7 |

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The EDTA can be replaced by the same amount of HEDP or DMDP, the  $\text{Na}_5\text{P}_3\text{O}_{10}$  by the same amount of a phosphorus-free phosphate substitute, as for example, the salts of citric acid or O-carboxymethyl-tartronic acid.

The process according to the invention and the composition for carrying it out have all the advantages of the compositions of the main patent; compared with this, however, they have a better ability to wash out fat. This is shown, for example, on collars and cuffs of dress shirts, especially in the case of those made of easy care cotton or of cotton-polyester mixed textiles and on fat-contaminated occupational washing, such as that of kitchen personnel, butchers, and of people employed in service stations and in car workshops and so on.

#### WHAT WE CLAIM IS:—

1. A process for the washing or bleaching of textiles by treatment thereof with an aqueous liquor, which contains in suspension a crystalline synthetically produced, finely-divided, water-insoluble aluminium or boron silicate cation exchanger, capable of binding the inorganic salts which cause hardness in water, possibly containing bound water and having a calcium binding capacity of at least 50 mg of  $\text{CaO/g}$  of water-free active substance (= AS), of the general formula



- in which Cat represents a cation of valency n and exchangeable with calcium; x is a number from 0.7 to 1.5, Me represents boron or aluminium and y is a number from 0.8 to 6 wherein the aqueous treatment liquor for the textiles contains a surface-active component consisting of 1 part by weight of non-ionic and 0 to 3 parts by weight of anionic surfactants, and wherein the non-ionic surfactant comprises a mixture of different ethoxylated condensates having an aliphatic hydrocarbon residue with 10 to 18 carbon atoms, in which 0.2 to 2 parts by weight of condensate having 2 to 6 ethyleneglycoether residues in the molecule are present per part by weight of condensate with 8 to 20 ethyleneglycoether residues in the molecule.

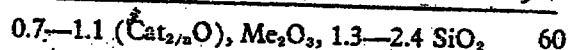
2. A process as claimed in claim 1 in which y in the formula:



is a number from 1.3 to 4.

3. A process as claimed in claim 1 or 2, in which the silicate cation exchanger has a calcium binding capacity of up to 200 mg  $\text{CaO/g}$  AS.

4. A process as claimed in claim 1, 2 or 3, in which the silicate cation exchanger containing bound water has the formula:



and a calcium binding capacity of 100—200 mg  $\text{CaO/g}$  AS.

5. A process as claimed in any one of claims 1 to 4, in which the silicate cation exchanger contains as cations sodium, lithium, potassium, ammonium, magnesium or cations of water-soluble organic bases.

6. A process as claimed in any one of claims 1 to 5, in which the silicate cation exchanger has an initial particle size of 0.1 to 100  $\mu$ .

7. A process as claimed in any one of claims 1 to 5 in which the silicate cation exchanger has an initial particle size of 1 to 50  $\mu$ .

8. A process as claimed in any one of claims 1 to 4, in which the treatment liquor contains dissolved therein complex-forming or calcium-precipitating builders selected from meta- and poly-phosphates, and the following organic acids or their salts: polycarboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids, carboxyalkylethers, polyanionic polymeric carboxylic acids and phosphonic acids.

9. A process as claimed in claim 8 in which the complex-forming or calcium-precipitating builders are used in concentrations of 0.05 to 2 g/litre.

10. A process as claimed in any one of claims 1 to 9, in which the surface-active component according to claim 1 is present in concentrations of 0.1 to 3 g/litre.

11. A process as claimed in any one of claims 1 to 10, in which the liquor contains inorganic or organic builder substances, including the complex-forming or calcium-precipitating builders as defined in claim 8, in amounts up to 6 g/litre.

12. A process as claimed in any one of claims 1 to 11, in which the liquor contains percompounds in amounts up to 0.4 g/litre of active oxygen.

13. A process as claimed in claim 12 which further contains stabilisers and/or activators for the percompounds.

14. A process as claimed in any one of claims 1 to 13, in which the bath liquor contains active chlorine compounds in amounts which are equivalent to 0.4 g/litre of active oxygen.

15. A process as claimed in any one of claims 1 to 14, in which the bath liquor contains inorganic and/or organic phosphorus compounds in amounts such that the phosphorus content of the treatment liquor does not exceed 0.6 g/litre.

16. A process as claimed in claim 16 in which the amount of phosphorus in the treatment bath does not exceed 0.3 g/litre.

17. A composition for carrying out the process as claimed in any one of claims 1 to 16



comprising a silicate cation exchanger as defined in any one of claims 1 to 7 and a surface-active component as defined in claim 1.

- 5 18. A composition as claimed in claim 17, which contains a surface-active component as defined in claim 1 in amounts of from 3 to 40% by weight.
- 10 19. A composition as claimed in claim 17 or 18, in which the silicate cation exchanger is present in amounts from 5 to 95% by weight.
- 15 20. A composition as claimed in claim 17 or 18, in which the silicate cation exchanger is present in amounts from 15 to 60% by weight.
- 20 21. A composition as claimed in any one of claims 17 to 20 which contain 2 to 15% by weight of the complex-forming or calcium-precipitating builders as defined in claim 8.
- 25 22. A composition as claimed in any one of claims 17 to 21 which further contains builder substances including the complex-forming or calcium-precipitating builders in amounts from 5 to 60% by weight.
- 30 23. A composition as claimed in any one of claims 17 to 22 which contains active oxygen compounds with a bleaching action in amounts from 10 to 40% by weight.
- 35 24. A composition as claimed in claim 23 which also contains stabilisers or activators for the active oxygen compounds.
25. A composition as claimed in any one of claims 17 to 24 which comprises,
- (A) 3—30% by weight of a surface-active component as defined in claim 1,
- (B) 15—60% by weight of a silicate cation exchanger as defined in any one of

- (C) 2—45% by weight of a complex-forming or calcium-precipitating builder as defined in claim 8,
- (D) 0—50% by weight of an inorganic or organic builder not being a complex-forming or calcium-precipitating builder,
- (E) 0—50% by weight of a bleaching agent as well as other detergent additives.
26. A composition as claimed in claim 25 in which component (C) is 2 to 15% by weight of a complex-forming or calcium-precipitating builder for calcium as defined in claim 8.
27. A composition as claimed in any one of claims 17 to 26 which contains organic and/or inorganic phosphorus compounds in amounts such that the total phosphorus content of the agent does not exceed 6% by weight.
28. A composition as claimed in claim 27 in which the total phosphorus content does not exceed 3% by weight.
29. A process for the preparation of a composition for washing or bleaching textiles as claimed in any one of claims 18 to 28, in which the pulverulent silicate cation exchanger as defined in any one of claims 1 to 7 is mixed with the remaining constituents of the composition.
30. A composition as claimed in claim 17 substantially as hereinbefore described with reference to any one of the Examples.

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# SPECIFICATION NO 1473572

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, a German Company, of 67 Henkelstrasse, 4000 Dusseldorf-Holthausen, Germany.

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