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(54) PARTICULATE BLEACHING OR CLEANING COMPOSITIONS CONTAINING ALUMINOSILICATES

TEILCHENFÖRMIGE, ALUMOSILIKATHALIGE BLEICH- ODER REINIGUNGSMITTELZUSAMMENSETZUNGEN

COMPOSITIONS NETTOYANTES OU DE BLANCHIMENT PARTICULAIRES CONTENANT DES ALUMINOSILICATES

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(73) Proprietors:
- **UNILEVER PLC**
  London EC4P 4BQ (GB)
  Designated Contracting States:
  GB
- **UNILEVER N.V.**
  3013 AL Rotterdam (NL)
  Designated Contracting States:
  CH DE ES FR IT LI NL SE

(72) Inventor: **CHAPPLE, Andrew Paul**
Wrexham, Clwyd LL11 5LP (GB)

(74) Representative: **Fransella, Mary Evelyn et al**
Unilever PLC
Patent Division
Colworth House
Sharnbrook
Bedford MK44 1LQ (GB)

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- **DATABASE WPI, Section Ch, Derwent Publications Ltd., London, GB; Class E33, AN 81-31774D & JP,A,56 026 715 (MISUZAWA KAGAKU) 14 March 1981**

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Description

TECHNICAL FIELD

The present invention relates to particulate detergent, bleaching or cleaning compositions containing crystalline aluminosilicates (zeolites), and also containing bleach ingredients sensitive to moisture, for example, inorganic persalts such as sodium percarbonate, organic or inorganic peroxyacids, bleach precursors, or bleach catalysts.

BACKGROUND AND PRIOR ART

The ability of crystalline aluminosilicates (zeolites) to sequester calcium ions from aqueous solution by an ionexchange mechanism has led to their becoming a well-known replacement for phosphates as detergency builder. Many particulate detergent compositions currently sold commercially in Europe, Japan and the USA contain zeolite.

Although many crystal forms of zeolite are known, the preferred zeolite for detergents use has always been zeolite A, used in sodium form.

Examples of prior art documents disclosing detergent compositions containing zeolites are EP 456 515A (Procter & Gamble), EP 38 591A and EP 21 491A (Procter & Gamble), EP 87 035A (Union Carbide), US 4 604 224 and CA 1 072 853 (Colgate). The use of zeolites A, X, B (P) and Y is disclosed, and general formulae with a range of possible cations given, but sodium is always the highly preferred cation and all specific disclosure relates to zeolites in sodium form.

Sodium percarbonate is a well-known bleaching ingredient in bleaching and detergent compositions and is widely disclosed in the literature, although in recent years its use in commercial products has been abandoned in favour of sodium perborate. Sodium percarbonate is less stable than sodium perborate in the presence of moisture, and its stabilisation in detergent powders has long been recognised as a problem. This problem becomes especially acute if sodium percarbonate is to be included in a detergent powder with a high mobile water content, when it tends to become deactivated in storage. This situation applies in particular to powders containing zeolites, because those materials contain a large amount of relatively mobile water.

This problem is addressed in GB 2 013 259A (Kao), which suggests as one solution the use of a zeolite in which the sodium cations have been partially exchanged for calcium or magnesium ions. This measure improves the stability of sodium percarbonate, but at the cost of reduced building (calcium and magnesium ion-exchanging) efficacy.

An alternative approach to the problem of percarbonate stability in particulate zeolite-containing detergent compositions is disclosed in EP 522 726A (Unilever), according to which conventional zeolite A is replaced by maximum aluminium zeolite P (zeolite MAP), a material described and claimed in EP 384 070A (Unilever). Use of this zeolite gives substantially improved sodium percarbonate storage stability.

Similar improvements have been observed in the storage stability of sodium perborate monohydrate, as disclosed in EP 552 053A (Unilever); bleach precursors, as disclosed in EP 552 054A (Unilever); peroxyacids, as disclosed in our copending International Patent Application No. EP/93/03369 filed on 29 November 1993; and certain manganese bleach catalysts, as disclosed in our copending British Patent Application No. 93 05599.4 filed on 18 March 1993.

The present invention is based on the discovery that further significant improvements in the storage stability of sodium percarbonate and other moisture-sensitive ingredients in particulate zeolite-containing detergent and cleaning compositions can be achieved by the use of zeolites in which the sodium ions have been wholly or partially exchanged for other cations. This is surprising because the ion-exchanged forms do not, in general, have lower moisture contents than their sodium counterparts and, in the present invention, they are used in fully hydrated form in environments where there is no control of mobile water content. Improvements are observed both with zeolite A and with zeolite MAP.

EP 364 184A (Unilever) discloses non-aqueous cleaning compositions containing dispersed aluminosilicate particles which have been deactivated by treatment with an ammonium or substituted ammonium compound and thereafter heated to reduce the water content below 24 wt%. The treatment reduces the aluminosilicate-catalysed decomposition of bleach precursors such as tetraacetylethylenediamine in the liquid product. Unlike the present invention, EP 364 184A is concerned with an environment (a non-aqueous liquid) in which the water content is strictly limited and controlled, and with aluminosilicates which must be partially dehydrated.

DEFINITION OF THE INVENTION

The present invention provides a particulate detergent, bleaching or cleaning composition comprising a bleach ingredient sensitive to moisture and a crystalline aluminosilicate having exchangeable cations, wherein the exchangeable cations of the aluminosilicate include ammonium, lithium or hydrogen ions or combinations thereof.

More specifically, the invention provides a particulate bleaching detergent composition comprising an organic detergent surfactant, a bleach ingredient sensitive to moisture and a crystalline aluminosilicate, wherein the aluminosilicate is as defined in the previous paragraph.

The invention further provides the use of an aluminosilicate as defined above to improve the stability of a bleach ingredient sensitive to moisture in a particulate detergent, bleaching or cleaning composition.

The invention further provides, as a novel material, zeolite P having a silicon to aluminium ratio not exceeding 1.33, preferably not exceeding 1.15 and more preferably not exceeding 1.07, having exchangeable cations wherein the exchangeable cations include ammonium, lithium or hydrogen ions or combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

The composition of the invention has two essential ingredients: the aluminosilicate, and the moisture-sensitive bleach ingredient.

The ion-exchanged zeolite

The compositions of the invention require as an essential ingredient a crystalline aluminosilicate (zeolite) in which the exchangeable cations consist at least in part of ammonium, lithium or hydrogen ions or combinations thereof.

Such a zeolite may readily be prepared by ion exchange from a sodium zeolite, and for convenience will be referred to as an ion-exchanged zeolite, although in principle the invention would also encompass the use of directly synthesised wholly non-sodium zeolites not prepared by ion-exchange, to the extent that such materials can be prepared.

Zeolites capable of ion exchange are represented by the following general formula:

$$M_x\ (SiO_2)_y(AlO_2)_x\ .\ z\ H_2O$$

where M is a monovalent cation. The ratio of silicon to aluminium (y:x) can vary, as can the amount of water of hydration.

A partially exchanged zeolite may be represented as:

$$M^1{}_{x'}.M^2{}_{(x\,-\,x')}\ (SiO_2)_y(AlO_2)_x\ .\ z\ H_2O$$

wherein M^1 and M^2 are two different exchangeable monovalent cations.

The (molar) percentage extent of exchange quoted hereafter can then be defined, for cation M^1, as

$$\frac{x'}{x} \times 100$$

The values of x and x' can be determined by conventional analytical methods, for example, atomic absorption spectroscopy.

The cations M^1 for the zeolites used in the present invention are ammonium, lithium and hydrogen. Zeolites in hydrogen and ammonium form are preferred, and zeolites in hydrogen form are especially preferred. Potassium ions, derived from a strong base, have been found to have the opposite effect, potassium zeolites giving worse stability of moisture-sensitive ingredients than the corresponding sodium zeolites.

The preferred cation M^2 is sodium.

Where M^1 is the hydrogen ion, the value of x' is best determined by difference between the aluminium content (x) and the second cation (M^2) content.

The zeolite may be of any crystal form suitable for detergents use. As indicated previously, zeolite A is the most popular detergent zeolite. The art also discloses the possible use of zeolites X, Y and P(B) although in practice those have not found favour because their calcium ion exchange is either inadequate or too slow.

Zeolite A has the advantage of being a "maximum aluminium" structure containing the maximum possible proportion of aluminium to silicon (or the minimum possible Si:Al ratio of 1.0) so that its capacity for taking up calcium ions from aqueous solution is intrinsically greater than those of zeolite X, Y and P which generally contain a lower proportion of aluminium (or have a higher Si:Al ratio).

Accordingly, in one preferred embodiment of the invention the partially or wholly ion-exchanged zeolite is zeolite A.

Alternatively, and most preferably, the partially or wholly ion-exchanged zeolite may be zeolite MAP as described and claimed in EP 384 070B (Unilever) as discussed above. This is maximum aluminium zeolite P, that is to say, zeolite P having a Si:Al ratio not greated than 1.33, preferably not greater than 1.15 and more preferably not greater than 1.07. Zeolite MAP has various advantages over zeolite A, one of which is that, even in sodium form, it improves the stability of sodium percarbonate and various other bleach ingredients stability as discussed previously.

Ion-exchanged zeolites are described in the literature, for example, by D W Breck and E M Flanagan, "Molecular Sieves", Soc Chem Ind (London), 1968, pages 47-61; US 4 346 067 (Exxon Corporation) describes ammonium-exchanged zeolites, and EP 223 396A (Mobil Oil Corporation) describes hydrogen-exchanged zeolites, both useful as catalysts in hydrocarbon conversion reactions.

However, zeolite MAP in ion-exchanged form is believed to be a novel material and is claimed as part of the present invention.

Extent of exchange

It appears that the zeolites should desirably be in the ion-exchanged form to an extent of at least 5%, preferably at least 10% and more preferably at least 20 wt%, in order for the benefit of improved moisture-sensitive ingredient stability to be fully realised. Greater extents of ionexchange do not appear to give further improvements, but neither does the benefit fall again.

Accordingly, the zeolites used in accordance with the present invention should preferably be in ion-exchanged form to an extent of at least 5%, more preferably at least 10% and most preferably at least 20%.

Zeolite A has been found to give good results when in 10-50% ion-exchanged form, more especially 20-50% ion-exchanged form, while zeolite MAP has been found to give good results when in 10-90% ion-exchanged form, more especially 20-90% ion-exchanged form.

The lower limits quoted here are specifically applicable to ammonium-exchanged zeolites. The corresponding limit for other cations may not necessarily be identical but could readily be determined by one skilled in the art by the methods described in the Examples herein.

Preparation of the ion-exchanged zeolite

The ion-exchanged zeolite may conveniently be prepared by immersing the corresponding sodium zeolite in an aqueous solution of a salt of the desired cation, for example, an ammonium or lithium salt.

Hydrogen-exchanged zeolites may be prepared similarly, by immersion in a aqueous solution of a strong acid, for example, hydrochloric acid.

The percentage extent of exchange can be controlled by varying the concentration of the salt or acid, and the amount of zeolite added, as described in more detail by D W Breck et al in JACS 78 5963 et seq (1956).

Compositions of the invention

The detergent, bleaching or cleaning compositions of the invention contain a builder system based on crystalline aluminosilicate (zeolite), and also contain at least one moisture-sensitive ingredient. While the invention is believed to be applicable to any moisture-sensitive ingredient, initial work has been concentrated on moisture-sensitive bleach ingredients.

Moisture-sensitive bleach ingredients

Examples of moisture-sensitive bleach ingredients include peroxy bleach compounds, for example, inorganic or organic persalts and peroxyacids, bleach activators (bleach precursors), and bleach catalysts.

Inorganic persalts

Inorganic persalts include the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Inorganic persalts susceptible to moisture, to which the present invention is especially applicable, include sodium perborate monohydrate, and, more especially, sodium percarbonate.

Inorganic persalts may advantageously be used in conjunction with a bleach precursor or bleach activator. Bleach precursors may themselves be susceptible to moisture and their stability therefore improved by means of the present invention.

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (Trade Mark), EDTMP.

Bleach precursors

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxycarbonic acid precursors.

Examples of peroxyacid bleach precursors suitable for use in the present invention include:

N,N,N',N'-tetracetyl ethylenediamine (TAED);

2-(N,N,N-trimethylammonium) ethyl sodium-4-sulphophenyl carbonate chloride (SPCC), also known as cholyl-p-sulphophenyl carbonate (CSPC);

sodium nonanoyloxybenzene sulphonate (SNOBS);

sodium 4-benzoyloxybenzene sulphonate (SBOBS);

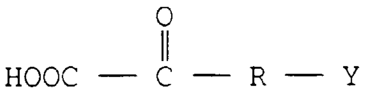
sodium 3,5,5-trimethylhexanoyloxybenzene sulphonate (STHOBS);

and glucose pentaacetate (GPA).

Peroxyacids

Peroxyacids to which the invention is applicable may be organic or inorganic.

Organic peroxyacids normally have the general formula:



$$HOOC - \overset{\overset{O}{\|}}{C} - R - Y$$

wherein R is an alkylene or substituted alkylene group containing from 1 to 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a carboxylic acid or percarboxylic acid group, or a quaternary ammonium group.

Typical monoperoxy acids useful in the compositions of the invention include, for example:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, eg peroxy-alpha-naphthoic acid;

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, eg peroxylauric acid, peroxystearic acid and N, N'-phthaloylaminoperoxy caproic acid (PAP);

(iii) 6-octylamino-6-oxoperoxyhexanoic acid.

Typical diperoxyacids useful in the compositions of the invention include, for example:

(iv) 1,12-diperoxydodecanedioic acid (DPDA);

(v) 1,9-diperoxyazelaic acid;

(vi) diperoxybrassilic acid, diperoxysebacic acid and diperoxyisophthalic acid;

(vii) 2-decyldiperoxybutane-1,4-dioic acid; and

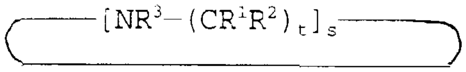
(viii) 4,4'-sulphonylbisperoxybenzoic acid.

(ix) N,N'-terephthaloyl-di(6-aminoperoxycaproic acid), also known as N,N'-di(5-percarboxypentyl) terephthalamide (TPCAP).

Bleach catalysts

A class of bleach catalysts to which the present invention is applicable is described and claimed in EP 458 397A and EP 458 398A (Unilever).

The bleach catalyst is defined as comprising a source of Mn and/or Fe ions and a ligand which is a macrocyclic organic compound of formula I:



$$\left[NR^3-(CR^1R^2)_t\right]_s \qquad (I)$$

wherein t is an integer from 2 to 3; s is an integer from 3 to 4; and R^1, R^2 and R^3 are each independently selected from H, alkyl and aryl, both optionally substituted.

Examples of preferred ligands are:

1,4,7-triazacyclononane (TACN);
1,4,7-trimethyl-1,4,7-triazacyclononane (1,4,7-Me_3TACN);
2-methyl-1,4,7-triazacyclononane (2-MeTACN);
1,2,4,7-tetramethyl-1,4,7-triazacyclononane (1,2,4,7-Me_4TACN);
1,2,2,4,7-pentamethyl-1,4,7-triazacyclononane (1,2,2,4,7-Me_5TACN);
1,4,7-trimethyl-2-benzyl-1,4,7-triazacyclononane; and
1,4,7-trimethyl-2-decyl-1,4,7-triazacyclononane.

Especially preferred is 1,4,7-trimethyl-1,4,7-triazacyclononane (1,4,7-Me_3TACN).

The aforementioned ligands may be synthesised by the methods described in K. Wieghardt et al., Inorganic Chemistry 1982, 21, page 3086.

The source of iron and/or manganese ions and ligand may be added separately or in the form of a mono-, di- or tetranuclear manganese or iron complex. When added separately, the ligand may be in the form of an acid salt such as 1,4,7-Me_3TACN hydrochloride. The source of iron and manganese ions may be a water soluble salt such as iron or manganese nitrate, chloride, sulphate or acetate or a coordination complex such as manganese acetylacetonate. The source or iron and/or manganese ions should be such that the ions are not too tightly bound, ie all those sources from which the ligand of formula (I), as hereinbefore defined, may extract the Fe and Mn in a wash liquor.

Preferred mononuclear complexes have the formula

$$\text{(a)} \qquad [LMn^{IV}(OR)_3]Y$$

wherein

Mn is manganese in the +4 oxidation state;

R is a C_1-C_{20} radical selected from the group alkyl, cycloalkyl, aryl, benzyl and radical combinations thereof;

at least two R radicals may also be connected to one another so as to form a bridging unit between two oxygens that coordinate with the manganese;

L is a ligand of formula (I) as hereinbefore defined;

and Y is an oxidatively-stable counterion;

or the formula

$$\text{(b)} \qquad [LMnX_p]^zY_q$$

wherein Mn can be either in the II, III or IV oxidation state;

each X independently represents a coordinating species with the exception of RO-, such as Cl^-, Br^-, I^-, F^-, NCS^- N_3^-, I_3^-, NH_3, $RCOO^-$, RSO_3^-, RSO_4^- in which R is alkyl or aryl, both optionally substituted, OH^-, O_2^{2-}, HOO^-, H_2O, SH, CN^-, OCN^-, S_4^{2-} and mixtures thereof;

p is an integer from 1-3;

z denotes the charge of the complex and is an integer which can be positive, zero or negative;

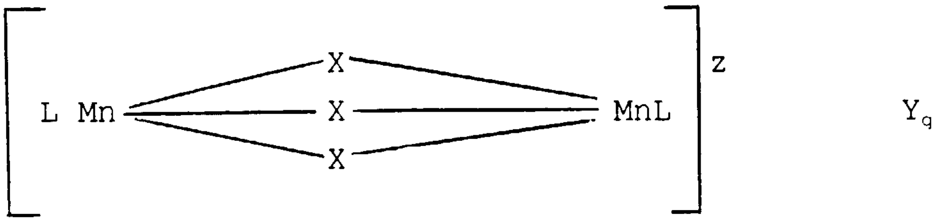
Y is a counterion the type of which is dependent upon the charge z of the complex;

q = z/[charge Y];

and L is a ligand as hereinbefore defined.

Such mononuclear complexes are further described in our copending European Patent Application EP 549 272A, filed on 18 September 1992 and published on 30 June 1993.

Preferred dinuclear complexes have the formula



wherein

Mn is manganese which can independently be in the III or IV oxidation state;

X is independently a coordinating or bridging species selected from the group consisting of H_2O, O_2^{2-}, OH^-, HO_2^-, SH^-, S^{2-}, >SO, Cl^-, SCN^-, N_3^-, RSO_3^-, $RCOO^-$, NH_2^- and NR_3, with R being H, alkyl, aryl, both optionally substituted, and R^1COO, where R^1 is an alkyl or aryl radical, both optionally substituted;

L is a ligand of formula (I) as hereinbefore defined;

z denotes the charge of the complex and is an integer which can be positive or negative, or is zero;

Y is a monovalent or multivalent counterion, leading to charge neutrality, which is dependent upon the charge z ofthe complex; and

q = z / [charge Y].

Such dinuclear complexes of this type are further described in EF 458 397A and EP 458 398A (Unilever).

The bleach catalyst is advantageously in the form of granules as described and claimed in WO 95 06710A (Unilever). These granules comprise:

(i) from 0.5 to 20 wt%, preferably from 1 to 15 wt%, of the catalyst itself,

(ii) from 5 to 90 wt% of a soluble core material, preferably selected from sodium bicarbonate, magnesium and potassium nitrates, and magnesium sulphate,

(iii) from 5 to 91 wt% of a binding agent selected from silicone oils, fatty acids, fatty esters, tri-, di- and monoglycerides, waxes and solid hydrocarbons.

An especially preferred binding agent is cetostearyl stearate.

Preferably, these granules will also comprise an inert solid. Preferred inert materials include silicas such as Gasil, Aerosil and Sorbosil (Trade Marks); clays such as kaolin; alumina; and titanium dioxide.

Other preferred granules are described and claimed in our British Patent Application No. 93 18295.4 filed on 3 September 1993.

Alternatively, the bleach catalyst may be in the form of granules as described and claimed in our copending application EP 544 440A filed on 18 November 1992 and published on 2 June 1993. These granules comprise:

(i) from 0.5 to 8 wt% of the catalyst itself,

(ii) optionally from 0 to 90 wt% of a inert salt selected from chlorides, carbonates and mixtures thereof, and

(iii) from 5 to 91 wt% of a binding agent selected from water-soluble non-oxidisable polymers, alkali metal silicates, saturated fatty acid soap mixtures, and combinations of these.

A preferred binding agent is sodium silicate, and a preferred inert salt is sodium carbonate.

Preferred granules include catalyst/sodium stearate/lauric acid granules, and catalyst/sodium carbonate/sodium silicate/zeolite granules.

Preferably, the manganese catalyst within the granules is of an average particle size as small as possible, preferably below 250 micrometres for proper distribution and to ensure fast delivery to the wash, although particles which are too small may cause handling problems during the granulation process. A preferred and optimum manganese catalyst particle size is within a range of from 50 to 150 micrometres.

Bleaching compositions

The composition of the invention may, for example, be a detergent additive wholly or predominantly constituted by aluminosilicate builder and one or more moisture-sensitive bleach ingredients.

An additive of this type may be used in conjunction with a conventional product under conditions where high water-hardness and/or a heavily soiled load require extra building and/or extra bleaching capacity.

Such an additive may also form part of a Baukasten (building block) system, for example, as described in EP 419 036A (Unilever), where it may be used together with an underbuilt and/or non-bleaching main wash powder.

Detergent compositions

Detergent compositions of the invention containing moisture-sensitive bleach ingredients may suitably contain the following ingredients:

(a) one of more organic detergent surfactants,

(b) a builder system comprising a crystalline aluminosilicate as defined above,

(c) a bleach system comprising one or more ingredients sensitive to moisture,

(d) optionally other detergent ingredients.

Preferred detergent compositions according to the invention may contain the following ingredients in the following proportions:

(a) from 2 to 60 wt% of one or more detergent surfactants,

(b) from 10 to 80 wt% of one or more detergency builders, including zeolite in partially or wholly ion-exchanged form,

(c) from 5 to 40 wt% of a bleach system comprising a bleach ingredient sensitive to moisture, and

(d) optionally other detergent ingredients to 100 wt%.

The bleach ingredient sensitive to moisture may be, as previously indicated, a persalt, a bleach precursor, a peroxyacid or a bleach catalyst; more particularly, sodium percarbonate, a peroxyacid, or a bleach catalyst as defined above.

Detergent surfactants

The detergent compositions of the invention will contain, as essential ingredients, one or more detergent-active compounds (surfactants) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and

II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkyl sulphates, particularly C_{12}-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_9-C_{15} primary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

Also of interest are non-ethoxylated nonionic surfactants, for example, alkylpolyglycosides; O-alkanoyl glucosides as described in EP 423 968A (Unilever); and polyhydroxyamides.

The choice of detergent-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition: different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

The total amount of surfactant present will also depend on the intended end use, but may generally range from 2 to 60 wt%, preferably from 5 to 40 wt%.

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or nonionic surfactant, or combinations of the two in any ratio, optionally together with soap.

The detergency builder system

The detergent compositions of the invention also contains one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 10 to 80 wt%.

The detergency builder system of the compositions of the invention is based on zeolite, optionally in conjunction with one or more supplementary builders.

The amount of zeolite present may suitably range from 5 to 60 wt%, more preferably from 15 to 40 wt%, calculated on an anhydrous basis (equivalent to from 6 to 75 wt%, preferably from 19 to 50 wt%, calculated on a hydrated basis).

The zeolite may, if desired, be used in conjunction with other inorganic or organic builders. Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever). Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Preferred supplementary builders for use in conjunction with zeolite include citric acid salts, more especially sodium citrate, suitably used in amounts of from 3 to 20 wt%, more preferably from 5 to 15 wt%. The combination of zeolite MAP with citrate as a detergency builder system is described and claimed in EP 448 297A (Unilever).

Also preferred are polycarboxylate polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%, of the detergent composition; the combination of zeolite MAP with polymeric builders is described and claimed in EP 502 675A (Unilever).

The bleach system

As previously indicated, the detergent compositions of the invention contain a bleach system which includes at least one bleach moisture-sensitive ingredient. The bleach system may generally comprise a peroxy bleach compound, for example, an inorganic or organic persalt, optionally in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures; or an inorganic or organic peroxyacid. A bleach stabiliser (heavy metal sequestrant) may also be present. According to a preferred embodiment of the invention, a bleach catalyst as previously defined may also be present.

Preferred inorganic persalts are sodium perborate monohydrate and sodium percarbonate. As indicated above, sodium percarbonate is especially sensitive to moisture and benefits particularly from the present invention.

In detergent compositions according to the invention, sodium percarbonate or other persalts may suitably be present in an amount of from 5 to 30 wt%, preferably from 10 to 25 wt%, based on the whole composition.

Bleach precursors are suitably used in amounts of from 1 to 8 wt%, preferably from 2 to 5 wt%.

Organic or inorganic peroxyacids are normally used in an amount within the range of from 2 to 10 wt%, preferably from 4 to 8 wt%.

The amount of the bleach catalyst described above present in the detergent compositions of the invention is suitably from 0.02 to 0.08 wt%.

Other ingredients

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; pigments; and perfumes. This list is not intended to be exhaustive.

Preparation of the detergent compositions

The particulate detergent compositions of the invention may be prepared by any suitable method.

One suitable method comprises spray-drying a slurry of compatible heat-insensitive ingredients, including the zeolite, any other builders, and at least part of the detergent-active compounds, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry, including sodium percarbonate and any other bleach ingredients. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

The compositions of the invention may also be prepared by wholly non-tower procedures, for example, dry-mixing and granulation, or by so-called "part-part" processes involving a combination of tower and non-tower processing steps.

The benefits of the present invention are observed in powders of high bulk density, for example, of 700 g/l or above. Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

EXAMPLES

The invention is further illustrated by the following Examples, in which parts and percentages are by weight unless otherwise indicated. Examples identified by numbers are in accordance with the invention, while those identified by letters are comparative.

EXAMPLES 1 to 14, COMPARATIVE EXAMPLES A and B

Preparation of ion-exchanged zeolites

Example 1

Preparation of ammonium-exchanged zeolite A

Sodium zeolite 4A powder (Wessalith (Trade Mark) P ex Degussa) was converted to a partially ammonium-exchanged form as follows.

150 g of hydrated sodium zeolite 4A were slurried with 1 litre of 0.2 molar ammonium sulphate solution (adjusted to pH 9 with ammonium hydroxide) for 1 hour at 60°C. The slurry was then filtered, and the filter cake re-slurried in a further 1 litre of fresh ammonium sulphate solution. This procedure was repeated to give a total of 3 exchange steps. The zeolite was finally filtered and washed with demineralised water then oven dried at 100°C. The dried zeolite was ground in a pestle and mortar and stored under ambient conditions for several days to fully rehydrate.

The calculated ammonium (NH_4) content for full exchange of zeolite A is 10.0 wt% NH_4. The material prepared as described above had an ammonium (NH_4) content of 5.04 wt%, corresponding to 50.4% exchange.

Example 2

Preparation of ammonium-exchanged zeolite MAP

Ammonium-exchanged zeolite MAP was prepared, by the method described in Example 1, from sodium zeolite MAP prepared by a method similar to that described in Examples 1 to 3 of EP 384 070A (Unilever). The starting zeolite MAP had a silicon to aluminium ratio of 1.0.

The calculated ammonium content for full exchange of zeolite MAP is 10.4 wt%. The exchanged material had an ammonium (NH_4) content of 7.95 wt%, corresponding to 76.4% exchange.

Example 3

Preparation of lithium-exchanged zeolite A

Sodium zeolite 4A was converted to (partially) lithium-exchanged form by a method similar to that used in Example 1, using 0.2 molar lithium chloride solution instead of ammonium sulphate solution.

Example 4

Preparation of lithium-exchanged zeolite MAP

Lithium zeolite MAP was prepared from the sodium zeolite MAP used in Example 2, by the method described in Example 3.

Example 5

Preparation of hydrogen-exchanged zeolite A

150 g of hydrated sodium zeolite 4A were slurried in 3 litres of demineralised water. The pH of the slurry was monitored using a pH electrode, and the pH adjusted to a value of 8.0 by the slow addition of 0.1 molar hydrochloric acid. Following addition of the acid, the zeolite was filtered, washed with demineralised water, and oven dried at 100°C. The dried zeolite was ground in a pestle and mortar and stored under ambient conditions for several days to rehydrate fully.

Example 6

Preparation of hydrogen-exchanged zeolite MAP

Partially hydrogen-exchanged zeolite MAP was prepared from the sodium zeolite MAP used in Example 2 by the method described in Example 5.

Comparative Example A

Preparation of potassium-exchanged zeolite A

Partially potassium-exchanged zeolite A was prepared from the sodium zeolite A used in Example 1 by the method described in Example 3, except that the lithium chloride solution was replaced by 0.2 molar potassium chloride solution.

Comparative Example B

Preparation of potassium-exchanged zeolite MAP

Partially potassium-exchanged zeolite MAP was prepared from the sodium zeolite MAP used in Example 2 by the method described in Example 4, except that the lithium chloride solution was replaced by 0.2 molar potassium chloride solution.

Examples 7 to 10

Preparation of a range of partially exchanged sodium/ammonium zeolite 4A samples

150 g samples of hydrated sodium zeolite were slurried with ammonium sulphate solutions (1 litre) having different concentrations, at pH 9 for 1 hour at 40°C. The zeolites were then filtered, washed with water, and dried in an oven at 100°C. The dried zeolite samples were then ground in a pestle and mortar and allowed to hydrate fully under ambient conditions for several days. The resulting products were analysed to determine the actual level of ammonium exchange achieved.

Example	Ammonium sulphate concentration	Ammonium content	Extent of exchange
	(molar)	(wt %)	(%)
7	0.10	1.31	13
8	0.21	2.35	23
9	0.41	3.60	35
10	0.82	4.74	46

Examples 11 to 13

Preparation of a range of partially exchanged sodium/ammonium zeolite MAP samples

Four samples of partially exchanged sodium/ammonium zeolite MAP were prepared by the method described in Examples 7 to 10. Preparative and analytical details were as follows:

Example	Ammonium sulphate concentration	Ammonium content	Extent of exchange
	(molar)	(wt %)	(%)
11	0.11	1.13	11
12	0.21	2.47	24
13	0.42	5.89	57.5
14	0.84	8.74	85

EXAMPLES 15 to 30, COMPARATIVE EXAMPLES C to K

Sodium percarbonate stability

Examples 15 to 17, Comparative Examples C and D

Sodium percarbonate stability of zeolite A/percarbonate mixtures

Test samples were prepared by mixing 3.75 g of each of the following zeolites with 1.25 g of sodium percarbonate (the 500-710 micrometre sieve fraction of Oxyper (Trade Mark) ex Interox), to give mixtures consisting of 75 wt% zeolite and 25 wt% percarbonate.

Example	Zeolite type
C	Sodium zeolite A (Wessalith P)
15	Ammonium-exchanged zeolite A (Example 1)
16	Lithium-exchanged zeolite A (Example 3)
17	Hydrogen-exchanged zeolite A (Example 5)
D	Potassium-exchanged zeolite A (Comparative Example A)

Storage stability was assessed by means of the following accelerated storage test under extremely severe conditions which is designed to show up differences in a shorter period of time than would be possible in a test using more realistic conditions and normal product packaging.

The samples were stored in open-topped glass bottles at 37°C and 70% relative humidity. Bottles were removed from storage at regular intervals and the powder mixtures analysed for remaining available oxygen (AvO). The results were as follows:

Example	AvO after time (days)				
	0	3	6	10	14
C	100	62.7	47.7	33.4	16.6
15	100	92.3	86.4	78.0	68.6

(continued)

Example	AvO after time (days)				
	0	3	6	10	14
16	100	85.0	75.7	60.9	55.7
17	100	85.0	67.0	50.0	36.6
D	100	54.0	34.5	19.5	12.3

It will be noted that the ammonium-exchanged, lithium-exchanged and hydrogen-exchanged zeolites all greatly improved the storage stability of the sodium percarbonate, the ammonium-exchanged material giving the largest benefit; while the potassium-exchanged material gave rather worse results than the all-sodium zeolite.

Examples 18 to 20, Comparative Examples E and F

Sodium percarbonate stability of zeolite MAP/percarbonate mixtures

Test samples were prepared as described in Examples 15 to 17, each containing 3.75 g (75 wt%) of zeolite and 1.25 g (25 wt%) of sodium percarbonate:

Example	Zeolite type
E	Sodium zeolite MAP (starting material for Examples 2 and 4)
18	Ammonium-exchanged zeolite MAP (Example 2)
19	Lithium-exchanged zeolite MAP (Example 4)
20	Hydrogen-exchanged zeolite MAP (Example 6)
F	Potassium-exchanged zeolite MAP (Comparative Example B).

Storage stability at 37°C and 70% relative humidity in open-topped glass bottles was measured as described in Examples 15 to 17. The results were as follows:

Example	AvO after time (days)				
	0	3	6	10	14
E	100	73.7	59.1	37.7	27.3
18	100	94.3	91.4	90.2	90.9
19	100	92.1	90.9	83.0	73.6
20	100	93.4	84.0	73.3	62.1
F	100	61.5	40.9	24.5	14.1

Comparison of these results with those of Examples 15 to 17 shows how the stability improvement achieved by replacement of zeolite A by zeolite MAP can be taken further by means of the present invention.

It will be noted that use of ammonium zeolite MAP (Example 18) resulted in virtually no percarbonate loss even after 14 days' open storage in very unfavourable conditions.

As with zeolite A, the potassium-exchanged material gave worse results than the sodium zeolite.

Examples 21 to 24, Comparative Example G

Sodium percarbonate stability in mixtures with differently exchanged sodium/ammonium zeolite A samples

The procedure of Examples 15 to 17 was repeated using the partially exchanged sodium/ammonium zeolites of Examples 7 to 10. The storage stability results were as follows, Comparative Example G being the starting all-sodium zeolite A.

Example	AvO after time (days)			
	3	5	10	17
G	68.2	54.6	29.8	12.7
21 (7)	94.6	89.8	73.9	56.4
22 (8)	94.1	90.5	83.0	69.8
23 (9)	90.9	90.5	82.5	66.4
24 (10)	97.3	93.6	87.0	74.5

It will be seen that a very significant benefit is achieved even at only 11% exchange (Example 21).

Examples 25 to 28, Comparative Example H

Sodium percarbonate stability in mixtures with differently exchanged sodium/ammonium zeolite MAP samples

The procedure of Examples 21 to 24 was repeated using the partially exchanged sodium/ammonium zeolite MAP of Examples 11 to 14. The storage stability results were as follows, Comparative Example H being the starting all-sodium zeolite MAP.

Example	AvO after time (days)			
	3	5	10	17
H	74.6	61.4	38.4	26.8
25 (11)	95.5	91.6	81.8	77.7
26 (12)	93.2	91.6	88.6	80.9
27 (13)	96.8	90.2	82.3	73.6
28 (14)	95.2	90.0	80.5	72.7

The pattern is similar to that observed with the partially exchanged zeolite A, with the maximum benefit apparently being achieved when the extent of ammonium exchange is 23% or more (Examples 26, 27 and 28).

Examples 29 and 30, Comparative Examples J and K

Sodium percarbonate stability in detergent granules

Detergent granules were prepared by granulating zeolite with nonionic surfactant in a laboratory-scale granulator, using in each case just sufficient nonionic surfactant to achieve granulation. The nonionic surfactant used was Synperonic (Trade Mark) A7 ex ICI, a C_{12}-C_{15} primary alcohol ethoxylated with an average of 7 moles of ethylene oxide per mole of alcohol.

The zeolites used were the ammonium-exchanged zeolites of Examples 1 and 2, and the corresponding sodium zeolites (the starting materials used in Examples 1 and 2). The compositions of the granules were as follows:

Example	Zeolite Type	Nonionic surfactant (g/200g zeolite)
J	Na A	61.5
29	NH_4 A (Ex 1)	64.8
K	Na MAP	75.3
30	NH_4 MAP (Ex 2)	82.0

The granules were sieved, and the 250-700 micrometre fraction was used in the test described below to determine percarbonate storage stability.

Each test sample was prepared by mixing detergent granules (8.75 g) with sodium percarbonate (1.25 g). The percentage compositions of the test samples were therefore as follows:

Example	Composition (wt%)		
	Zeolite	Nonionic	Percarbonate
J	66.9	20.6	12.5
29	66.1	21.4	12.5
K	63.6	23.9	12.5
30	62.1	25.4	12.5

As in previous Examples, the samples were stored in open-topped glass bottles at 37°C and 70% relative humidity. The results were as follows:

Example	AvO after time (days)			
	0	6	9	14
J	100	30.2	20.5	4.1
29	100	83.9	77.7	51.6
K	100	50.0	42.0	10.5
30	100	90.0	90.9	79.5

Examples 31 to 35, Comparative Examples L to O Bleach catalyst stability

Example 31, Comparative Example L

Detergent base powders were prepared by mixing zeolite A, in sodium or ion-exchanged form, with a liquid surfactant blend - coconut alcohol sulphate (cocoPAS), coconut alcohol 3EO nonionic surfactant, coconut alcohol 7EO nonionic surfactant and water - in a laboratory-scale granulator. The zeolites were as used in previous Examples: the ammonium zeolite A was that of Example 1, and the sodium zeolite the raw material of Example 1. The differences in formulation reflect the different carrying capacities of the two zeolites.

The base powders were mixed with manganese catalyst granules to give powders having the following formulations:

	Example L	Example 31
Zeolite A (Na)*	65.5	-
Zeolite A (NH_4)* (Ex 1)	-	68.6
CocoPAS	7.5	6.7
Coco 7EO	7.5	6.7
Coco 3EO	9.6	8.5
Soap	2.9	2.6
Water	2.0	1.8
Total base powder	95.0	95.0
Catalyst granules	5.0	5.0
	100.0	100.0

* hydrated basis

The catalyst granules had the following formulation:

Catalyst (Mn 1,4,7-Me_3TACN)	1.8
Zeolite MAP	46.6
Soap/fatty acid*	20.5
Citric acid	22.2

*30% neutralised mixture of C_{12}-C_{18} saturated fatty acids (about 60% C_{12}, 17% C_{16}, 20% C_{18}, 3% C_{10}+ C_{14}).

(continued)

Titanium dioxide	8.9 100.0

Samples of each powder were stored in open-topped glass jars at 37°C and 70% relative humidity. After a period of 28 days, the samples were removed from storage, and pairs of samples of Powders 31 and L were compared visually by a panel of eight assessors, to assess relative discoloration. The results were as follows:

Panellists showing a preference for Powder 31	8
Panellists showing a preference for Powder L	0

The powder of Example 31 showed slight discoloration, while the powder of Comparative Example L was quite badly discoloured. On an arbitrary scale of 0 to 10, panellists allocated the following discoloration scores:

Powder 31	3
Powder L	6

Example 32, Comparative Example M

Detergent base powders were prepared by mixing zeolite MAP, in sodium or ion-exchanged form, with the liquid surfactant blend used in Examples 31 and L, in a laboratory-scale granulator. The ammonium-exchanged zeolite MAP was that of Example 2, and the sodium zeolite MAP the raw material of Example 2. Again, the differences between the formulations reflect the different carrying capacities of the two zeolites.

The base powders were mixed with manganese catalyst granules to give powders having the following formulations:

	Example M	Example 32
Zeolite MAP (Na)*	58.9	-
Zeolite MAP (NH_4)* (Ex 2)	-	63.6
CocoPAS	9.2	8.0
Coco 7EO	9.2	8.0
Coco 3EO	11.7	10.1
Soap	3.5	3.1
Water	2.5	2.2
Total base powder	95.0	95.0
Catalyst granules	5.0	5.0
	100.0	100.0

* hydrated basis

Storage tests and assessment of discoloration were carried out as described in Examples 31 and L. The results were as follows:

Panellists showing a preference for Powder 32	6
Panellists showing a preference for Powder M	2

The powder of Comparative Example M (containing sodium zeolite MAP) was significantly less discoloured that the powder of Comparative Example L (containing sodium zeolite A), the discoloration score being 2.

Example 33, Comparative Example N

The procedure of Examples 31 and L was repeated using different catalyst granules, having the following composition:

Catalyst (Mn 1,4,7-Me$_3$TACN)	2.0
Cetocetylstearate	31.0
Silica*	26.4
Sodium bicarbonate	39.6
Titanium dioxide	1.0
	100.0

* Gasil (Trade Mark) 200TP ex Crosfield.

Example 33 contained 95 wt% of the base powder of Example 31 (ammonium-exchanged zeolite A), and Comparative Example N contained 95 wt% of the base powder of Comparative Example A (sodium zeolite A). Each powder also contained 5 wt% of the catalyst granules. Storage tests were carried out as in earlier Examples, and the panel assessment results were as follows:

Panellists showing a preference for Powder 33	8
Panellists showing a preference for Powder N	0

The discoloration scores were as follows:

Powder 33	0
Powder N	8

Example 34, Comparative Example P

The procedure of Examples 33 and N was repeated using ammonium-exchanged zeolite MAP (Example 34) and sodium zeolite MAP (Example P).

Example 34 contained 95 wt% of the base powder of Example 32 (ammonium-exchanged zeolite MAP), and Comparative Example P contained 95 wt% of the base powder of Comparative Example M (sodium zeolite MAP). Each powder also contained 5 wt% of the catalyst granules. Storage tests were carried out as in earlier Examples, and the panel assessment results were as follows:

Panellists showing a preference for Powder 34	7
Panellists showing a preference for Powder P	1

The discoloration scores were as follows:

Powder 34	0
Powder P	3

Example 35, Comparative Example O

This Example describes an accelerated storage test to show the effect of zeolite type on the decomposition of the manganese catalyst Mn 1,4,7-Me$_3$TACN. In this test, the catalyst, not in granular form, was in direct contact with zeolitic base powder.

Crystalline catalyst (0.26 g) was granulated with 7EO nonionic surfactant (3 g) and zeolite (10 g) to give the following compositions:

Example	O	35
Catalyst	1.96	1.96
Zeolite A (Na)*	75.42	-
Zeolite A (NH$_{4)}$)* (Ex 1)	-	75.42

*hydrated basis

(continued)

Example	O	35
Nonionic 7EO**	22.62	22.62
	100.00	100.00

**C_{12-15}oxo alcohol, 7EO: Synperonic (Trade Mark) A7 ex ICI.

The granules were stored at 37°C and 70% relative humidity and their colour assessed visually at regular time intervals.

The granules of Comparative Example Q showed significant levels of brown discoloration after 24 hours' storage. The granules of Example 35, however, showed no discoloration even after 7 days' storage.

Claims

1. A particulate detergent, bleaching or cleaning composition comprising a bleach ingredient sensitive to moisture and a crystalline aluminosilicate having exchangeable cations, characterised in that the exchangeable cations of the aluminosilicate include ammonium, lithium or hydrogen ions or combinations thereof.

2. A composition as claimed in claim 1, characterised in that at least 5% of the exchangeable cations of the aluminosilicate comprise ammonium, lithium or hydrogen ions or combinations thereof.

3. A composition as claimed in any preceding claim, characterised in that the aluminosilicate is zeolite A wherein from 10 to 50% of the exchangeable cations comprise ammonium, lithium or hydrogen ions or combinations thereof.

4. A composition as claimed in claim 1 or claim 2, characterised in that the aluminosilicate is zeolite P having a silicon to aluminium ratio not exceeding 1.33 (zeolite MAP), wherein from 10 to 90 wt% of the exchangeable cations comprise ammonium, lithium or hydrogen ions or combinations thereof.

5. A composition as claimed in any preceding claim, characterised in that the bleach ingredient sensitive to moisture is an inorganic persalt.

6. A composition as claimed in claim 5, characterised in that the bleach ingredient sensitive to moisture is sodium percarbonate.

7. A composition as claimed in any preceding claim, which is a particulate detergent composition comprising:

   (a) from 2 to 60 wt% of one or more organic detergent surfactants,

   (b) from 10 to 80 wt% of a builder system comprising a crystalline aluminosilicate having exchangeable cations,

   (c) from 5 to 40 wt% of a bleach system comprising a bleach ingredient sensitive to moisture,

   (d) optionally other ingredients to 100 wt%,

   characterised in that the exchangeable cations of the aluminosilicate (b) include ammonium, lithium or hydrogen ions or combinations thereof.

8. Zeolite P having a silicon to aluminium ratio not exceeding 1.33 (zeolite MAP) having exchangeable cations, characterised in that the exchangeable cations include ammonium, lithium or hydrogen ions or combinations thereof.

9. Zeolite MAP as claimed in claim 8, characterised in that from 10 to 90 wt% of the exchangeable cations comprise ammonium, lithium or hydrogen ions or combinations thereof.

10. Use of a crystalline aluminosilicate having exchangeable cations to stabilise a bleach ingredient sensitive to moisture in a particulate detergent, bleaching or cleaning composition, characterised in that the exchangeable cations include ammonium, lithium or hydrogen ions or combinations thereof.

Patentansprüche

1. Teilchenförmige Reinigungs-, Bleich- oder Waschmittelzusammensetzung, die einen feuchtigkeitsempfindlichen Bleichmittelbestandteil und ein kristallines Aluminiumsilicat mit austauschbaren Kationen umfaßt, dadurch gekennzeichnet, daß die austauschbaren Kationen des Aluminiumsilicats Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon einschließen.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß mindestens 5% der austauschbaren Kationen des Aluminiumsilicats Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon umfassen.

3. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Aluminiumsilicat der Zeolith A ist, worin von 10 bis 50% der austauschbaren Kationen Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon umfassen.

4. Zusammensetzung nach einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß das Aluminiumsilicat der Zeolith P mit einem Silicium zu Aluminium Verhältnis, das 1,33 nicht übersteigt, (Zeolith MAP) ist, worin von 10 bis 90 Gew.-% der austauschbaren Kationen Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon umfassen.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der feuchtigkeitsempfindliche Bleichmittelbestandteil ein anorganisches Persalz ist.

6. Zusammensetzung nach Anspruch 5, dadurch gekennzeichnet, daß der feuchtigkeitsempfindliche Bleichmittelbestandteil Natriumpercarbonat ist.

7. Zusammensetzung nach einem der vorhergehenden Ansprüche, die eine teilchenförmige Reinigungsmittelzusammensetzung ist, umfassend:

   (a) von 2 bis 60 Gew.-% eines oder mehrerer organischer oberflächenaktiver Reinigungsmittel,

   (b) von 10 bis 80 Gew.-% eines Gerüststoffsystems, das ein kristallines Aluminiumsilicat mit austauschbaren Kationen umfaßt,

   (c) von 5 bis 40 Gew.-% eines Bleichmittelsystems, das einen feuchtigkeitsempfindlichen Bleichmittelbestandteil umfaßt,

   (d) wahlweise andere Bestandteile bis auf 100 Gew.-%,

   dadurch gekennzeichnet, daß die austauschbaren Kationen des Aluminiumsilicats (b) Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon einschließen.

8. Zeolith P mit einem Silicium zu Aluminium Verhältnis, das 1,33 nicht übersteigt, (Zeolith MAP) mit austauschbaren Kationen, dadurch gekennzeichnet, daß die austauschbaren Kationen Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon einschließen.

9. Zeolith MAP nach Anspruch 8, dadurch gekennzeichnet, daß von 10 bis 90 Gew.-% der austauschbaren Kationen Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon umfassen.

10. Verwendung eines kristallinen Aluminiumsilicats mit austauschbaren Kationen zur Stabilisierung eines feuchtigkeitsempfindlichen Bleichmittelbestandteils in einer teilchenförmigen Reinigungs-, Bleich- oder Waschmittelzusammensetzung, dadurch gekennzeichnet, daß die austauschbaren Kationen Ammonium-, Lithium- oder Wasserstoffionen oder Kombinationen davon einschließen.

Revendications

1. Une composition nettoyante ou de blanchiment détergente particulaire, comprenant un ingrédient de blanchiment sensible à l'humidité et un aluminosilicate cristallin présentant des cations échangeables, caractérisée en ce que

les cations échangeables de l'aluminosilicate comprennent des ions d'hydrogène, de lithium ou d'ammonium, ou des combinaisons de ceux-ci.

2. Une composition selon la Revendication 1, caractérisée en ce qu'au moins 5% des cations échangeables de l'aluminosilicate comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.

3. Une composition selon l'une quelconque des Revendications précédentes, caractérisée en ce que l'aluminosilicate est une zéolite A, dans laquelle 10 à 50 % des cations échangeables comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.

4. Une composition selon la Revendication 1 ou 2, caractérisée en ce que l'aluminosilicate est une zéolite P présentant un rapport entre silicium et aluminium n'excédant pas 1,33 (zéolite MAP), dans laquelle 10 à 90 % en masse des cations échangeables comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.

5. Une composition selon l'une quelconque des Revendications précédentes, caractérisée en ce que l'ingrédient de blanchiment sensible à l'humidité est un persel inorganique.

6. Une composition selon la Revendication 5, caractérisée en ce que l'ingrédient de blanchiment sensible à l'humidité est un percarbonate de sodium.

7. Une composition selon l'une quelconque des Revendications précédentes, qui est une composition détergente particulaire comprenant :

(a) 2 à 60 % en masse d'un ou de plusieurs agent(s) tensioactif(s) détergent(s) organique(s),

(b) 10 à 80 % en masse d'un système d'édificateur de détergence comprenant un aluminosilicate présentant des cations échangeables,

(c) 5 à 40 % en masse d'un système de blanchiment comprenant un ingrédient de blanchiment sensible à l'humidité,

(d) optionnellement, d'autres ingrédients jusqu'à 100 % en masse.

caractérisée en ce que les cations échangeables de l'aluminosilicate (b) comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.

8. Zéolite P présentant un rapport entre silicium et aluminium n'excédant pas 1,33 (zéolite MAP) et présentant des cations échangeables, caractérisée en ce que les cations échangeables comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.

9. Zéolite MAP selon la Revendication 8, caractérisée en ce que 10 à 90 % en masse des cations échangeables comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.

10. Utilisation d'un aluminosilicate cristallin présentant des cations échangeables destiné à stabiliser un ingrédient de blanchiment sensible à l'humidité dans une composition nettoyante ou de blanchiment détergente particulaire, caractérisée en ce que les cations échangeables comprennent des ions d'ammonium, de lithium ou d'hydrogène, ou des combinaisons de ceux-ci.