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(54) Title: DETERGENT COMPOSITION

(57) Abstract: The invention provides a granular detergent composition which comprises (i) from 20 to 50 wt %, preferably from 30 to 40 wt %, of an alkyl ether sulphate, (ii) from 40 to 75 wt %, preferably from 50 to 65 wt %, of a solid carrier, (iii) from 1 to 10 wt %, preferably from 1 to 5 wt %, of an inorganic non-builder salt, and (iv) optionally water to 100 wt % and a method for preparing such a granular detergent composition. A laundry detergent composition which comprises 1 to 20 wt% of a granular detergent composition as defined above is also provided as well as a process for laundering textile fabrics utilising such a laundry detergent composition and the use of such a laundry detergent composition to facilitate oily-stain removal from a fabric. The invention further provides the use of a tri-surfactant system to improve oily-stain removal performance in a zeolite-built laundry detergent composition.

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DETERGENT COMPOSITION

Technical Field

The present invention relates to a granular detergent composition and a method for preparing such a granular detergent composition. A laundry detergent composition comprising such a granular detergent composition is also provided as well as a process for laundering textile fabrics utilising such a laundry detergent composition and the use of such a laundry detergent composition to facilitate oily-stain removal from a fabric. The invention also relates to the use of a tri-surfactant system to improve oily-stain removal performance in a zeolite-built laundry detergent composition.

Background of the invention

Laundry detergent compositions have for many years contained anionic sulphonate and/or sulphate surfactant, such as linear alkylbenzene sulphonate (LAS) and/or an alkyl ether sulphate, together with ethoxylated alcohol non-ionic surfactants. Examples of such compositions are common in the published literature.

Such laundry detergent compositions are often in powder form. These powders are commonly manufactured by preparing a slurry of all or the majority of the ingredients, spray-drying the slurry, and optionally post dosing (dry-mixing) further ingredients. If an alkyl ether sulphate is to be included in the powder formulation, it is conventional for

this to be added in the slurry stage. However, such alkyl ether sulphates, especially sodium lauryl ether sulphate (SLES), tend to decompose under the higher temperature conditions of spray-drying and cause handling difficulties when added to the slurry due to their high stickiness. Moreover, the latter characteristic also makes post-dosing of this ingredient impractical.

It has now been found that these problems can be overcome by using a new process to produce granules containing an alkyl ether sulphate. These granules have good flow properties and good stability/compatibility. Thus, they can easily be post-dosed into the spray-dried composition.

In addition, it has surprisingly been found that laundry detergent compositions containing such granules, especially in conjunction with a linear alkyl benzene sulphonate and an alkoxylated alcohol, show a significant improvement in oily-stain removal performance, particularly under washing conditions where the washing liquor is at ambient temperature, that is, 20 - 30°C. This improvement in oily-stain removal performance is particularly noticeable in zeolite-built laundry detergent powders.

Definition of the Invention

According to a first aspect of the invention there is provided a granular detergent composition which comprises (i) from 20 to 50 wt %, preferably from 30 to 40 wt %, of an alkyl ether sulphate, (ii) from 40 to 75 wt %, preferably from 50 to 65 wt %, of a solid carrier, (iii)

from 1 to 10 wt %, preferably from 1 to 5 wt %, of an inorganic non-builder salt, and (iv) optionally water to 100 wt %.

According to a second aspect of the invention there is provided a method for preparing a granular detergent composition as defined in the first aspect, which comprises mixing the alkyl ether sulphate, solid carrier, inorganic non-builder salt and any water in a suitable mixer; extruding the mixture to form granules; drying the granules; and screening the dried granules to obtain granules of a specific particle size.

According to a third aspect of the invention there is provided a laundry detergent composition which comprises from 1 to 20 wt% , preferably from 1 to 10 wt%, of a granular detergent composition as defined in the first aspect.

According to a fourth aspect of the invention there is provided a process for laundering textile fabrics by machine or hand, which includes the step of immersing the fabrics in a wash liquor comprising water in which a laundry detergent composition as defined in the third aspect is dissolved or dispersed.

According to a fifth aspect of the invention there is provided use of a laundry detergent composition as defined in the third aspect to facilitate oily-stain removal from a fabric.

According to a sixth aspect of the invention there is provided use of a surfactant system to improve oily-stain removal performance in a zeolite-built laundry detergent composition characterised in that the surfactant system comprises: (i) a linear alkyl benzene sulphonate or a salt thereof, (ii) an alkyl ether sulphate or a salt thereof, and (iii) an alkoxylated alcohol.

Detailed Description of the Invention

Granular Detergent Composition

The granular detergent composition of the invention contains a combination of an alkyl ether sulphate, a solid carrier, an inorganic non-builder salt and optionally water. Further optional detergent ingredients may also be present.

The alkyl ether sulphate may be present as a sodium, potassium, calcium or magnesium salt or a mixture of these. Sodium salts are generally preferred.

The alkyl ether sulphate is typically present in an amount from 20 to 50 wt%, preferably from 30 to 40 wt%, based on the weight of the granular detergent composition.

Preferably, the alkyl ether sulphate is a C_{11-14} alkyl ether sulphate, especially a C_{12-13} alkyl ether sulphate. Sodium lauryl ether sulphate (SLES) is particularly preferred.

It is preferred that the alkyl ether sulphate has a degree of alkoxylation, especially ethoxylation, from 0 to 9,

preferably 0 to 2. Preferably, the alkyl ether sulphate has an average degree of ethoxylation of 1. A particularly preferred alkyl ether sulphate is SLES.1EO.

The solid carrier may be any suitable, preferably inert, solid material. Preferably, the solid material has a high liquid carry capacity. In a preferred embodiment, the solid carrier is an aluminosilicate, preferably an alkali metal, especially sodium, aluminosilicate. It is preferred that the solid carrier is a zeolite, especially one of the well-known commercially available zeolites A and X, or a mixture thereof. The zeolite may also be a zeolite of the P type, such as zeolite MAP as described and claimed in EP 384070A (Unilever). However, it is particularly preferred that the zeolite is zeolite 4A.

The solid carrier is typically present in an amount from 40 to 75 wt%, preferably from 50 to 65 wt%, especially from 55 to 60 wt%, based on the weight of the granular detergent composition.

The inorganic non-builder salt serves to strengthen the structure of the granular detergent composition and keeps it from breaking down and caking. The inorganic non-builder salt may be any of those listed later in this specification. These include alkaline agents such as alkali metal, preferably sodium, carbonates, sulphates, silicates, metasilicates etc. However, it is preferred that the inorganic non-builder salt is an alkali metal silicate, especially alkaline sodium silicate.

The inorganic non-builder salt is typically present in an amount from 1 to 10 wt%, preferably from 1 to 5 wt%, especially from 1 to 3 wt%, based on the weight of the granular detergent composition.

The granular detergent composition of the invention may also contain water. Typically, this will constitute about 1 to 10 wt%, preferably 3 to 6 wt%, based on the weight of the granular composition.

Preferably, the granular detergent composition has a bulk density of from 460 to 500 g/l, preferably from 470 to 490 g/l.

The granular detergent composition typically has a particle size specification as follows:

>	1000 µm (% cumulative)	3.0 max
>	500 µm (% cumulative)	85.0 max
<	180 µm (% cumulative)	5.0 max

The granules therefore have a main particle size in the range of 150-1000µm, with a main particle size controlled at the range of 500-1000 µm.

Preparation of the granular detergent composition

The granular detergent composition of the present invention is prepared using a process in which the liquid ingredients are agglomerated with powder carriers in a mixer and the granulated mixture is then converted into a free flowing granule using a fluid bed. Specifically, the process

comprises mixing the alkyl ether sulphate, solid carrier, inorganic non-builder salt and any water in a suitable mixer; extruding the mixture to form granules; drying the granules; and screening the dried granules to obtain granules of a specific particle size.

Preferably, a suitable mixer is a convection mixer such as a ribbon mixer, especially a horizontal ribbon mixer. A horizontal ribbon mixer is composed of a container, screw stirring paddles and transitional parts. There are three layers of screw paddles. The outer screw converges the material to the centre from two sides and the inner layer of screw paddles conveys the material to the two sides from the centre, so as to produce convection mixing.

Ideally, the (sticky and wet) mixture is extruded by pressing the mixture through a sieve to form noodles which are then cut to form granules (noodle granules). This is conveniently accomplished using a granulator in which, under the action of clockwise and counter-clockwise rotation of a roller, the damp powder mixture will be forced to pass through a sieve and then become a granule. Granules with different specifications can be made by adjusting the size of the sieve. However, it is particularly preferred that the mesh size of the sieve is from 600-700μm.

Preferably, the granules are dried by hot air in a fluid bed. Typically, the feedstock is fed into the machine from the inlet and moves forward continuously along with the level of fluid bed under the action of vibration. The hot air passes through the fluid bed and carries out hot heat

exchange with the damp granules. The damp air is exhausted out through a cyclone separator and belt filter and the dry granule is discharged through the discharge outlet. The hot air exchanger heats the inlet air using steam. Thus, the inlet temperature range has a maximum of 140°C. Ideally, the hot air has a temperature of about 70 to 90°C, preferably about 75 to 85°C. The granule is heated evenly and the thickness of the granule layer, the speed of movement inside the machine and the amplitude can be adjusted continuously. The dried granule can also be cooled by the fluid bed depending on the granule character to remove extra moisture.

Finally, the dried granules are screened by the use of a sieve having an appropriate mesh size. The resultant granules were white and free-flowing and suitable for manual handling due to less dust.

Laundry detergent composition

The granular detergent composition described above can be used to form laundry detergent compositions. Thus, a laundry detergent composition of the present invention comprises from 1 to 20 wt%, preferably from 1 to 10 wt%, of a granular detergent composition as defined above, based on the weight of the total composition. Preferably, the amount of granular detergent composition is selected to give an amount of from 1 to 5 wt% of alkyl ether sulphate based on the weight of the total composition.

Laundry detergent compositions of the invention may further comprise

(i) from 5 to 25 wt%, preferably from 10 to 15 wt%, of an anionic surfactant,

(ii) from 1 to 10 wt%, preferably from 1 to 5 wt%, of a non-ionic surfactant,

(iii) from 10 to 30 wt%, preferably from 15 to 25 wt%, of a detergency builder,

(iv) from 40 to 60 wt%, preferably from 45 to 55 wt%, of an inorganic non-builder salt,

(v) from 0.5 to 3 wt%, preferably from 1 to 2 wt%, of a polycarboxylate polymer, and

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

The anionic surfactant (i)

Anionic surfactants are well-known to those skilled in the art. 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.

Examples include alkylbenzene sulphonates, branched or linear alkyl benzene sulphonates, primary and secondary alkylsulphates, particularly C_8-C_{16} primary alkyl sulphates; olefin sulphonates, including alpha olefin sulphonates, fatty alcohol sulphates such as primary alcohol sulphates, alkane sulphonates, alkyl xylene sulphonates, dialkyl sulphosuccinates, and fatty acid ester sulphonates, and alkyl carboxylates. These may be present as sodium,

potassium, calcium or magnesium salts or mixtures of these. Sodium salts are generally preferred.

The anionic surfactant is preferably a sulphonate or sulphate anionic surfactant. More preferably the anionic surfactant is linear alkylbenzene sulphonate or primary alcohol sulphate. Most preferably the anionic surfactant is linear alkylbenzene sulphonate. The linear alkyl benzene sulphonate may be present as sodium, potassium, or alkaline earth metal salts, or mixtures of these salts. Sodium salts are generally preferred.

The anionic surfactant is present in an amount of from 5 to 20 wt %, preferably from 10 to 15 wt %, based on the weight of the total composition.

The nonionic surfactant (ii)

Nonionic surfactants are also well-known to those skilled in the art. Many such nonionic surfactants 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.

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

Non-ethoxylated non-ionic surfactants include alkylpolyglycosides, glycerol monoethers. and polyhydroxyamides (glucamides).

It is preferred that the level of nonionic surfactant is from 1 to 10 wt%, preferably from 1 to 5 wt%, based on the weight of the total composition.

The detergency builder (iii)

The compositions of the invention may contain a detergency builder. Preferably the builder is present in an amount of from 10 to 30 wt % based on the weight of the total composition. More preferably the amount of builder is from 15 to 25 wt %.

The builder may be selected from strong builders such as phosphate builders, aluminosilicate builders and mixtures thereof. One or more weak builders such as calcite/carbonate, beryllium/carbonate, citrate or polymer builders may be additionally or alternatively present. However, it is preferred that the detergency builder is an aluminosilicate builder.

Phosphate builders may for example be selected from alkali metal, preferably sodium, pyrophosphate, orthophosphate and tripolyphosphate, and mixtures thereof.

Aluminosilicate builders may be, for example, selected from one or more crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel),

amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst).

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: 0.8-1.5 Na_2O. Al_2O_3. 0.8-6 SiO_2.

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite is preferably the commercially available zeolite 4A now widely used in laundry detergent powders. However, the zeolite builder incorporated in the compositions of the invention may also be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to

1.33, and more preferably within the range of from 0.90 to 1.20.

Zeolite MAP may be used, having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

The inorganic non-builder salt (iv)

The compositions of the invention may contain from 40 to 60 wt % of an inorganic non-builder salt, preferably from 45 to 55 wt %, based on the weight of the total composition.

These are included in order to increase detergency and ease processing.

Suitable inorganic non-builder salts include alkaline agents such as alkali metal, preferably sodium, carbonates, sulphates, silicates, metasilicates as independent salts or as double salts etc, which for the purposes of this specification, are not to be considered as builders.

Preferably the inorganic non-builder salt (iv) is selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sulphate, burkeite, sodium silicate and mixtures thereof.

A preferred alkali metal carbonate is sodium carbonate. The sodium carbonate may be present in a dense or light form. Sodium carbonate may suitably be present in amounts ranging

from 1 to 30 wt %, preferably from 10 to 25 wt %, based on the weight of the total composition.

However, compositions containing little or no sodium carbonate are also within the scope of the invention.

Sodium sulphate may suitably be present in an amount of from 10 to 50 wt %, preferably from 20 to 40 wt %, based on the weight of the total composition. Compositions containing little or none of the independent solid sodium sulphate are also within the scope of the invention.

The composition according to the invention preferably may comprise sodium carbonate and sodium sulphate, wherein the total amount of sodium carbonate and sodium sulphate is from 20 to 80 wt %, and preferably from 40 to 60 wt %, based on the weight of the total composition.

The composition according to the invention may comprise a ratio of sodium carbonate to sodium sulphate within the range of from 0.1:1 to 5:1, preferably 0.5:1 to 1.5:1, most preferably from 1:1.

Burkeite may suitably be present in an amount of from 20 to 80 wt %, preferably from 40 to 60 wt %, based on the weight of the total composition. Compositions containing burkeite as the only non-builder salt are within the scope of the invention, as are compositions containing little or no burkeite. Burkeite is of the formula $Na_2CO_3.2Na_2SO_4$, and this is different from sodium carbonate and sodium sulphate as

previously described as it is a double salt comprised of the combination of sodium carbonate and sodium sulphate.

In addition to the inorganic non-builder salts listed above the detergent composition according to the invention may further comprise sodium silicate, the sodium silicate may be present at levels of from 0.5 to 10 wt %, preferably from 1 to 5 wt %, based on the weight of the total composition. Preferably the total amount of sodium carbonate, sodium sulphate, burkeite and sodium silicate is from 25 to 85 wt %, most preferably from 45 to 80 wt %, based on the weight of the total composition.

Further suitable inorganic non-builder salts include sodium sesquicarbonate, sodium chloride, calcium chloride and magnesium chloride.

The polycarboxylate polymer (v)

The compositions of the invention may contain a polycarboxylate polymer. These include homopolymers and copolymers of acrylic acid, maleic acid and acrylic/maleic acids. The publication 'Polymeric Dispersing Agents, Sokalan', a printed publication of BASF Aktiengesellschaft, D-6700 Ludwigshaven, Germany describes organic polymers which are useful.

Preferably the polycarboxylate polymer is selected from the group consisting of sodium polyacrylate, sodium acrylate maleate and mixtures thereof.

Suitable polymers are generally at least partially neutralised in the form of their alkali metal ammonium or other conventional cation salts. The alkali metal especially sodium salts are most preferred. The molecular weight of such polymers can vary over a wide range, it is preferably from 1,000 to 500,000, more preferably from 2,000 to 250,000, and most preferably from 3,000 to 100,000.

Unsaturated monomeric acids that can be polymerised to form suitable polymeric polymeric polycarboxylates include maleic acid (or maleic anhydride), fumaric acid itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence of monomeric segments containing no carboxylate groups such as vinylmethyl ether, styrene, ethylene etc is suitable. Another suitable polymer is copolymers of acrylamide. Also acrylate/maleate copolymers. Other suitable copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are also suitable.

Examples of suitable polymers include ISP Gantrez AN 119 maleic polyvinyl ether anhydride, also Ciba Versicol E5 polyacrylate, and Sokalan CP5, ex BASF polyacrylate, namely maleic acid-acrylic acid copolymer, with a sodium salt. Especially preferred is Sokalan PA 40, ex BASF a sodium polyacrylate with a molecular weight of 30,000.

The laundry detergent composition may contain from 0.5 to 3 wt%, preferably from 1 to 2 wt%, of a polycarboxylate polymer, based on the weight of the total composition.

The other optional detergent ingredients (vi)

As well as the surfactants and builders discussed above, the compositions may optionally contain other active ingredients to enhance performance and properties.

The detergent composition may further comprise one or more additional surfactants in an amount of from 0 to 50 wt %, and preferably from 0 to 10 wt %. Additional surfactants or detergent active compounds may comprise other nonionics such as alkylpolyglucosides, polyhydroxyamides (glucamide), and glycerol monoethers. Also amphoteric surfactants and/or zwitterionic surfactants may be present. Preferred amphoteric surfactants are amine oxides, for example coco dimethyl amine oxide. Preferred zwitterionic surfactants are betaines, and especially amidobetaines. Preferred betaines are C8 to C18 alkyl amidoalkyl betaines, for example coco amido betaine. These may be included as co-surfactants. 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 detergent compositions of the invention may comprise one or more optional ingredients selected from soap, peroxyacid and persalt bleaches, bleach activators, air bleach catalysts, sequestrants, cellulose ethers and esters, cellulosic polymers, other antiredeposition agents, sodium chloride, calcium chloride, sodium bicarbonate, other inorganic salts, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam

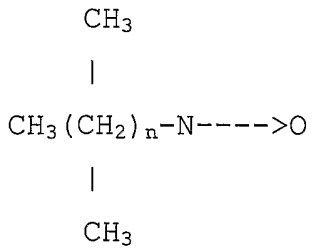
controllers, foam boosters, acrylic and acrylic/maleic polymers, proteases, lipases, cellulases, amylases, other detergent enzymes, citric acid, soil release polymers, silicone, fabric conditioning compounds, coloured speckles such as blue speckles, and perfume. This list is not intended to be exhaustive.

It is preferred that the compositions do not contain bleach.

Yet other materials that may be present in detergent compositions of the invention lather control agents or lather boosters as appropriate; dyes and decoupling polymers.

Suitable lather boosters for use in the present invention include cocamidopropyl betaine (CAPB), cocomonoethanolamide (CMEA) and amine oxides.

Preferred amine oxides are of the general form:-



where, n is from 7 to 17.

A suitable amine oxide is Admox (Trademark) 12, supplied by Albemarle.

Enzymes

The detergent compositions may also contain one or more enzymes. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

In particulate detergent compositions, detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt %. However, any suitable physical form of enzyme may be used in any effective amount.

Other

Antiredeposition agents, for example cellulose esters and ethers, for example sodium carboxymethyl cellulose, may also be present. An example of a commercially available sodium carboxymethyl cellulose is Finnfix BDA (trademark), ex Noviant.

The compositions may also contain soil release polymers, for example sulphonated and unsulphonated PET/POET polymers, both end-capped and non-end-capped, and polyethylene glycol/polyvinyl alcohol graft copolymers such as Sokalan (Trade Mark) HP22. Especially preferred soil release polymers are the sulphonated non-end-capped polyesters described and claimed in WO 95 32997A (Rhodia Chimie).

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate

copolymer, or sodium silicate. One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt %, based on the weight of the total composition.

Form of the composition

The compositions of the invention may be of any suitable physical form, for example, particulates (powders, granules, tablets), liquids, pastes, gels or bars. However, it is preferred that the compositions are in particulate form, that is, in the form of powders, granules or tablets, especially powders.

According to one especially preferred embodiment of the invention, the detergent composition is in particulate form, preferably powder form. Preferably, such a powder has a bulk density from 400 to 480 g/l, more preferably from 400 to 460 g/l.

The composition can be formulated for use as hand wash or machine wash detergents.

Preparation of the compositions

The compositions of the invention may be prepared by any suitable process.

Powders of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally postdosing (dry-mixing) further ingredients. "Concentrated" or "compact"

powders may be prepared by mixing and granulating processes, for example, using a high-speed mixer/granulator, or other non-tower processes.

Tablets may be prepared by compacting powders, especially "concentrated" powders.

Liquid detergent compositions may be prepared by admixing the essential and optional ingredients in any desired order to provide compositions containing the ingredients in the requisite concentrations.

The choice of processing route may be in part dictated by the stability or heat-sensitivity of the surfactants involved, and the form in which they are available.

In all cases, ingredients such as the granular detergent composition, enzymes, bleach ingredients, sequestrants, polymers and perfumes may be added separately.

Use of the compositions

The laundry detergent compositions described above are particularly useful for removing oily-stains from a fabric. Thus, the invention provides use of a laundry detergent composition as defined above to facilitate oily-stain removal from a fabric.

The invention also provides a process for laundering textile fabrics, especially cotton, by machine or hand, which includes the step of immersing the fabrics in a wash liquor

comprising water in which a laundry detergent composition as previously defined is dissolved or dispersed. This process shows improved stain removal across a range of fabrics and water hardnesses. It is particularly effective when the wash liquor is at ambient temperature (about 20-30°C).

Tri-surfactant systems comprising a linear alkyl benzene sulphonate or a salt thereof, an alkyl ether sulphate or a salt thereof, and an alkoxylated alcohol (especially an ethoxylated alcohol) have been found to be particularly effective in improving oily-stain removal performance in a zeolite-built laundry detergent composition as previously described.

Examples

The invention will now be explained in more detail by reference to the following non-limiting examples, in which parts and percentages are by weight.

Table A: Materials used in the examples

Chemical	Trade Name
Acrylic Acid/Maleic Acid Copolymer Sodium Salt	Sokalan CP-5 or Acusol 479N
NI Alcohol Ethoxylate (9EO)	AEO-9
Distyryl Biphenyl (DSBP)	Tinopal CBS-X , CF-351

Bis(triazinylamino)stilbene disulphonic acid derivative	Tinopal DMA-X or Optiblanc
Sodium carbonate	Soda Ash
Protease	Savinase 12TXT
Perfume	YaoMing 114R

Example 1

Preparation of SLES.1EO granules

Granular detergent compositions were prepared according to Table 1 below using the method set out in the description.

Table 1

Component	Weight %	
	IA	IB
SLES.1EO	35.0	35.0
Alkaline Sodium Silicate	3.0	2.0
Zeolite 4A	59.0	57.0
Water	to 100	to 100

The resultant granules were white and free-flowing.

Example 2

Preparation of Laundry Detergent Compositions

Laundry detergent compositions were prepared according to Table 2 below. Example A is a comparative example (i.e. not according to the invention) and Example 2 is in accordance with the invention.

Component	Weight %	
	A	2
Sodium linear alkylbenzene sulphonate	16.00	13.00
NDOM	0.31	0.13
NI AEO-9 (C12,14)	2.00	2.00
Sodium Carbonate	14.00	20.00
Sodium Bicarbonate	2.00	-
Sodium Silicate	2.00	1.83
Sodium Carboxy Methyl Cellulose	0.70	0.70
4A Zeolite	26.00	19.80
Acrylic Acid/Maleic Acid Copolymer, Na salt	1.50	1.50
Bis(triazinylamino)stilbene disulphonic acid derivate	0.10	0.08
DSBP	0.04	0.04

Protease	0.25	0.25
Perfume	0.13	0.17
Blue Speckle	0.60	0.60
Sodium sulphate	31.37	31.19
SLES.1EO granules	-	5.71
Water	3.00	3.00

Example 3

Evaluation of laundry compositions: Removal of soil from fabric (Tergotometer test)

The tergotometer was set up in accordance with standard operating procedure. Each pot was filled with an appropriate amount of demineralised water and calcium chloride solution for the required hardness and allowed to equilibrate to the test temperature. Test cloths were prepared with appropriate stains. The test cloths used were cotton or polycotton and 8cm x 8cm in size. Once the test cloths had been prepared and the tergotometer had equilibrated, the test compositions described in Table 2 were added to the tergotometer pots and mixed for 1 minute to give 2g/l solutions of the test compositions. The test cloths were then added and washed for 15 minutes (Liquor: Cloth ratio = 50:1). 4 replicates were carried out per test. After 15 minutes had elapsed, the test cloths were removed and rinsed in the same water hardness as used in the test. The cloths were then removed, any excess water was squeezed out and the cloths were then rinsed 3 times in a further litre of water of the correct hardness (10 seconds

for each rinse). The cloths were then dried by line drying in a cabinet at 40°C. The reflectance of the cloths at 460nm was measured before washing and after washing using a Macbeth Coloreye 7000 Spectrophotometer. The difference in the reflectance values at 460nm before and after washing for each test cloth was then calculated to give the Delta R460 value. The results are set out in Table 3 below:-

Table 3

Water Hardness	Temperature	Test cloth	Delta R460	
			Ex A	Ex 2
300 ppm (Ca:Mg mol.ratio =6:4)	25°C	AS-12	20.64	22.70
		WFK-10D	20.43	22.64
		AS-12	21.14	22.80
		WFK-10D	19.23	21.63
		Artificial sebum/ Polycotton	11.03	14.57

Test Cloth AS-12 is a cotton cloth stained with pigment and oil having a low milk content.

Test Cloth WFK-10D is a cotton cloth stained with soil/sebum

It will be apparent from the above test results that the test composition of Example 2 (in accordance with the invention) exhibited better stain removal properties than the test composition of Comparative Example A.

Example 4

Evaluation of laundry compositions: Removal of soil from fabrics (Real Machine Wash)

Test cloths were prepared with appropriate stains and washed in a top loading washing machine (Little Swan) under the following conditions:-

Wash dosage: 1g/litre (sample solution)
Stain aging time: 4 days
Liquor:cloth ratio=20:1 (8 stain pieces/white sheet, 8 stain pieces/white sheet, ballast = 1.75 kg)
Wash program: Standard (Disperse for 1 minute, wash for 12 minutes, rinse two times for 9 minutes each, dry in a cabinet at 40°C)
Replication: 4

The reflectance at 460nm wavelength (R460 value) was measured for AS-12 test cloth, and the E(CMC) value was measured for other test cloths except AS-12 using a Macbeth Coloreye 7000 Spectrophotometer before and after washing. The difference between the R460 or E(CMC) values before and after washing is marked as Delta R460 or Delta E for performance evaluation.

The results are set out in Table 4A below:-

Table 4A

Water hardness	Temperature	Test cloth	Measurement (Delta R460 or Delta E)	
			Ex A	EX 2
Shanghai Tap Water	25°C	Bean oil/cotton	16.31	17.93
		Artificial sebum/cotton	9.82	13.06
		Chocolate/cotton	36.02	37.78
		Chocolate/polycotton	32.85	35.67
		Blood/cotton	37.62	37.94
		Blood/polycotton	33.24	33.52
		Lipstick/cotton	7.57	9.83
		Mud/polycotton	27.29	28.86
		AS-12	17.59	18.33

The above test was then repeated at a lower temperature. The only other variation in the test procedure was that a liquor:cloth ratio of 20:1 was used again but with 15 stain pieces/white sheet, 15 stain pieces/white sheet and a ballast of 1.75 kg.

The results are set out in Table 4B below:-

Table 4B

Water hardness	Temperature	Test cloth	Measurement (Delta R460 or Delta E)	
			Ex A	EX 2

Shanghai Tap Water	9°C	Peanut oil (fried) knitted cotton	5.11	5.60
		Peanut oil (raw)/knitted cotton	4.02	4.65
		Rape oil (fried) knitted cotton	3.95	4.50
		Rape oil (raw)/knitted cotton	3.64	4.43
		Vegetable oil (fried) knitted cotton	1.63	2.34
		Bean oil/knitted cotton	5.56	6.28
		Chocolate/woven cotton	37.44	37.97
		Chocolate/woven polycotton	28.73	29.26
		Mud/woven cotton	28.62	29.99
		Mud/woven polycotton	28.60	29.52
		Chilli oil/woven cotton	18.12	19.19
		Chilli oil/woven polycotton	11.59	12.98
		Gravy oil/woven cotton	35.45	37.91
		Gravy oil/woven polycotton	42.08	44.99
		AS-12	10.2	12.26

It will be apparent from the above test results that the test composition of Example 2 exhibits better stain removal properties than the test composition of Comparative Example A, particularly on oily stains.

Example 5

Evaluation of laundry compositions: Removal of soil from fabrics (Real Handwash)

Test cloths were prepared with appropriate stains and the stains were aged for 4 days. Water of the required hardness was prepared and placed in a wash basin. The test formulation was then added to the water in the basin and dispersed for 1 minute to give a 3g/l sample solution. The test cloth and ballast load were then placed in the basin and soaked for 15 minutes. The liquor:cloth ratio was 5:1 (26 stain pieces per wash basin; ballast of 400g white cotton). Each monitor was then rubbed by hand for 10 seconds followed by dipping the cloth in the wash solution and this cycle was repeated 3 times. The test cloth was then rinsed 3 times in water of the appropriate hardness (10 seconds for each rinse) and dried in a cabinet at 40°C. 4 replicates were carried out. The test cloths were then assessed for stain removal.

The reflectance at 460nm wavelength (R460 value) was measured for AS-12 test cloth, and the E(CMC) value was measured for other test cloths except AS-12 using a Macbeth Coloreye 7000 Spectrophotometer before and after washing. The difference between the R460 or E(CMC) values before and after washing is marked as Delta R460 or Delta E for performance evaluation.

The results are set out in Table 5A below:-

Table 5A

Water hardness	Temperature	Test cloth	Measurement (Delta R460 or Delta E)	
			Ex A	EX 2
300ppm (Ca:Mg mol ratio= 6:4)	25°C	Bean Oil/cotton	11.58	17.98
		Bean oil/polycotton	14.10	14.78
		Artificial sebum/cotton	24.94	34.84
		Artificial sebum/polycotton	12.63	21.19
		Chocolate/cotton	25.74	35.48
		Chocolate/polycotton	37.5	37.98
		Blood/cotton	33.74	34.03
		Blood/polycotton	33.86	34.17
		Lipstick/cotton	12.58	16.97
		Lipstick/polycotton	9.88	9.93
		Mud/cotton	30.91	31.86
		AS-12	23.30	27.72
100 ppm (Ca:Mg mol ratio= 6:4)	25°C	Artificial sebum/cotton	32.54	34.61
		Artificial sebum/polycotton	27.6	28.38
		Chocolate/cotton	25.11	25.58
		Chocolate/polycotton	41.68	42.79
		Blood/cotton	36.19	36.38
		Lipstick/polycotton	12.98	15.12
		Mud/cotton	31.22	32.09
		Mud/polycotton	33.12	33.69
		AS-12	30.71	32.66

The above handwash test was then repeated except that the liquor: cloth ratio was 6:1 (30 stain pieces per wash basin and ballast of 400g white cotton), the test formulation was

dispersed for 2 minutes and the soaking step was omitted. 3 replicates were carried out and other variations in the test conditions are listed in Table 5B below:-

Table 5B

Water hardness	Temperature	Test cloth	Measurement (Delta R460 or Delta E)	
			Ex A	EX 2
Shanghai Tap Water	25°C	Peanut oil (fried)knitted cotton	2.67	2.69
		Peanut oil (raw)/knitted cotton	2.51	2.96
		Rape oil (fried)knitted cotton	2.37	3.06
		Rape oil (raw)/knitted cotton	2.41	3.01
		Vegetable oil (fried)knitted cotton	2.13	2.30
		Bean oil/knitted cotton	3.47	4.25
		Chocolate/woven cotton	30.6	30.76
		Chocolate/woven polycotton	2.59	3.07
		Mud/woven cotton	31.88	32.78
		Mud/woven polycotton	32.67	33.72
		Chilli oil/woven cotton	7.86	8.92
		Chilli oil/woven polycotton	2.59	3.07
		Gravy oil/woven cotton	31.88	33.11
		Gravy oil/woven polycotton	32.33	33.73
		AS-12	19.53	22.11

It will be apparent from the above test results that the test composition of Example 2 exhibits better stain removal properties than the test composition of Comparative Example A, particularly on oily stains.

CLAIMS

1. A granular detergent composition which comprises
(i) from 20 to 50 wt %, preferably from 30 to 40 wt %, of an alkyl ether sulphate,
(ii) from 40 to 75 wt %, preferably from 50 to 65 wt %, of a solid carrier,
(iii) from 1 to 10 wt %, preferably from 1 to 5 wt %, of an inorganic non-builder salt, and
(iv) optionally water to 100 wt %.

2. A granular detergent composition according to claim 1, in which the alkyl ether sulphate is a C_{11-14} alkyl ether sulphate.

3. A granular detergent composition according to claim 1 or claim 2, in which the alkyl ether sulphate is a C_{12-13} alkyl ether sulphate

4. A granular detergent composition according to any one of the preceding claims, in which the alkyl ether sulphate is sodium lauryl ether sulphate (SLES).

5. A granular detergent composition according to any one of the preceding claims in which the alkyl ether sulphate has a degree of ethoxylation from 0 to 9, preferably 0 to 2.

6. A granular detergent composition according to any one of the preceding claims in which the alkyl ether sulphate is SLES.1EO.

7. A granular detergent composition according to any one of the preceding claims in which the solid carrier is an aluminosilicate.

8. A granular detergent composition according to any one of the preceding claims, in which the solid carrier is a zeolite, preferably 4A Zeolite.

9. A granular detergent composition according to any one of the preceding claims in which the inorganic non-builder salt is an alkali metal silicate, preferably alkaline sodium silicate.

10. A granular detergent composition according to any one of the preceding claims in which the granules have a main particle size in the range of 150-1000μm, preferably 500-1000μm.

11. A method for preparing a granular detergent composition as defined in any one of the preceding claims, which comprises mixing the alkyl ether sulphate, solid carrier, inorganic non-builder salt and any water in a suitable mixer; extruding the mixture to form granules; drying the granules; and screening the dried granules to obtain granules of a specific particle size.

12. A method according to claim 11, in which the suitable mixer is a ribbon mixer, preferably a horizontal ribbon mixer.

13. A method according to claim 11 or claim 12, in which the mixture is extruded by pressing the mixture through a sieve to form noodle granules.

14. A method according to any one of claims 11 to 13, in which the granules are dried by hot air in a fluid bed.

15. A method according to claim 14, in which the hot air has a temperature of about 70 to 90°C, preferably about 75 to 85°C.

16. A method according to any one of claims 11 to 15, in which the dried granules are screened by use of a sieve.

17. A laundry detergent composition which comprises from 1 to 20 wt%, preferably from 1 to 10 wt%, of a granular detergent composition as defined in any one of claims 1 to 10.

18. A laundry detergent composition according to claim 17 which further comprises

(i) from 5 to 25 wt%, preferably from 10 to 15 wt%, of an anionic surfactant,

(ii) from 1 to 10 wt%, preferably from 1 to 5 wt%, of a non-ionic surfactant,

(iii) from 10 to 30 wt%, preferably from 15 to 25 wt%, of a detergency builder,

(iv) from 40 to 60 wt%, preferably from 45 to 55 wt%, of an inorganic non-builder salt,

(v) from 0.5 to 3 wt%, preferably from 1 to 2 wt%, of a polycarboxylate polymer, and

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

19. A laundry detergent composition according to claim 17 or claim 18 which is in powder form.

20. A laundry detergent composition according to claim 19 which has a bulk density from 400 to 480 g/l, preferably from 400 to 460 g/l.

21. A process for laundering textile fabrics by machine or hand, which includes the step of immersing the fabrics in a wash liquor comprising water in which a laundry detergent composition according to any one of claims 17 to 20 is dissolved or dispersed.

22. Use of a laundry detergent composition according to any one of claims 17 to 20 to facilitate oily-stain removal from a fabric.

23. Use of a surfactant system to improve oily-stain removal performance in a zeolite-built laundry detergent composition characterised in that the surfactant system comprises:

(i) a linear alkyl benzene sulphonate or a salt thereof,

(ii) an alkyl ether sulphate or a salt thereof, and

(iii) an alkoxylated alcohol.

24. Use according to claim 23, in which the zeolite-built laundry detergent composition is a composition according to any one of claims 17 to 20.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/000924

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D1/29 C11D1/83 C11D17/06 C11D11/00 C11D3/08
C11D3/12 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/31223 A (UNILEVER PLC; UNILEVER NV; HINDUSTAN LEVER LIMITED) 2 June 2000 (2000-06-02)	1-10, 17-24
Y	claims examples	11-16
X	EP 0 623 593 A (SUED-CHEMIE AG; DALLI-WERKE WAESCHE- UND KOERPERPFLEGE GMBH & CO. KG) 9 November 1994 (1994-11-09) claims 1-4,9-15	1-10,17, 21,22
Y	examples 1,2,5-7 page 5, line 3 - line 26 page 6, line 47 - line 58	11-16

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/000924

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	examples 3,5 page 2, line 1 - line 14 page 12, paragraph 1	11-16
A	EP 0 651 050 A (THE PROCTER & GAMBLE COMPANY) 3 May 1995 (1995-05-03) claims examples	1-24
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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