⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 339 997**
A2

⑫ # EUROPEAN PATENT APPLICATION

㉑ Application number: **89304206.9**

㉒ Date of filing: **27.04.89**

(51) Int. Cl.^{4}: **C 11 D 3/12**
C 11 D 3/39

㉚ Priority: **29.04.88 GB 8810189**

㊸ Date of publication of application:
02.11.89 Bulletin 89/44

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ (GB)

(84) Designated Contracting States: **GB**

(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam (NL)

(84) Designated Contracting States:
CH DE ES FR IT LI NL SE

(72) Inventor: **Schepers, Frederik Jan**
Albertine Agneslaan 234
NL-3136 NE Vlaardingen (NL)

Verburg, Charles Cornelis
Drs. Stijkelstraat 42
NL-3132 BV Vlaardingen (NL)

(74) Representative: **Gambell, Derek et al**
UNILEVER PLC Patents Division P.O. Box 68 Unilever House
London EC4P 4BQ (GB)

(54) **Liquid cleaning products.**

(57) In substantially non-aqueous liquid cleaning products comprising dispersed particles of aluminosilicate builder, components sensitive to decomposition catalysed by aluminosilicate can be protected if the aluminosilicate particles are surface-deactivated with an acid.

EP 0 339 997 A2

Bundesdruckerei Berlin

Description

LIQUID CLEANING PRODUCTS

The present invention is concerned with substantially non-aqueous liquid cleaning products of the kind comprising dispersed particles of aluminosilicate builder and one or more other components having a sensitivity to decomposition caused by catalytic action of the aluminosilicate. It also extends to a process of preparing such compositions.

Substantially non-aqueous liquid cleaning products are those comprising little or no water, e.g. 5% by weight or less. They comprise a liquid (solvent) phase which is composed of a liquid surfactant, another non-aqueous solvent or a mixture of both types of liquid. When an aluminosilicate builder is incorporated, it is present as dispersed particles. Other components may also be present, either as dispersed particles or dissolved in the solvent phase. Particles are maintained as a dispersion by virtue of their small size and the viscosity of the liquid phase (i.e. as governed by Stokes' law), by the van der Waals attractive forces between the small particles, and/or by the action of a dispersant incorporated for that purpose.

The aluminosilicate is used in cleaning products as a builder, i.e. to counter the effects of calcium ion water hardness in the wash. However, outside the cleaning/detergent field, it is also well known that aluminosilicates can be used as non-specific catalysts for a wide variety of chemical reactions.

We have found that the presence of aluminosilicate particles in such non-aqueous compositions can lead to severe problems when certain other components are also present, namely decomposition which can be said to be catalysed by the aluminosilicate in that it does not occur (or occurs to a much lesser extent) when the aluminosilicate is not present.

Surprisingly, we have now also found that such decomposition is inhibited if the aluminosilicate particles are surface-deactivated with an acid. These novel compositions, not suffering from the aforementioned drawback, can be prepared by the steps of:-

a) treating the aluminosilicate particles with an acid; and
b) intimately admixing the thus treated particles with the other components of the composition.

Acid treatment of the aluminosilicate causes partial destruction of the zeolite lattice, especially at the surface thereof, as can be observed with X-ray powder diffraction, electron microscopy and other known surface sensitive techniques.

The surface-deactivated particles also differ from regular untreated particles in that they yield a lower pH when dried and dispersed at 1% by weight in water.

In the literature of catalytic chemistry it is known to pre-treat aluminosilicates with hydrogen chloride to enhance their ability to catalyse reactions in the gas phase, i.e. in H Matsumoto et al, Journal of Catalysis, 12 (1968) 84-89. However there is no suggestion that such a pre-treatment could inhibit their ability to catalyse decomposition of components in non-aqueous liquid detergents.

Whilst not being bound by any particular interpretation or theory, we believe that the kinds of problem encountered with the aluminosilicates typically occur along the following lines, although the precise mechanism by which the present invention provides the solution is not clear.

When particulate aluminosilicate is added to a non-aqueous liquid medium, an initial release of gas from the particles is observed for several hours. This could be due to the escape of gas trapped in the highly porous surface of the aluminosilicate. However, once such escape has ceased, there is no longer a problem. Nevertheless, there can be further difficulties when an aluminosilicate-sensitive component is present.

A common aluminosilicate-sensitive component is a dispersed particulate oxygen bleach system comprising an inorganic persalt and a bleach precursor. Such systems are well known to those skilled in the art. They function by release of hydrogen peroxide from the peroxygen compound when in contact with water, e.g. in the wash. The hydrogen peroxide reacts with the precursor to form a peroxyacid as an effective bleach. The use of the activator thus makes bleaching more effective at lower temperatures.

The aluminosilicate causes profound gassing in the presence of the inorganic persalt, for example sodium perborate, monohydrate or tetrahydrate. This is probably due to release of oxygen and so effectively reduces the bleach capacity of the product. Moreover, when certain dispersants for the particles are used, the evolved gas can be suspended, forming a mousse of unacceptably high viscosity.

The aluminosilicate also promotes decomposition of the precursor. The precursors are often acetic acid esters (e.g. glyceryl tri-acetate or N, N, N^1, N^1-tetraacetyl ethylene diamine, otherwise known as TAED). Decomposition of the precursor is measurable by a titration technique and clearly is another factor which will degrade the bleaching capability of the product.

Whilst the degree of both these decompositions is partly dependent on the solvent phase, in particular the kind of any nonionic surfactant therein, we have also found that the amount of water present in the aluminosilicate particles has a profound effect. Here it is convenient to define three levels of water (degrees of hydration) for the aluminosilicates, e.g. for 4A zeolite. These can be termed 'fully hydrated', corresponding to about 24% of water by weight of the aluminosilicate which is approximately the maximum theoretical water level, 'partially hydrated', corresponding to about 18% by weight of water and 'activated', corresponding to about 4-6% by weight of water. In the latter case (activated) the water seems to be bound to the aluminosilicate and cannot be driven off. The amount of water may therefore represent the maximum amount of dehydration which may be achieved.

In the applicants' unpublished European patent application no. 87309568.1, filed 29 October 1987 it is stated that initial gassing due to trapped gas and undesired setting are worsened by increased water levels in the aluminosilicate. However, in that context, the setting due to the water can be mitigated or stopped by use of an additional material in accordance with the invention claimed in that application.

The applicants have now found that in the context of the present invention, water levels around that of the partially hydrated material are preferable to those in the activated material but most preferred is a degree of hydration around that at the fully hydrated aluminosilicate. In general, they have observed that the higher water level has a much more beneficial effect on the stability of the precursor than in prevention of degradation of the persalt bleach compound.

In the compositions according to the present invention, it is preferred that the average particle size of all dispersed solids is 10 microns or less. If the solids are not already suitably small, they can be reduced to the required size by milling. They can be milled prior to dispersion in the solvent phase or they can be milled after mixing with the solvent phase (e.g. in a colloid mill). Even if some or all of the particles are already sufficiently small, they can be passed through a mill after mixing with the solvent phase, in order to improve homogeneity of the composition. It is also possible to mill some solids before mixing with the solvent phase and some afterwards.

However, when the sensitive components comprise an oxygen bleach system of the kind hereinbefore described, to maximise inhibition of gassing, it is preferred that at least the persalt and the treated aluminosilicate are dispersed in the solvent phase (most preferably also with the bleach precursor) and then passed through a mill to provide a homogeneous, non-sedimenting, liquid. When the composition also contains further components, it is most preferred that substantially all components are brought together with the solvent phase and then milled. These requirements apply even when some or all of the solids are already sufficiently small and/or have been milled previously.

Thus during manufacture, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In particular it is preferred that the aluminosilicate builder contains less than 24% water. In the aforementioned most preferred process, the dry, substantially anhydrous solids are blended with the solvent in a dry vessel. This blend is passed through a grinding mill or a combination of mills, e.g. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill, to achieve a particle size of 0.1 to 100 microns, preferably 0.5 to 50 microns, ideally 1 to 10 microns. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if desired, can be incorporated during a later stage of processing.

It may also be desirable to de-aerate the product before addition of any heat sensitive ingredients. Although in the most preferred process, all components are passed through the mill, sometimes it may be convenient to add certain highly heat sensitive components (usually minor) after milling and a subsequent cooling step. Typical heat sensitive ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of aeration. Suitable equipment for cooling (e.g. heat exchangers) and de-aeration will be known to those skilled in the art.

It follows that all equipment used in this process should be completely dry, special care being taken after any cleaning operations. The same is true for subsequent storage and packing equipment.

Although liquid cleaning products according to the present invention need not contain a surfactant, it is envisaged that in many embodiments they will. These surfactant compositions are liquid detergent products, e.g. for fabrics washing, machine warewashing or hard surface cleaning (with or without abrasives). However, the wider term 'liquid cleaning product' also includes non-surfactant liquids which are still useful in cleaning, for example non-aqueous bleach products or those in which the liquid phase (solvent) consists of one or more light, non-surfactant solvents for greasy stain pre-treatment of fabrics prior to washing. Such pre-treatment products can contain in addition to the aluminosilicate builder, solid bleaches, dispersed enzymes and the like. The liquid cleaning products according to the invention may also be in the form of specialised cleaning products, such as for surgical apparatus or artificial dentures. They may also be formulated as agents for washing and/or conditioning of fabrics.

As with compositions according to the prior art, in those of the present invention, solid particles can be maintained in dispersion (i.e. resist settling, even if not perfectly) by a number of means. For example, settling may be inhibited purely by virtue of the relative small size of the particles and the relatively high viscosity of the solvent phase. The effect is that utilised in the compositions described in patent specifications EP-A-30 096 and GB 2 158 838A. Alternatively, they may be dispersed, according to any of several prior proposals to utilise additional means to enhance solid-suspending properties in such non-aqueous liquids. These are somewhat analogous to so-called external structuring techniques used in aqueous systems; i.e., in addition to the particulate solids and the liquid solvent phase in which they are to be suspended, an additional dispersant is used which by one means or another, acts to aid stable dispersion or suspension of the solids for a finite period.

One such known means of promoting dispersion is to use nonionic surfactant as the solvent and to add an inorganic carrier material as the dispersant, in particular, highly voluminous silica. This acts by forming a separate solid-suspending network. This silica was highly voluminous by virtue of having an extremely small particle size, hence high surface area. This is described in GB patent specifications 1,205,711 and 1,270,040.

However, there can be a problem with these compositions in that they may set after prolonged storage.

A similar structuring means is use of fine particulate chain structure-type clay, as described in specification EP-A-34,387.

Another suitable substance known as a dispersant for particles in nonionic-based non-aqueous compositions is a hydrolyzable co-polymer of maleic anhydride with ethylene or vinylmethylether, which co-polymer is at least 30% hydrolyzed. This is described in specification EP-A-28,849.

Most preferably however, the dispersions can be stabilised is the use of a dispersant material which has been termed 'a deflocculant', according to the disclosure of European Patent Specification EP 266199-A (Unilever). As described there, for deflocculation to occur, an appropriate combination of solids, solvent and deflocculant must be identified. The deflocculant can be solid or liquid before it is added to the remainder of the composition. It can be mono-functional (i.e. act only to deflocculate the particulate solids) or it can be bi-functional (i.e. also have properties beneficial in the relevant cleaning application, e.g. a surfactant). Many of the deflocculants described are inorganic or organic acids (including the free acid form of anionic surfactants). Two mentioned as particularly preferred are dodecyl benzene sulphonic acid (as the free acid) and lecithin.

In the case of hard-surface cleaning, the compositions according to the present invention may be formulated as main cleaning agents, or pre-treatment products to be sprayed or wiped on prior to removal, e.g. by wiping off or as part of a main cleaning operation.

In the case of warewashing, the compositions may also be the main cleaning agent or a pre-treatment product, e.g applied by spray or used for soaking utensils in an aqueous solution and/or suspension thereof.

Those products which are formulated for the cleaning and/or conditioning of fabrics constitute an especially preferred form of the present invention because in that role, there is a very great need to be able to incorporate substantial amounts of various kinds of solids. These compositions may for example, be of the kind used for pre-treatment of fabrics (e.g. for spot stain removal) with the composition neat or diluted, before they are rinsed and/or subjected to a main wash. The compositions may also be formulated as main wash products, being dissolved and/or dispersed in the water with which the fabrics are contacted. In that case, the composition may be the sole cleaning agent or an adjunct to another wash product. Within the context of the present invention, the term 'cleaning product' also embraces compositions of the kind used as fabric conditioners (including fabric softeners) which are only added in the rinse water (sometimes referred to as 'rinse conditioners').

Thus, the compositions will contain at least one agent which promotes the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, this agent will be selected from surfactants, enzymes, bleaches, microbiocides, (for fabrics) fabric softening agents and (in the case of hard surface cleaning) abrasives. Of course in many cases, more than one of these agents will be present, as well as other ingredients commonly used in the relevant product form.

The compositions will be substantially free from agents which are detrimental to the article(s) to be treated. For example, they will be substantially free from pigments or dyes, although of course they may contain small amounts of those dyes (colourants) of the kind often used to impart a pleasing colour to liquid cleaning products, as well as fluorescers, bluing agents and the like.

All ingredients before incorporation are either liquid, in which case, in the composition they will constitute all or part of the liquid phase, or they will be solids, in which case, in the composition they will either be dispersed as solid particles in the liquid phase or they will be dissolved in the liquid phase. Thus as used herein, the term solids is to be construed as referring to materials in the solid phase which are added to the composition and are dispersed therein in solid form, those solids which dissolve in the liquid phase and those in the liquid phase which solidify (undergo a phase change) in the composition, wherein they are then dispersed.

Some liquids are alone, unlikely to be suitable to perform the function of the liquid phase if it is desired to incorporate a deflocculant for the solids. However, in that case they still will be able to be incorporated if used with another liquid which does have the required properties, the only requirement being that where the liquid phase comprises two or more liquids, they are miscible when in the total composition or one can be dispersible in the other, in the form of fine droplets.

Where surfactants are solids, they will usually be dissolved or dispersed in the solvent. Where they are liquids, they will usually constitute all or part of the liquid phase. However, in some cases the solvents may undergo a phase change in the composition, Also, as mentioned earlier above, some surfactants are also eminently suitable as deflocculants.

In general however, surfactants may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol. I, by Schwartz & Perry, Interscience 1949 and 'surface Active Agents' Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the Mccutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Liquid surfactants are an especially preferred class of material to use in the solvent phase, especially polyalkoxylated types and in particular polyalkoxylated nonionic surfactants.

When it is desired to incorporate a deflocculant, as a general rule, the most suitable liquids to choose as the liquid phase are organic materials having polar molecules. In particular, those comprising a relatively lipophilic part and a relatively hydrophilic part, especially a hydrophilic part rich in electron lone pairs, tend to be well suited.

Many nonionic detergent surfactants suitable for use in compositions of the present inventions are well-known in the art. They normally consist of a water-solubilizing polyalkoxylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes. Also common are fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms. In any of the mono- and dialkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule. In all polyalkoxylene containing surfactants, the polyalkoxylene moiety preferably consists of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class, particularly preferred are those described in European patent specification EP-A-225,654, (Unilever) especially for use as all or part of the solvent. Also preferred are those ethoxylated nonionics which are the condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C_{11-13} alcohols with (say) 3 or 7 moles of ethylene oxide. These may be used as the sole nonionic surfactants or in combination with those of the described in the last-mentioned European specification, especially as all or part of the solvent.

Another class of suitable nonionics comprise the alkyl polysaccharides (polyglycosides/oligosaccharides) such as described in any of specifications US 3,640,998; US 3,346,558; US 4,223,129; EP-A-92,355; EP-A-99,183; EP-A-70,074, '75, '76, '77; EP-A-75,994, '95, '96.

Nonionic detergent surfactants normally have molecular weights of from about 300 to about 11,000.

Mixtures of different nonionic detergent surfactants may also be used, provided the mixture is liquid at room temperature. Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic or ampholytic detergent surfactants and soaps may also be used. If such mixtures are used, the mixture must be liquid at room temperature.

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamaine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphates having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphates having from 1 to 5 ethylene oxide groups, olefin sulphonates prepared by sulphonation of C_{10}-C_{24} alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product.

Other surfactants which may be used include alkali metal soaps of a fatty acid, preferably one containing 12 to 18 carbon atoms. Typical such acids are oleic acid, ricinoleic acid and fatty acids derived from caster oil, rapeseed oil, groundnut oil, coconut oil, palmkernal oil or mixtures thereof. The sodium or potassium soaps of these acids can be used. As well as fulfilling the role of surfactants, soaps can act as detergency builders or fabric conditioners, other examples of which will be described in more detail hereinbelow. It can also be remarked that the oils mentioned in this paragraph may themselves constitute all or part of the solvent, whilst the corresponding low molecular weight fatty acids (triglycerides) can be dispersed as solids or function as structurants.

Yet again, it is also possible to utilise cationic, zwitterionic and amphoteric surfactants such as referred to in the general surfactant texts referred to hereinbefore. Examples of cationic detergent surfactants b are aliphatic or aromatic alkyl-di(alkyl) ammonium halides and examples of soaps are the alkali metal salts of C_{12}-C_{24} fatty acids. Ampholytic detergent surfactants are e.g. the sulphobetaines. Combinations of surfactants from within the same, or from different classes may be employed to advantage for optimising structuring and/or cleaning performance.

Non-surfactants which are suitable as solvents include those having molecular forms referred to above as preferred for deflocculation to occur, although other kinds may be used, especially if combined with those of the former type. In general, the non-surfactant solvents can be used alone or with in combination with liquid surfactants. Non-surfactant solvents which have molecular structures which fall into the former, more preferred category include ethers, polyethers, alkylamines and fatty amines, (especially di- and tri-alkyl- and/or fatty- N-substituted amines), alkyl (or fatty) amides and mono- and di- N-alkyl substituted derivatives thereof, alkyl (or fatty) carboxylic acid lower alkyl esters, ketones, aldehydes, and glycerides. Specific examples include respectively, di-alkyl ethers, polyethylene glycols, alkyl ketones (such as acetone) and glyceryl trialkylcarboxylates (such as glyceryl tri-acetate), glycerol, propylene glycol, and sorbitol.

Suitable light solvents with little or no hydrophilic character include lower alcohols, such as ethanol, or higher alcohols, such as dodecanol, as well as alkanes and olefins. Usually, it is preferred to combine them with other liquid materials which are surfactants or non-surfactants having the aforementioned kinds of molecular structure preferred for the occurrence of deflocculation. Even though they may not to play a role in any deflocculation process, it is often desirable to include them tor lowering the viscosity of the product and/or assisting soil removal during cleaning.

The compositions of the invention may contain the liquid phase (whether or not comprising liquid surfactant) in an amount of at least 10% by weight of the total composition. The amount of the liquid phase present in the composition may be as high as about 90%, but in most cases the practical amount will lie between 20 and 70%

and preferably between 20 and 50% by weight of the composition.

Preferably, the compositions of the present invention do contain a deflocculant (as hereinbefore defined) which may be any of those referred to in the published prior art. Or these deflocculants, especially preferred are acids. In the narrowest sense, these are regarded as substances which in aqueous media are capable of dissociating to produce hydrogen ions (H^+), which in aqueous systems can be regarded as existing in the form H_3O^+. However, in the content of the present invention, the definition also extends to those materials which are capable of losing a proton (H^+) and are often termed 'Bronsted Acids', and even those according to the widest definition, that is, a substance which can accept a pair of electrons. Such an acid according to this definition is often called a Lewis acid.

Bronsted acids constitute a preferred group of the acid deflocculants, especially inorganic mineral acids and alkyl-, alkenyl-, aralkyl- and aralkenyl-sulphonic or mono-carboxylic acids and halogenated derivatives thereof, as well as acidic salts (especially alkali metal salts) of these.

Some typical examples from within the latter group include the alkanonic acids such as acetic, propionic and stearic and their halogenated counterparts such as trichloracetic and trifluoracetic as well as the alkyl (e.g. methane) sulphonic acids and aralkyl (e.g. paratoluene) sulphonic acids.

Examples or suitable inorganic mineral acids and their salts are hydrochloric, carbonic, sulphurous, sulphuric and phosphoric acids; potassium monohydrogen sulphate, sodium monohydrogen sulphate, potassium monhydrogen phosphate, potassium dihydrogen phosphate, sodium monohydrogen phosphate, potassium dihydrogen pyrophosphate, tetrasodium monohydrogen triphosphate.

In addition to the acids and acidic salts, other organic acids may also be used as deflocculants, for example formic, lactic, citric, amino acetic, benzoic, salicylic, phthalic, nicotinic, ascorbic, ethylenediamine tetraacetic, and aminophosphonic acids, as well as longer chain fatty carboxylates and triglycerides, such as oleic, stearic, lauric acid and the like. Peracids such as percarboxylic and persulphonic acids may also be used.

The class of acid deflocculants further extends to the Lewis acids, including the anhydrides of inorganic and organic acids. Examples oi these are acetic anhydride, maleic anhydride, phthalic anhydride and succinic anhydride, sulphur-trioxide, diphosphorous pentoxide, boron trifluoride, antimony pentachloride.

One particularly suitable sub-class of deflocculants comprises the anionic surfactants of formula (I) R-L-A-Y (I) wherein R is a linear or branched hydrocarbon group having from 8 to 24 carbon atoms and which is saturated or unsaturated;

L is absent or represents -O-, -S-, -Ph-, or -Ph-O-(where Ph represents phenylene), or a group of formula $-CON(R^1)-$, $-CON(R^1)R^2-$ or $-COR^2-$, wherein R^1 represents a straight or branched C_{1-4} alkyl group and R^2 represents an alkylene linkage having from 1 to 5 carbon atoms and is optionally substituted by a hydroxy group;

A is absent or represents from 1 to 12 independently selected alkenyloxy groups; and

Y represents $-SO_3H$ or $-CH_2SO_3H$ or a group of formula $-CH(R^3)COR^4$ wherein R^3 represents $-OSO_3H$ or $-SO_3H$ and R^4 independently represents $-NH_2$ or a group of formula $-OR^5$ where R^5 respresents hydrogen or a straight or branched C_{1-4} alkyl group and salts, particularly metal, more especially alkali metal salts thereof. However, the free acid forms thereof are the most preferred.

Especially preferred of the free acid forms are those wherein L is absent or represents -O-, -Ph- or -Ph-O-; A is absent or represents from 3 to 9 ethoxy, i.e. $-(CH_2)_2O-$or propoxy, i.e. $-(CH_2)_3O-$ groups or mixed ethoxy/propoxy groups; and Y represents $-SO_3H$ or $-CH_2SO_3H$.

The alkyl and alkyl benzene sulphates, and sulphonates, as well as ethoxylated forms thereof, and also analogues wherein the alkyl chain is partly unsaturated, are particularly preferred.

As well as anionic surfactants, zwitterionic-types can also be used as structurants/deflocculants. These may be any described in the aforementioned general surfactant references. One preferred example is lecithin which is a material having both acidic and basic sites on the molecule and contains a phosphorous linkage of formula $-O-P(-O)(O^-)-O-$.

The level of the deflocculant material in the composition can be optimised by the means described in the art but in very many cases is at least 0.01%, usually 0.1% and preferably at least 1% by weight, and may be as high as 15% by weight. For most practical purposes, the amount ranges from 2-12%, preferably from 4-10% by weight, based on the final composition.

The compositions according to the present invention must contain dispersed particles of surface-deactivated aluminosilicate builder and at least one sensitive component. However, they may also contain one or more other functional ingredients, for example selected from other detergency builders, bleaches or bleach systems (themselves, a sensitive component) and (for hard surface cleaners) abrasives.

The detergency builders are those materials which counteract the effects of calcium, or other ion, water hardness, either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders. They may also be sub-divided into the phosphorus-containing and non-phosphorus types, the latter being preferred when environmental considerations are important.

In general, the inorganic builders comprise the various phosphate-, carbonate-, silicate-, borate- and aliminosilicate-type materals, particularly the alkali-metal salt forms. Mixtures of these may also be used.

Examples of phosphorus-containing inorganic builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous alumino silicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxsulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the tradename of the Dequest range and alkanehydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and co-polymers known to have builder properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/polymaleic acid co-polymers and their salts, such as those sold by BASF under the Sokalan Trade Mark.

The aluminosilicates which are to incorporated when surface-deactivated, comprise for example, crystalline or amorphous materials having the general formula:

$Na_Z (AlO_2)_Z (SiO_2)_Y \ x \ H_2O$

wherein Z and Y are integers of at least 6, the molar ratio of Z to Y is in the range from 1.0 to 0.5, and x is an integer from 6 to 189 such that the moisture content is from about 4% to about 20% by weight.

The preferred range of aluminosilicate is from about 12% to about 30% on an anhydrous basis. The aluminosilicate preferably has a particle size of from 0.1 to 100 microns, ideally betweeen 0.1 and 10 microns and a calcium ion exchange capacity of at least 200 mg calcium carbonate/g.

Suitable bleaches include the halogen, particularly chlorine bleaches such as are provided in the form of alkalimetal hypohalites, e.g. hypochlorites. In the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt, preferably with an precursor, or as a peroxy acid compound.

In the case of the inorganic persalt bleaches, the precursor makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60° C, so that such bleach systems are commonly known as low-temperature bleach systems and are well known in the art. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the precursor is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound alone. The ratio by weight of the peroxy bleach compound to the precursor is from about 15:1 to about 2:1, preferably from about 10:1 to about 3.5:1. Whilst the amount of the bleach system, i.e. peroxy bleach compound and precursor, may be varied between about 5% and about 35% by weight of the total liquid, it is preferred to use from about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxy bleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the precursor is between about 0.5% and about 40%, most preferably between about 1% and about 5% by weight.

Typical examples of the suitable peroxybleach compounds are alkalimetal peroborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate is preferred.

Precursors for peroxybleach compounds have been amply described in the literature, including in British patent specifications 836,988, 855,735, 907,356, 907,358, 907,950, 1,003,310, and 1,246,339, US patent specifications 3,332,882, and 4,128,494, Canadian patent specification 844,481 and South African patent specification 68/6,344.

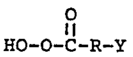
The exact mode of action of such precursors is not known, but it is believed that peracids are formed by reaction of the precursors with the inorganic peroxy compound, which peracids then liberate active-oxygen by decomposition.

They are generally compounds which contain N-acyl or O-acyl residues in the molecule and which exert their activating action on the peroxy compounds on contact with these in the washing liquor.

Typical examples of precursors within these groups are polyacylated alkylene diamines, such as N,N,N^1,N^1-tetraacetylethylene diamine (TAED) and N,N,N^1,N^1-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylgylcoluril (TAGU); triacetylcyanurate and sodium sulphophenyl ethyl carbonic acid ester.

A particularly preferred precursor is N,N,N^1,N^1-tetra- acetylethylene diamine (TAED).

The organic peroxyacid compound bleaches are preferably those which are solid at room temperature and most preferably should have a melting point of at least 50° C. Most commonly, they are the organic peroxyacids and water-soluble salts thereof having the general formula



$$HO{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R{-}Y$$

wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution.

Another preferred class of peroxygen compounds which can be incorporated to enhance dispensing/dispersibility in water are the anhydrous perborates described for that purpose in European patent specification EP-A-217,454 (Unilever).

When the composition contains abrasives for hard surface cleaning (i.e. is a liquid abrasive cleaner), these will inevitably be incorporated as particulate solids. They may be those of the kind which are water insoluble, for example calcite. Suitable materials of this kind are disclosed in patent specifications EP-A-50,887; EP-A-80,221; EP-A-140,452; EP-A-214,540 and EP 9,942 (Unilever) which relate to such abrasives when suspended in aqueous media. Water soluble abrasives may also be used.

The compositions of the invention optionally may also contain one or more minor ingredients such as fabric conditioning agents, enzymes, perfumes (including deoperfumes), micro-biocides, colouring agents, fluorescers, soil-suspending agents (anti-redeposition agents), corrosion inhibitors, enzyme stabilizing agents, and lather depressants.

In general, the solids content of the product may be within a very wide range, for example from 1-90%, usually from 10-80% and preferably from 15-70%, especially 15-50% by weight of the final composition. The alkaline salt should be in particulate form and have an average particle size of less than 300 microns, preferably less than 200 microns, more preferably less than 100 microns, especially less than 10 microns. The particle size may even be of sub-micron size. The proper particle size can be obtained by using materials of the appropriate size or by milling the total product in a suitable milling apparatus.

The compositions are substantially non-aqueous, i.e. they contain little or no free water, preferably no more than 5%, preferably less than 3%, especially less than 1% by weight of the total composition. It has been found by the applicants that the higher the water content, the more likely it is for the viscosity to be too high, or even for setting to occur. However, this may at least in part be overcome by use of higher amounts of, or more effective deflocculants or other dispersants.

The present invention will now be illustrated by way of the following examples.

Example 1

Preparation of Aluminosilicates

Two 'control' samples were prepared:-

A. Partially hydrated Zeolite, ex Degussa, water content ca. 18% by weight. This was dried at 120° C for 24 hours. The resultant water level was found to be 11.2% and the pH of a 1% by weight dispersion of the dried material in water was 11.3.

B. The same Degussa Zeolite was dispersed at 30% by weight in water in which was dissolved 10% by weight of sodium chloride. After one hour, the solids were filtered and dried. The pH of a 1% by weight dispersion of the dried material in water was 10.9.

Two surface-deactivated samples were also prepared for use in compositions according to the present invention:-

1. The same Degussa Zeolite as used in samples A and B was exposed to hydrogen chloride gas by being supported above a concentrated hydrochloric acid solution for 3 days in a dessicator. It was then dried at 120° C for 24 hours. The pH of a 1% by weight dispersion of the dried material in water was 7.0.
2. The same Degussa Zeolite was dispersed at 30% by weight in water in which was dissolved 10% by weight of citric acid. After one hour, the solids were filtered and dried. The pH of a 1% by weight dispersion of the dried material in water was 8.1.

Effects on Precursor Stability

Compositions were made up with 24% of each aluminosilicate dispersed in Dobanol 91-5T and the dispersion then was ball-milled. A 4:5 weight ration of TAED/Glyceryl Triacetate bleach precursor was then post-dosed to give a total precursor weight concentration in the product as measured by titration immediately after preparation as listed under T_0 in Table I. The corresponding concentration after 4 weeks storage at 37° C is given under T_4. In this and all subsequent examples, gassing was measured as the cumulative gas release in ml per 100g of product at various time intervals during storage at 37° C. Reference values were also recorded for samples without the precursor.

Table 1

	Gas released (ml)			Precursor (wt%) measured at:		
Aluminosilicate	Precursor Present	1 day	3 days	5 days	T_0	T_4
A	-	22	31	31	-	-
	+	25	29	33	8.0	7.3
B	-	20	24	24	-	-
	+	20	27	28	8.8	7.7
1	-	16	19	19	-	-
	+	19	19	22	8.4	8.4
2	-	24	33	33	-	-
	+	20	29	33	8.6	8.4

It can be seen that with the surface-deactivated aluminosilicate, precursor stability was considerably improved. There was little effect on gassing which in any event was not too severe with or without surface-deactivation of the aluminosilicate.

Example 2: Effects when Post-dosed Bleach also present

The experiments of Example 1 were repeated but with post-dosing (after the milling step) of 15% by weight milled sodium perborate monohydrate bleach. The concentration of the bleach was also measured by titration at T_0 and T_4 during storage at 37° C. The results are given in Table II. The reference samples contained neither bleach nor precursor.

It can be seen that the beneficial effects on precursor stability are substantially identical to those found in Example 1. However, presence of the bleach resulted in worse gassing which was not inhibited, or even exacerbated by surface-deactivation of the aluminosilicate.

The stability of the bleach was satisfactory with or without surface pre-treatment of the aluminosilicate.

Table II

Aluminosilicate	Precursor Present	Gas Released (ml) after: 1 day	3 days	5 days	Precursor (wt%) Measured at: T_0	T_4	Bleach (wt%) Measured at: T_0	T_4
A	-	42	71	68	-	-	-	-
	+	39	67	71	8.8	3.8	14.3	13.0
B	-	31	66	68	-	-	-	-
	+	29	67	70	8.1	1.9	14.6	13.7
1	-	76	106	*	-	-	-	-
	+	71	102	*	8.8	7.9	14.1	12.7
2	-	49	89	92	-	-	-	-
	+	44	84	85	8.4	6.8	14.3	13.1

* very large - not measured.

To show that the loss of TAED stability in the control examples given above is due to the catalytic effect of the zeolite on the bleach, similar compositions were prepared containing:

partially hydrated zeolite	0 or 24%
sodium perborate monohydrate	0 or 15%
TAED	4%
Dobanol 91-5T	balance

The TAED activity was measured after 1 week at 37°C with the following results.

Perborate monohydrate	Zeolite	TAED activity (1 week)
absent	absent	88%
present	absent	89%
absent	present	95%
present	present	5%

Example 3: Effect on Gassing of Processing and Presence of Other Ingredients

Gassing was investigated in the same way but with the following variations. First, both milled and un-milled bleach were used. Second, in some options, 5% by weight Sokalan CP5 polymer builder and 4.5% by weight sodium carbonate were also included. Third, all components were ball milled together. Compositions were otherwise as Example 2 (compositions with bleach and precursor) except that the nonionic used was Imbentin-C-91/35 OFA and 0.25% dodecyl benzene sulphonic acid (free acid) deflocculant was incorporated.

Results are shown in Table III. Compared to those of Example 2, they show an overall improvement on gassing. Thus, even without surface-deactivation of the aluminosilicate, gassing is satisfactory when the bleach is milled simultaneously with the aluminosilicate and the nonionic. However, when other components are also present, the gassing rises unacceptably unless the aluminisolicate is surface-deactivated. There is no significant difference, whether or not the bleach is initially milled.

Table III

Aluminosilicate	Bleach Milled (+) or Unmilled (-)	Polymer and Carbonate	Gas Reseased (ml) after:		
			1 day	3 days	6 days
A	-	-	45	73	77
1	-	-	62	80	84
A	+	-	57	91	93
1	+	-	63	80	80
A	-	+	57	93	120
1	-	+	46	79	81
A	+	+	64	110	120
1	+	+	49	78	81

Example 4: Complete Formulations

	% by weight
Dobanol 91-5T Nonionic	39.55 or 38.55
Glyceryl Triacetate	5.0
Aluminosilicate (as specified)	24.0
Sokalan CP5	6.0
Sodium Perborate Monohydrate	15.0
Sodium Carbonate	4.5
Tylose MH20	0.5
TAED	4.0
Sodium Carboxy Methyl Cellulose	1.0
Ethylene Diamine Tetraacetic Acid	0.15
Tinopal DMS	0.3
ABSA* Deflocculant	0 or 1.0

* Dodecyl benzene sulphonic acid as free acid.

With variations in the aluminosilicate and presence or absence of the deflocculant as shown in Table IV, precursor and bleach stability and gassing performance were determined as in Examples 1-3. Product viscosity at 25°C was substantially constant throughout the experiment. The value at a shear rate of $21s^{-1}$ is also recorded.

The results are each an average for 3 separate batches of composition. They clearly show the beneficial effects of surface-deactivation of the aluminosilicate on bleach and precursor stability and upon gassing.

Table IV

Aluminosilicate	ABSA	Viscosity (m Pas) at $21s^{-1}$	Bleach (wt%) Measured at:		Precursor Measured at:		Gas Released (ml) after:		
			T_0	T_4	T_0	T_4	3 days	5 days	10 days
A	+	*	14.3	8.8	7.7	1.6	71(1)	>100(2)	*
1	-	1029	15.1	12.6	9.0	5.8	0	0	0
1	+	1136	15.0	12.6	9.0	6.4	55	60	60
1	+	1189	14.3	12.6	8.9	6.5	42(1)	51	53(3)

(1) after 1 day
(2) after 4 days
(3) after 7 days
* not measured because of profound gassing

Claims

1. A substantially non-aqueous liquid cleaning composition comprising a liquid phase having dispersed therein particles of aluminosilicate builder and one or more components sensitive to decomposition catalysed by aluminosilicate, characterised in that the aluminosilicate particles are surface-deactivated with an acid.

2. A composition according to claim 1, wherein the components sensitive to catalytic decomposition comprise an oxygen bleach system comprising an inorganic persalt and a bleach precursor.

3. A composition according to claim 2, wherein the persalt is an alkali metal perborate and the precursor comprises N, N, N^1, N^1 tetraacetylethylene diamine.

4. A process of preparing a substantially non-aqueous cleaning composition comprising a liquid phase having dispersed therein particles of aluminosilicate builder and one or more components sensitive to decomposition catalysed by aluminosilicate, characterised in that said process comprises

a) treating the aluminosilicate particles with an acid; and

b) intimately admixing the thus treated particles with the other components of the composition.

5. A process according to claim 4, wherein the acid comprises an inorganic material.

6. A process according to claim 4, wherein step a) comprises exposing the particles to an acidic gas.

7. A process according to claim 6, wherein the gas is hydrogen chloride.

8. A process according to claim 4, wherein the acid comprises an organic.

9. A process according to claim 4, wherein step a) comprises contacting the particles with the acid in the liquid medium and removing the liquid medium before effecting step b).

10. A process according to claim 9, wherein step a) comprises contacting the particles with a solution of a solid acid in a solvent and removing the solvent before step b).

11. A process according to claim 10, wherein the acid is citric acid.

12. A process according to claim 4, wherein the components sensitive to catalytic decomposition comprise a particulate oxygen bleach system comprising an inorganic persalt and a bleach precursor, the treated aluminosilicate particles and the bleach system particles being mixed in dispersion and then reduced in size by milling.

13. A process according to claim 12, wherein the composition contains further components, substantially all ingredients of the composition being mixed and then subjected to milling.

14. A substantially non-aqueous liquid base for receiving one or more components sensitive to decomposition by aluminosilicate, said base comprising a liquid phase having dispersed therein particles of aluminosilicate builder, which particles are surface - deactivated with an acid.