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(54) **DETERGENT COMPOSITION**

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COMPOSITION DETERGENTE

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Description

TECHNICAL FIELD

The present invention relates to liquid detergent compositions, in particular to aqueous lamellar structured liquid detergent compositions comprising non-ionic surfactant material.

BACKGROUND & PRIOR ART

Liquid detergent compositions are well-known in the art and offer several advantages over solid compositions. For example, liquid compositions are easier to measure, to dispense and to dissolve into a laundering liquor. Further, liquid compositions give more confidence to the consumer of being safer and less harsh to the washed or laundered textile than solid compositions. This may be the reasons why heavy duty and light duty built laundry liquid detergent products are gaining in popularity ever since their introduction on the market at the expense of powdered detergent products.

Two general and separate classes of liquids compositions, isotropic and structured liquids, are known in the art. Isotropic liquids are liquids in which all ingredients are dissolved and, contrary to structured liquids, there is no structure present in isotropic liquid.

Structured liquids are well-known in the art. They can either be internally structured, whereby the structure is formed by primary ingredients, preferably by surfactant material, and/or by providing a three dimensional matrix structure using secondary additives, preferably polymers and/or silicate material. Structuring may be brought about to endow properties such as consumer preferred flow properties and/or turbid appearance. Many structured liquids are also capable of suspending particulate solids, such as particles of clay that may be used to provide a fabric-softening effect to fabrics. Examples of structured liquids without suspended solids are given in US-A-4,244,840, whilst examples where solid particles are suspended are disclosed in EP-A-160 342; EP-A-38 101; EP-A-140 452 and also in the aforementioned US-A-4,244,840.

EP-A-0,225,142 discloses aqueous liquid detergent compositions comprising surfactant and builder material and a clay material which has low swellability in sodium tripolyphosphate solutions and high swellability in water. There is no direct disclosure of the use of clay material in structured compositions. Liquids according to this reference may be or may become viscous.

EP-A-0,291,261 discloses aqueous structured liquid detergent composition comprising a fabric softening clay material, wherein the viscosity of the liquid is reduced by incorporation of a non-peptising/non-building electrolyte. Examples of such electrolytes are formate, acetate, halide and sulphate.

WO 91/08281 discloses aqueous structured liquid detergent compositions comprising a dispersion of lamellar droplets of surfactant material materials in an aqueous continuous phase and clay material wherein the viscosity and stability of the liquid is improved by incorporation of a deflocculating polymer.

EP-A-0,580,245 discloses aqueous liquid detergent compositions comprising surfactants, electrolyte and clay material. The liquids are said to have a polymer structure. The document does however not disclose liquids with a low molar ratio of sodium:potassium.

EP 50887 discloses aqueous liquids comprising electrolyte, surfactant, clay and high molar ratios of sodium:potassium ions.

EP 4111 discloses aqueous liquids comprising surfactant, electrolyte and clay. The liquids do not comprise a lamellar structure.

EP 3625 discloses aqueous liquids comprising surfactant, electrolyte and clay. The liquids are stablised by using a suspending agent.

EP 541,203 discloses aqueous liquids comprising surfactant, electrolyte and clay. The liquids are structured by way of polymeric thickening agents such as Carbopol.

EP 75813 discloses aqueous liquids comprising surfactant, electrolyte and clay. The liquids are structured by a thickening agent.

Incorporation of the particles of clay material in liquids of the art may however still lead to high viscosity and/or instability of the liquid detergent composition. This is especially true for compositions that are structured, i.e. for liquids that are externally structured (e.g. by using polymers or silicate), and in particular, for liquids that have an internal structure (e.g. by using surfactant material).

We have now found that the problems of the art can be overcome by careful selection of the salts that are present in the clay containing liquid detergent compositions. In particular we have found that swelling and/or delamination of the clay material in liquid detergents is considerably reduced, when potassium ions are present in liquids.

DEFINITION OF THE INVENTION

Therefore, the present invention relates to an aqueous lamellar structured liquid detergent composition comprising nonionic surfactant material, electrolyte material and suspended clay particles, characterised in that the composition further comprises sodium and potassium ions in a molar ratio of 10:1 or lower.

Preferably, the molar ratio between Na^+ and K^+ in the liquid according to the invention is 10:1 or lower, e.g. 9:1 or lower, more preferably 8:1 or lower, most preferably 5:1 or lower, or even 3:1 or lower or in particular 1.5:1 or lower. Suitable ratios are 1.3:1 or lower, 1:1 or lower and 0.8:1 or lower. Preferably, the ratio is 1:20 or higher, more preferably 1:5 or higher, most preferably 1:3 or higher.

Preferably the K^+ ions are added in the form of a soluble salt. Examples of such salts are citrate, hydroxide, (bi) carbonate, anionic surfactant material, nitrate, sulphate and chloride.

Althought it is possible to pretreat the clay with a K^+ before incorporation in compositions according to the present invention, it is preferred to add the clay along with the K^+ source. This is not only the most straightforward route, but incorporation of K^+-clays may sometimes have adverse effects on the viscosity of the liquid.

For the purpose of the invention, the Na^+ and K^+ concentrations in the structured liquid are defined as the concentrations that are determined in the liquid phase of the product and also include the Na^+ and K^+ ions that are present in solid materials that are capable of contributing ions to the structured liquid, e.g. zeolite. Inert solid materials, which do not contribute to ion-exchange are not included when determining the Na^+ and K^+ concentrations.

CLAY MATERIAL

The clay material according to the present invention is suspended in particle form in the structured liquid.

Clays of interest in the present invention are swelling types, which expand and delaminate in liquid media. These clays belong to the group of phyllosilicates and are three-layer sheet type crystalline materials. The sheet structures are composed of three layer arrangements of tetrahedral silica, octahedral alumina and tetrahedral silica. The central layer may be dioctahedral or triotahedral and the three layer sheet structures are separated by an interlamellar space.

Clays are defined as crystalline and amorphous hydrated silicates of Al, Mg Li and Fe. They comprise fine colloidal particles. The following key features distinguish the different varieties on:

a) chemical composition; and

b) the degree of isomorphic substitution (replacement of one framework ion with another of similar size, usually of different valence).

Point b) offers the opportunity for a permanent charge on the lattice which must be balanced by cations present in close proximity. These features can be clearly illustrated with reference to talc and hectorite (magnesium silicates) and pyrophyllite and montmorillonite (aluminosilicates); details of which are given in table 1:

TABLE 1

Clay	Isomorphic substitution	Formula
Talc	NO	$Mg_3\ Si_4\ O_{10}\ (OH)_2$
Hectorite	YES	$(M+)_a\ (Mg)_{6-a}\ (Li)_a\ Si_8\ O_{20}\ (OH)_4$
Pyrophyllite	NO	$Al_2\ Si_4\ O_{10}\ (OH)_2$
Montmorillonite	YES	$(M+)_{..}(Al)_{4-a}\ (Mg)_a\ Si_8\ O_{20}\ (OH)_4$

In the table M+ refers to the charge balancing cations introduced as a result of the isomorphic substitution. The degree of isomorphic substitution determines the magnitude of the layer charge, a crucial factor in the swelling of clays.

The layer structure has many variants in nature. For example the central octahedral layer may have the two aluminium ions (Al^{3+}) (dioctahedral) replaced by three magnesium ions (Mg^{2+}) (trioctahedral) or the octahedral layer may be partially occupied by the substitution of one Al^{3+} for one Mg^{2+} (dioctahedral) or one Mg^{2+} for one Li^+ (trioctahedral) resulting in a residual surplus of negative charge in the structure. A residual surplus of negative charge can also arise when silicon ions (Si^{4+}) in the tetrahedra layer are replaced by aluminium ions (Al^{3+}).

The surplus of negative charge requires the present of balancing cations which are located in the interlamellar space between the sheet structures A measure of the degree of the surplus charge is given by the number of exchangeable cations, as reflected by the cation exchange capacity (CEC) of the pure mineral. The CEC of a mineral is directly related to the lattice charge deficiency of the mineral.

This can be further explained by general representation of clays useful in the present invention which fall into the formulae:

$$(Si_{4-y}\ Al_y)\ (M^{III}{}_a\ N^{II}{}_b)\ O_{10}\ (OH)_2\ X^{n+}{}_{(y+b)/n}\ \text{(dioctahedral clays)}$$

or:

$$(Si_{4-y}\ Al_y)\ (N^{II}{}_a\ L^{I}{}_b)\ O_{10}\ (OH)_2\ X^{n+}{}_{(y+b)/n}\ \text{(trioctahedral clays)}$$

Where X^{n+} is a balancing exchangeable cation which can be univalent or divalent;

y + b is the lattice charge deficiency of the mineral per half unit cell;
M^{III} is a trivalent metal ion e.g. Al^{3+}, Fe^{3+} and Cr^{3+};
N^{II} is a divalent metal ion e.g. Mg^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+};
L^{II} is a univalent metal ion e.g. Li^{+};
y is zero or a positive number less than four; and

a and b are separately or together zero or positive numbers.

CEC measurements indirectly determine the number of $X^{n+}{}_{y+b/n}$ present in 100g and quote these as meg.

The value of y+b (the lattice charge deficiency) in gram equivalents per half unit cell is therefore directly related to CEC.

Swelling is the process in which solvent molecules penetrate the inter layer space between individual crystals, and occurs very readily in clays containing exchangeable cations such as hectorites and montmorillonites. The factors which most influence the swelling behaviour is aqueous suspension are:

i) the origin of the layer charge - ie. whether the substitution is in the octahedral (Mg or Al) layer or the tetrahedral (Si) layer;
ii) the magnitude of the layer charge; and
iii) the identity of the inter layer cation.

Point i) is important because substitution in the tetrahedral layer creates a localised charge and in the octahedral layer a delocalised charge. The latter interacts only weakly with water molecules.

Clays used in through the wash fabric softening are generally montmorillonites. Although it has been shown that softening performance is a function of lattice charge, the detailed mechanism of the action of clays in fabric softening is not fully understood. Both delamination (swelling) behaviour, and electrostatic forces between the clay particles and the fabric substrate are thought to govern the overall process, and both are influenced by layer charge.

Montmorillonites occur in nature with a range of layer charges (see point ii)), and optimum softening is observed with a limited number of clays of poor colour which have layer charges at the lower end of the range. The lattice charge of clays can, however, be modified by chemical treatment. Controlled incorporation of Li^{+} cations in the crystal lattice (by ion exchange/calcination) is described in EP-A-0,401,047 (Unilever) and leads to an improvement in the performance of the clay through charge reduction.

Layer charge reduction of montmorillonite requires neutralisation of a delocalised negative charge. This is thought to be achieved when Li cations penetrate the crystal lattice upon dehydration. They are thought to move into octahedral vacancies in the aluminous region of the montmorillonite lattice. This process requires an expensive calcination step to achieve the dehydration of the Li^{+} cation before penetration into the lattice can take place.

Soil scientists recognise close association of certain cations with clay surfaces and call it cation fixation. Potassium is the most closely studied ion. Its ionic diameter closely matches the diameter of the ring of six oxygen atoms characteristic of clay crystal surfaces. Good coordination of potassium by the clay surface can therefore be reasonably expected.

Preferably the clay material is selected from Bentonite, Kaolinite, Attapulgite, Hectorite, and derivative thereof. Most preferably the clay material is a Bentonite clay.

Preferably the clay material particles in the product have an average weight particle size (D(3,2)) of at least 0.1 μm, more preferably at least 1μm, most preferably at least 5μm and preferably at most 100 μm, more preferably at most 50 μm, most preferably at most 10μm. Preferably the clay has a white colour.

Preferably the level of clay material is at least 0.5% by weight of the composition, preferably at least 1%, more

preferably at least 3%, most preferably at least 5%. Preferably the clay level is at most 20%, more preferably at most 10%, most preferably at most 8% by weight of the composition.

SURFACTANT MATERIAL

Compositions of the invention also comprise surfactant materials, preferably at a level of at least 1% by weight of the composition, more preferred at least 5% by weight, most preferred at least 10% by weight of the composition; and preferably at a level of at most 70% by weight, more preferably at most 40%, most preferably at most 35% by weight.

In the case of blends of surfactants, the precise proportions of each component which will result in lamellar structures will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids.

In the widest definition the surfactant material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they 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.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkyl oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-di-amine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Surprisingly, we have found a way to prepare low viscous aquoeus structured liquids according to the invention when the surfactant material comprises nonionic surfactant, in particular ethoxylated nonionic surfactants.

Preferably, the composition then comprises at most 25%, more preferably at most 20%, most preferably at most 15%, in particular at most 10% by weight of the total ethoxylated nonionic surfactants of long chain EO (ethylene oxide) nonionic surfactants. Long chain EO nonionic surfactants are defined as comprising 15 or more EO groups, preferably 10 or more EO groups, more preferably 8 or more EO groups per nonionic molecule. It is noted that commercially available ethoxylated nonionics always represent a nonionic mixture.

Although we do not wish to be bound by any theory, it is believed that the nonionic surfactants with a long chain of ethylene oxide groups form a complex with the clay material, in particular in the environment of concentrated liquids, in such a way that the complex tends to increase the viscosity of the structured liquid.

Preferably the level of nonionic surfactant materials is from 1 to 40 % by weight of the composition, more preferred from 2 to 20%.

Compositions of the present invention may contain synthetic anionic surfactant ingredients, which are preferably present in combination with the above mentioned nonionic materials. Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic surfactant compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glycerol ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-$_{20}$) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolysing the reaction product. The preferred anionic surfactant compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Generally the level of the above mentioned non-soap anionic surfactant materials is from 1-40 % by weight of the composition, more preferred from 2 to 25 %. It is also possible, and sometimes preferred, to include an alkali metal soap of a mono- or di-carboxylic acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, alk(en)yl succinate for example dodecyl succinate, and fatty acids derived from castor oil, rapeseed oil, groundnut oil,coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used. Preferably the level of soap in compositions of the invention is from 1-35% by weight of the com-

position, more preferred from 5-25%.

Also possible is the use of salting out resistant active materials such as for example described in EP-A-0,328,177, especially the use of alkylpolyglycoside surfactants such as for example disclosed in EP-A-0,070,074. Also alkyl mono glucosides may be used. Further, alkyl glucose ether may be used and/or polyhydroxy fatty acid amides as described in WO 92/06157, more particular the amides used in the Examples thereof.

ELECTROLYTE MATERIAL

Compositions according to the invention comprise electrolyte material, some or all of which may be builder material.

Preferably the total level of electrolyte is from 1 to 60% by weight of the composition, more preferably from 5 to 45% by weight, most preferably from 10 to 30% by weight.

Preferably the level of dissolved electrolytes is from 1 to 45% by weight of the composition, more preferably from 5 to 35% by weight, most preferably from 10 to 25% by weight.

It is noted that for the purpose of the invention, the term electrolytes including builder material.

Preferably the level of non-soap builder material is from 5 to 40 % by weight of the composition, more preferred from 5 to 25 % by weight of the composition.

Compositions according to the invention preferably contain a salting-out electrolyte that is able to bring about internal structuring of the liquid, preferably in the form of lamellar droplets of the surfactant material. Salting-out electrolyte has the meaning ascribed to in specification EP-A-0,079,646, i.e. salting-out electrolytes have a lyotropic number of less than 9.5, preferably less than 9.0. Examples are sulphate, citrate, NTA and carbonate. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included. Preferably the compositions contain from 1% to 60%, especially from 10 to 45% of salting-out electrolyte.

BUILDER MATERIAL

In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. In this context it should be noted that some surfactant materials such as for example soaps, also have builder properties.

Examples of phosphorous containing inorganic detergency builders include the water-soluble salts, especially alkali metalpyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used. It may however be preferred to minimise the amount of phosphate builders.

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

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, CMOS, tartrate mono succinate, tartrate di succinate and citric acid. Citric acids or salts thereof are preferred builder materials for use in compositions of the invention.

In the context of organic builders, it is also desirable to incorporate polymers which are only partly dissolved, in the aqueous continuous phase as described in EP-A-0,301,882. This allows a viscosity reduction (due to the polymer which is dissolved) whilst incorporating a sufficiently high amount to achieve a secondary benefit, especially building, because the part which is not dissolved does not bring about the instability that would occur if substantially all were dissolved. Typical amounts are from 0.5 to 4.5% by weight.

It is further possible to include in the compositions of the present invention, alternatively, or in addition to the partly dissolved polymer, yet another polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100 ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal to or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6000; said second polymer having a molecular weight of at least 1000. Use of such polymers is generally described in our EP-A-0,301,883. Typical levels are from 0.5 to 4.5% by weight.

DEFLOCCULATING POLYMERS

Preferably a deflocculating polymer is incorporated in liquid detergent compositions according to the present invention to further improve viscosity and stability. WO 91/06622 describes deflocculating polymers being a block copolymer consisting of alternating hydrophobic and hydrophillic groups, WO 91/06623 describes deflocculating polymers consisting of nonionic monomers and ionic monomers and GB-A-2,237,813 describes deflocculating polymers consisting of a hydrophobic backbone and one or more hydrophillic side-chains. WO 91/09109 discloses liquid detergent compositions comprising deflocculating polymers that are biodegradable. PCT Patent Application No EP/93/01882 discloses deflocculating polymer having a ketone group. Preferably deflocculating polymer are described in EP-A-0,346,995 having a hydrophillic backbone and one or more hydrophobic side-chains. In general the deflocculating polymer will be used at levels of from 0.01 to 5 % by weight of the composition, more preferably from 0.1 to 3.0, especially preferred from 0.25 to 2.0 %.

OPTIONAL INGREDIENTS

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase (Trade Mark) ex Novo), enzyme stabilizers, anti-redeposition agents, germicides and colorants. Obviously in selecting the materials other than the polymer for use in compositions of the invention, also biodegradable materials are preferred for environmental reasons.

PRODUCT FORM

As indicated, structured liquids, internally as well as externally, are well-known in the art. Some of the different kinds of liquids, that are internally structuring with surfactant material, are described in the reference H.A. Barnes, "Detergents", Ch.2. in K. Walters (Ed), "Rheometry: Industrial Applications", J. Wiley & Sons, Letchworth 1980. In general, the degree of ordering of such systems increases with increasing surfactant and/or electrolyte concentrations.

At very low concentrations of surfactant and/or electrolyte, the surfactant can exist as a molecular solution, or as a solution of spherical micelles, both of these solutions being isotropic, i.e. they are not structured.

With the addition of further surfactant and/or electrolyte structures of surfactant material may form. Various forms of such structures exists, e.g. bi-layers. They are referred to by various terms such as rod-micelles, anisotropic surfactant phase, planar lamellar structures, lamellar droplets and liquid crystalline phases. Often different workers have used different terminology to refer to the structures which are really the same. For instance, in European patent specification EP-A-0,151,884, lamellar droplets are called spherulites.

A preferred form of lamellar structures are lamellar droplets of surfactant material. The dispersed structuring phase in such liquids is generally believed to consist of an onion-like configuration comprising concentric bilayers surfactant molecules, between which water is trapped, the aqueous phase. Liquids with a lamellar droplets structure are preferred as systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties, i.e. low viscosity with stability. Such liquids have for example been described in A. Jurgens, Microstructure and Viscosity of Liquid Detergent, Tenside Surfactants Detergent 26 (1989) 222 and J.C. van de Pas, Liquid Detergents, Tenside Surfactants Detergents 28 (1991) 158.

The presence and identity of a surfactant structuring system in a liquid may be determined by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and sometimes, electron microscopy.

Externally structured liquids may provide a high viscosity, especially upon storage. Therefore, internally structured liquids are preferred over externally structured. The most preferred structured liquids are liquid detergent compositions comprising lamellar droplets of surfactant material.

Liquid compositions of the invention preferably have a viscosity of less than 2,500 mPas at 21 s-1, more preferred less than 1,500 mPas, most preferred less than 1,000 mPas and preferably higher than 100, more preferably higher than 500 mPas at 21 s-1.

Liquid compositions according to the invention are physically stable. In the context of the present invention, physical stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more than 10 %, preferably no more than 5 %, most preferred no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation.

Three common product forms in this type are liquids for heavy duty fabrics washing and liquid abrasive and general purpose cleaners.

In the first class, the suspended solid can comprise suspended solids which are substantially the same as the dissolved electrolyte, being an excess of same beyond the solubility limit. This solid is usually present as a detergency builder, i.e. to counteract the effects of calcium ion water hardness in the wash.

In the second class, the suspended solid usually comprises a particulate abrasive, insoluble in the system. In that case the electrolyte, present to contribute to the structuring of the active material in the dispersed phase, is generally different from the abrasive compounds. In certain cases, the abrasive can however comprise partially soluble salts which dissolve when the product is diluted.

In the third class, the structure is usually thickens the product to give consumer-preferred flow properties, and sometimes to suspend pigment particles.

Compositions of the first kind are described in for example our patent specification EP-A-0,038,101 whilst examples of those in the second category are described in our specification EP-A-0,140,452. Those in the third category are for example, described in US-A-4,244,840.

Preferably the compositions of the present invention are concentrated. Therefore, the water level in the liquid detergent compositions according to the present invention is preferably at least 10%, more preferably at least 20%, most preferably at least 30% by weight of the composition and preferably at most 60% by weight, more preferably at most 50%, most preferably at most 40% by weight of the composition.

Preferably the liquid compositions according to the invention have a product pH of at least 6, more preferably at least 6.5, most preferably at least 7 and preferably at most 14, more preferably at most 13, most preferably at most 12.

Preferably the pH, as provided to the wash liquor, is at least 6, more preferably at least 7.5, most preferably at least 8. Preferably the pH is at most 12, more preferably at most 10, most preferably at most 9.

METHOD OF PREPARATION

Liquid compositions of the invention may be prepared by any conventional method for the preparation of liquid detergent compositions.

However, we have found that a method that provides structured aqueous liquid detergent composition comprising clay material that show low swelling and/or delamination of the clay material.

Accordingly, a further embodiment of the present invention relates to a method of preparing a lamellar-structured aqueous liquid detergent composition comprising surfactant material, electrolyte and suspended clay material by mixing electrolytes, water, surfactant and clay material wherein the composition comprises sodium and potassium ions in a molar ratio of 10:1 or lower and the clay material is a Bentonite clay.

The preferred method for example involves the dispersing of the electrolyte ingredient together with the minor ingredients except for the temperature and pH sensitive ingredients, such as enzymes, perfumes, etc -if any- in water of elevated temperature, followed by the addition of the builder material -if any-, the surfactant material (possibly as a premix) under stirring and thereafter cooling the mixture and adding any temperature and pH sensitive minor ingredients. The deflocculating polymer may for example be added after the electrolyte ingredient or as the final ingredient. Preferably the deflocculating polymer are added prior to the formation of the lamellar structure.

It is preferred that at least 25% by weight of the total amount of clay material is added to the liquid after addition of at least 25% by weight of the total of electrolytes to further minimise swelling and/or delamination, more preferably at least 50% by weight of the total amount of clay material, most preferably at least 75% by weight, in particular 100% of clay is added after the electrolytes. Preferably the clay is added after addition of at least 50% by weight of the total of electrolytes, more preferably at least 75% by weight, most preferably 100% by weight of the total of electrolyte material.

In use, the detergent compositions of the invention will be diluted with wash water to form a wash liquor for instance for use in a washing machine. The concentration of liquid detergent composition in the wash liquor is preferably from 0.1 to 10 %, more preferred from 0.1 to 3% by weight.

The invention will be illustrated by way of the following non-limiting Examples.

EXAMPLES 1-5

Five model compositions were prepared, with Na^+, K^+ and mxitures thereof as the cation(s), with the aim of having the same viscosity in the absence of the clay material. After that similar compositions were made with the clay material to determine the effect of the clay material on the product viscosity.

The order of addition to water was citric acid, NaOH and/or KOH (for neutralising the citric acid and LAS-acid), polymer, premix of LAS-acid and Synperonic A7®, and clay (if present). The preparation was done without external heating. The temperature during processing rose to about 60°C due to release of neutralisation heat and heat of mixing.

All compositions were physically stable, i.e. showed no phase separation over a storage period of 1 month at room temperature.

The Examples clearly illustrates that incorporation of clay in compositions where K+-ions are present significantly reduces the viscosity of the composition. The clay containing compositions with K+ and K+/Na+ are readily pourable, whereas the full Na^+ composition is non-pourable.

Ingredient (parts by weight)	full Na+ composition		full K+ composition		Na+/K+ composition		Na+/K+ composition		Na+/K+ composition	
	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b
Na-LAS	31.4	31.4	---	---	20.3	20.3	26.7	26.7	26.7	26.7
K-LAS	---	---	36.1	36.1	13.5	13.5	5.9	5.9	3.8	3.8
Synperonic A7®	13.5	13.5	15.5	15.5	14.5	14.5	14.0	14.0	14.0	14.0
Na-citrate	13.8	13.8	---	---	7.7	7.7	10.9	10.9	11.8	11.8
K-citrate	---	---	12.1	12.1	5.2	5.2	2.4	2.4	1.6	1.6
Polymer (1)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
QCC 200 (2)	---	7.5	---	7.5	---	7.5	---	7.5	---	7.5
Water	41.4	41.4	36.4	36.4	38.7	38.7	40.0	40.0	40.0	40.0

Na+/K+ mole ratio	1:0	1:0	0.06:1 (3)	0.06:1 (3)	1.9:1	1.9:1	5.5:1	5.5:1	9.0:1	9.0:1
Viscosity (mPas at 21 s^{-1}) after 1 month storage	590	5120	600	1500	540	1050	570	1060	810	1160
Viscosity ratio (with clay/without clay)	8.7		2.5		1.9		1.9		1.4	

1) Deflocculating polymer with a chemical structure as polymer A11 in EP 346,995, see note 11 of Examples 10-15

2) Bentonite clay, ex Colin Stewart Minchem

3) The polymer is the source of the low level of Na+ in the formulation

EXAMPLE 6

The swellability of the clay (QC200) in electrolyte solutions representing product conditions and wash solution conditions were measured. 5% clay material was stirred for 5 minutes in a 25% citrate solution, representing the electrolyte concentration in the product. Another 5% clay material was stirred for 5 minutes in a 25% citrate solution, after which the dispersion was washed out in such a way that the citrate concentration was decreased while retaining the clay material in the dispersion. The clay dispersions were poured into a measuring cylinder. The clay sedimentation was measured after 2 weeks with the same method as described in EP-A-0,225,142. The amount of clay swelling was calculated by dividing the height of the clay sediment by the total height of the dispersion in the cylinder and multiplying that figure with 100%.

It was found that the clay swellability increased on decreasing the electrolyte concentration below a critical value. The critical value lies for the full Na^+ and K^+ containing electrolyte solutions well above the electrolyte concentration in the wash solution of about 0.1%. Below the above mentioned critical electrolyte concentration, the clay swellability rose to a value between 75 and 100%. The results of a number of these experiments are given below:

Citrate	Clay Swellability (%)	
	in 0.5% citrate	in 25% citrate
Na-citrate	>99	19
Na/K-citrate (3)	75-100	15
K-citrate	75-100	15

(3) mole ratio is 1.9:1

These experiments illustrate that clay swellability at low electrolyte concentration is hardly affected by the nature of the cation. The swelling is high, ensuring good softening benefits in the wash as demonstrated in EP-A-0,225,142.

The swelling of the clay in the high electrolyte solution is, however, lower in the K^+-containing compositions.

EXAMPLE 7

A fully formulated composition 7 was made (ingredients by weight %):

Water	balance
Silicon antifoam	0.3
Citric-acid	8.2
Glycerol	2.0
Borax	1.5
KOH	10.3
Zeolite 4A	7.5
Polymer (1)	1.0
QCC 200 (2)	7.5
Oleic-acid	4.7
LAS-acid	17.1
Synperonic A3®	4.7
Synperonic A7®	4.7
PVP	0.3
Protease	0.4
Lipase	0.2
Amylase	0.3
Perfume	0.5

The Na^+/K^+ molar ratio is 0.43:1 The viscosity is 820 mPas at 21 s^{-1}

(1) and (2) see Examples 1-5

Method of Preparation

The order of addition was according to the listed order of ingredients. During neutralisation of the surfactants the temperature rose to about 80°C. After addition of the surfactants the samples were cooled before addition of the temperature sensitive ingredients.

Both liquid detergents are showed no phase separation over 3 months when stored at temperatures between 0 and 37°C, have a low viscosity and are readily pourable. Similar compositions having the surfactants and citrate neutralised with NaOH (resulting in a full Na^+-composition) are highly viscous and not readily pourable.

EXAMPLES 8-11

Ingredient (% by weight)	8	9	10	11
LAS acid	11.67	11.67	11.67	11.67
Synperonic A7®	9.72	11.22	9.72	9.72
Oleic acid	6.80	6.80	6.80	6.80
Coconut fatty acid	4.53	4.53	4.53	4.53
Citric acid	9.0	9.0	9.0	9.0
NaOH	8.48	8.61	7.67	6.18
KOH	-	1.36	1.34	2.88
Bentonite clay	10(1)	10(2)	10(1)	10(1)
Polymer (3)	0.71	1.0	0.71	0.71
Glycerol	4.5	4.5	4.5	4.5
Borax (10aq)	3.15	3.15	3.15	3.15
Silicone antifoam	0.09	0.09	0.09	0.09
fluorescer	0.09	-	0.09	0.09
Perfume	0.32	0.32	0.32	0.32
Water	to 100	to 100	to 100	to 100
Na^+/K^+ mole ratio	1:0	9.5:1	8.7:1	3.3:1
Viscosity (mPas at 21/s)	5000	1500	1100	600

(1) Sodium Bentonite = calcium bentonite ion exchangedwith Na2CO3

(2) Calcium Bentonite

(3) Deflocculating polymer with chemical structure aspolymer A11 in EP-A-0,346,995, see note 11, Ex. 10-15

Method of Preparation

The order of addition to water was citric acid, glycerol, borax, fluorescer, caustic, clay, polymer, Synperonic A7®, fatty acids premix and LAS acid. Then after cooling from ca 50°C to 30°C or below, the silicone and perfume were added.

Material specification

LAS	Linear C12 alkyl benzene sulphonate
Synperonic A3®	C12-15 alcohol with 3 ethoxy groups, ex ICI
Synperonic A7®	C12-15 alcohol with 7 ethoxy groups, ex ICI
Zeolite 4A	Vegabond XD®, ex Sophralit
PVP	Polyvinylpyrollidone

EXAMPLES 10-15

The following formulations were prepared by adding the ingredients in the order listed to water.

	12	13	14	15	16	17
KOH	10.3	10.3	10.3	10.3	10.3	10.3
Citric acid	8.2	8.2	8.2	8.2	8.2	8.2
Glycerol	2.0	2.0	2.0	2.0	2.0	2.0
Borax	1.5	1.5	1.5	1.5	1.5	1.5
Silicone	0.3	0.3	0.3	0.3	0.3	0.3
Zeolite 4A [1]	7.5	10.0	10.0	7.5	7.5	7.5
Clay	7.5[2]	5.0[3]	6.8[3]	7.5[4]	7.5[2]	7.5[5]
Polymer [11]	1.0	1.0	1.0	1.0	1.0	1.0
LAS acid [6]	17.1	16.5	16.5	17.1	17.1	17.6
Nonionic 1 [7]	4.7	4.5	4.5	5.2	-	4.8
Nonionic 2 [8]	4.7	4.5	4.5	5.2	-	4.8
Nonionic 3 [9]	-	-	-	-	9.4	-

Oleic acid [10]	4.7	4.5	4.5	4.7	4.7	4.8
Minors	1.5	1.5	1.5	1.5	1.5	1.5
Water	<----------to 100---------->					
Na+:K+ molar ratio	0.43:1	0.52:1	0.52:1	0.42:1	0.43:1	0.43:1
Viscosity in mPa.s 21s-1 at 25°C)	820	620	940	850	1000	670

[1] Zeolite 4A Vegabond XD®, ex Sophralit

[2] QCC300 Ca Bentonite clay, ex CSM

[3] QCC200 Ca Bentonite clay, ex CSM

[4] QCC300/QPC300, Ca Bentonite clay, ex CSM

[5] Na Bentonite clay, ex CSM

[6] LAS Linear C12-15 alkyl benzene sulphonate

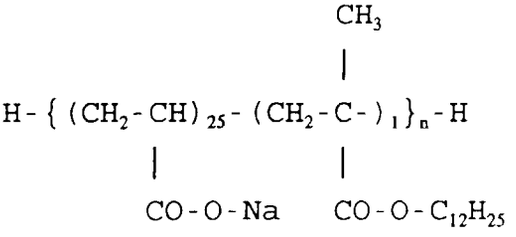
[7] Nonionic 1 C12-15 alcohol with 3 ethoxy groups, Synperonic A3®, ex ICI

[8] Nonionic 2 C12-15 alcohol with 7 ethoxy groups, Synperonic A7®, ex ICI

[9] Nonionic 3 Vista 1012-6.2®

[10] Oleic acid Priolene 6907®, ex Unichema

(11) Deflocculating polymer with chemical structure as polymer A11 in EP-A-0,346,995 having a Mw of 400 (n is about 1.5) and having the following formula:



The D50% of the clay particles in the liquids was in the region of 10 to 20 microns. The liquids of these Examples are low viscous and have good stability.

Claims

1. Aqueous lamellar non-ionic structured liquid detergent composition comprising surfactant material, electrolyte material and suspended clay particles, characterised in that the composition further comprises sodium and potassium ions in a molar ratio of 10:1 or lower.

2. A liquid detergent composition according to claim 1 characterised in that the molar ratio is 5:1 or lower.

3. A liquid detergent composition according to claims 1-2 characterised in that the K^+-ions are added in the form of (bi)carbonate, citrate, hydroxide, anionic surfactant material, nitrate, sulphate and chloride.

4. A liquid detergent composition according to claims 1-3 characterised in that the clay material is selected from Bentonite, Kaolinite, Attapulgite, Hectorite and derivative thereof.

5. A liquid detergent composition according to claims 1-4 characterised in that the viscosity of the liquid is less than 2,500 mPas at 21 s^{-1}.

6. A liquid detergent composition according to claims 1-5 characterised in that the liquid yields less than 10% by volume phase separation when stored at 25°C for 21 days from the day of preparation.

7. A liquid detergent composition according to claims 1-6 characterised in that the clay material particles have an average size of between 0.1 μm to 10 μm.

8. A liquid detergent composition according to claims 1-7 characterised in that the composition comprises at most 25% by weight of the total ethoxylated nonionic surfactants of long chain EO nonionic surfactants comprising 15 or more EO groups.

9. Method of preparing a lamellar-structured aqueous liquid detergent composition comprising non-ionic surfactant material, electrolyte and suspended clay material by mixing water, electrolytes, surfactant and clay material wherein the composition comprises sodium and potassium ions in a molar ratio of 10:1 or lower and wherein the clay material is a Bentonite clay.

10. Method according to claim 9 characterised in that at least 25% by weight of the total amount of clay material is added after at least 25% by weight of the total electrolytes.

Patentansprüche

1. Wässerige lamellarstrukturierte, flüssige Waschmittelzusammensetzung, enthaltend nichtionisches Tensid-Material, Elektrolyt-Material und suspendierte Tonteilchen, dadurch gekennzeichnet, daß die Zusammensetzung ferner Natrium- und Kalium-Ionen in einem molaren Verhältnis von 10 : 1 oder niedriger, enthält.

2. Eine flüssige Waschmittelzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das molare Verhältnis 5 : 1 oder niedriger ist.

3. Eine flüssige Waschmittelzusammensetzung nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, daß die K^+-Ionen in der Form von (Bi)carbonat, Citrat, Hydroxid, anionischem Tensid-Material, Nitrat, Sulfat und Chlorid zugesezt sind.

4. Eine flüssige Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Tonmaterial aus Bentonit, Kaolinit, Attapulgit, Hectorit und Derivaten derselben, ausgewählt ist.

5. Eine flüssige Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Viskosität der Flüssigkeit kleiner als 2500 mPa.s bei 21 s^{-1} ist.

6. Eine flüssige Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Flüssigkeit weniger als 10 Volumprozent Phasentrennung liefert, wenn sie bei 25°C für 21 Tage ab dem Tag der Herstellung gelagert worden ist.

7. Eine flüssige Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 6, dadurch qekennzeichnet, daß die Tonmaterial-Teilchen eine durchschnittliche Größe von zwischen 0,1 μm bis 10 μm haben.

8. Eine flüssige Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Zusammensetzung höchstens 25 Gewichtsprozent der gesamten ethoxylierten nichtionischen Tenside von

langkettigen EO-nichtionischen Tensiden, enthaltend 15 oder mehr EO-Gruppen, enthält.

9. Verfahren zur Herstellung einer lamellarstrukturierten wässerigen, flüssigen Waschmittelzusammensetzung, enthaltend nichtionisches Tensid-Material, Elektrolyt und suspendiertes Tonmaterial, durch Mischen von Wasser, Elektrolyten, Tensid und Tonmaterial, worin die Zusammensetzung Natrium- und Kalium-Ionen in einem molaren Verhältnis von 10 : 1 oder niedriger enthält und worin das Tonmaterial ein Bentonit-Ton ist.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß zumindest 25 Gewichtsprozent der Gesamtmenge des Tonmaterials nach zumindest 25 Gewichtsprozent der gesamten Elektrolyte zugesetzt sind.

Revendications

1. Composition détergente liquide structurée lamellaire aqueuse comprenant un tensioactif non ionique, un électrolyte et des particules d'argile en suspension, caractérisée en ce que la composition comprend en outre des ions sodium et potassium en un rapport molaire de 10:1 ou plus bas.

2. Composition détergente liquide selon la revendication 1, caractérisée en ce que le rapport molaire est de 5:1 ou plus bas.

3. Composition détergente liquide selon les revendications 1 à 2, caractérisée en ce qu'on ajoute les ions K^+ sous forme de (bi)carbonate, citrate, hydroxyde, tensioactif anionique, nitrate, sulfate et chlorure.

4. Composition détergente liquide selon les revendications 1 à 3, caractérisée en ce qu'on choisit l'argile parmi la Bentonite, la Kaolinite, l'Attapulgite, l'Hectorite et leurs dérivés.

5. Composition détergente liquide selon les revendications 1 à 4, caractérisée en ce que la viscosité du liquide est inférieure à 2500 mPas à 21 s^{-1}.

6. Composition détergente liquide selon les revendications 1 à 5, caractérisée en ce que le liquide donne moins de 10% en volume de séparation de phases quand on le stocke à 25°C pendant 21 jours à partir du jour de préparation.

7. Composition détergente liquide selon les revendications 1 à 6, caractérisée en ce que les particules d'argile ont une dimension moyenne entre 0,1 et 10 µm.

8. Composition détergente liquide selon les revendications 1 à 7, caractérisée en ce que la composition comprend au plus 25% en poids des tensioactifs non ioniques éthoxylés totaux de tensioactifs non ioniques à chaîne longue OE comprenant 15 groupes OE ou plus.

9. Procédé de préparation d'une composition détergente liquide aqueuse à structure lamellaire comprenant un tensioactif non ionique, un électrolyte et une argile en suspension en mélangeant l'eau, les électrolytes, le tensioactif et l'argile, dans lequel la composition comprend des ions sodium et potassium en un rapport molaire de 10:1 ou plus bas et dans lequel l'argile est une argile Bentonite.

10. Procédé selon la revendication 9, caractérisé en ce qu'on ajoute au moins 25% en poids de la quantité totale de l'argile après au moins 25% en poids des électrolytes totaux.